Teacher's Reference Handbook

CHEMISTRY

AN ROINN OIDEACHAIS AGUS EOLAÍOCHTA
DEPARTMENT OF EDUCATION AND SCIENCE

Department of Education and Science: *Intervention Projects in Physics and Chemistry*
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INTRODUCTION

This handbook has been produced as part of the Department of Education and Science's Equality of Opportunity Programme. The project developed out of the Department's scheme of ***Intervention Projects in Physics and Chemistry*** which was implemented from 1985 with a view to increasing the participation of girls in the study of the physical sciences. It is hoped that the material contained in this book will assist teachers in presenting chemistry in a manner which will give due cognisance to gender differences in relation to interests and attitudes. It is also hoped that the material will help teachers in their continuing quest to develop new approaches to their teaching which will make chemistry more interesting and exciting for all their students.

International trends in chemical education show attempts being made to develop syllabi which incorporate an appreciation of the social, environmental and technological aspects of chemistry. Chemical educators throughout the world are attempting to make students aware of how mankind benefits from the advances being made in chemistry. In developing this handbook close attention has been paid to these international trends.

The importance of science in general, and chemistry in particular, in today's society should be considered when relevant throughout the course. As in the syllabus, considerable emphasis has been placed on the social and applied aspects of chemistry. In engaging the interest of students in chemistry it is very important that significant emphasis be placed on the 'human face' of chemistry. Students should be aware that chemistry has an increasingly important role to play in industry, medicine, entertainment and in the home. The chemical industry has added immeasurably to the quality of our lives through the development of new materials, new and improved pharmaceuticals, improved quality of drinking water and food products, etc.

The individual modules making up this handbook have been selected around the content and structure of the syllabus to provide easy access to resource material in a way which supports the implementation of the course. However, it is important to realise that these modules do not define the syllabus. They do not determine the scope of the syllabus nor the depth of treatment that is required or recommended. Rather, each module is designed to provide additional background information for teachers. Each module contains suggestions on the teaching methods that the authors have found beneficial over the years and gives details of student experiments and teacher demonstrations. Worked examples are included which the teacher may find useful in the class room or for homework.

It is not intended that this book be used as a textbook or be read from cover to cover. Rather, it is intended that it be used as a reference handbook to assist teachers in their task of conveying the excitement and fascination of chemistry.

Chemistry is an experimental subject. General principles and concepts are more easily understood if they are demonstrated in the laboratory. The properties of particular substances are more fully appreciated if the student has the opportunity to examine them and investigate relevant reactions at the laboratory bench. There is no better way to ‘bring chemistry to life’ than with suitable laboratory practical work. While it is vitally important that appropriate safety precautions be taken at all times it is also important that students be encouraged to approach practical chemistry in a positive and enthusiastic manner.

The material in this handbook is arranged into ten modules plus a section on Gender and Science (see Contents). Each module is paginated independently. One index is provided for all the material, with page numbers preceded by a number to indicate the module. Thus, for example, ‘**2**: 47’ refers to Module 2, page 47.

All of the content is also provided on the attached CD, along with the material from the Physics Handbook. It is intended that this will facilitate teachers in finding specific items of interest and in maximising on the use of the material in their classes. To this end teachers may print selected sections from the CD for class handouts or overhead transparencies. They may also incorporate selected topics into on-screen presentations and into class materials prepared in other software packages.

GENDER AND SCIENCE

DR SHEELAGH DRUDY

Introduction

The Department of Education introduced the scheme of Intervention Projects in Physics and Chemistry in the 1980s. It formed part of the Department's programme for Equality of Opportunity for Girls in Education, and it arose from the observation that, though half the population is female, the majority of scientists and engineers are male. In particular, it was a response to a concern in many quarters that females were very under-represented among Leaving Certificate Physics and Chemistry candidates. The lack of representation and participation of females in the physical sciences, engineering and technology is not confined to Ireland. For the past two decades it has been a major concern throughout most of the industrialised world.

Although girls and women are well represented in biological science, their participation and achievement at all levels of education in Physics and Chemistry have been the focus of much research. This research has sought not only to describe and analyse female participation in Physics and Chemistry but to identify ways of improving it.

It is essential that girls and women orient themselves to the physical sciences and related areas for two principal reasons. Firstly there is the question of women's relationship to the natural world. It is vital that women's and girls' participation in the physical sciences is improved in order to increase women's comprehension of the natural world and their appreciation of the contribution of Physics and Chemistry to human well-being. It is also important to improve women's capacity to control nature and to appreciate the beauty of Physics and Chemistry.

Just as important is the issue of employment. There is no doubt that, in the future, the potential for job opportunities and careers in the scientific and technological areas will increase in significance for women, in comparison to the 'traditional' areas of female employment. In so far as women are under-represented in scientific and technological areas, they are disadvantaged in a labour market increasingly characterised by this form of employment.

Achievement and Participation

International Comparisons

In order to put the issue of female participation in Physics and Chemistry into context, it is useful to consider the international trends. Since the 1970s a number of international comparisons of girls' and boys' achievements in science have been conducted. The earliest of these indicated that boys achieved better than girls in all branches of science at ages ten and fourteen, and at pre-university level. Studies also showed that while girls were more likely to take Biology as a subject, they were a lot less likely than boys to take Physics, Chemistry or Higher Mathematics.

A recent international comparison focused on the performance of girls and boys in science at age thirteen. This study indicated that in most of the 20 countries participating, 13 year old boys performed significantly better than girls of that age. This significant gender difference in performance was observed in Ireland, as well as in most of the other participating countries. This difference was observed in spite of the fact that in Ireland, as in the majority of countries, most students had positive attitudes to science and agreed with the statement that ‘science is important for boys and girls about equally’.

Let us now consider the Irish context. Firstly, we should remember that relatively little science is taught in schools before this age, so it could be suggested that boys have greater socialisation into scientific ‘culture’ by early adolescence (for example, through very gender-differentiated toys, comics and television programmes). In addition, the international tests mentioned above relied heavily on the use of multiple-choice. There is evidence that the multiple-choice mode of assessment disadvantages girls.

Junior and Leaving Certificates: Achievement[1]

The important relationship between mode of assessment and performance in the sciences becomes evident when we examine the performance of girls in *public examinations* in Ireland. Analysis of recent results from the Junior Certificate and the Leaving Certificate examinations reveals some interesting patterns. For example, at Junior Certificate level, of the candidates taking science, a higher proportion of girls are entered at Higher Level than is the case with boys. A higher proportion of girls than boys receive grades A, B or C. This is also the case at Ordinary Level.

At Leaving Certificate level, while fewer girls than boys are entered for Physics, a higher proportion of the girls who do take the subject are entered at Higher Level. Traditionally, Chemistry has also been a male-dominated subject, though to a lesser extent than Physics. More recently, the numbers of girls taking the subject has equalled, or even slightly exceeded, the numbers of boys. However, as for Physics, a higher proportion of the girls who take the subject do so at Higher Level. As regards grades awarded, boys are generally somewhat more likely to receive an award in the A categories on the Higher Level papers. However, a higher proportion of girls than boys receive awards at the B and C levels, so overall a higher proportion of girls are awarded the three top grades in Physics and Chemistry at Higher Level. The same is true at Ordinary Level. Grade Point Average for girls in Physics and Chemistry is higher for girls than for boys at both Higher and Ordinary levels. Thus, in public examinations in Ireland, girls outperform boys in Physics, Chemistry and Junior Certificate Science. There is, therefore, no support for the notion that girls underachieve in the physical sciences in Ireland, when results are based on performance in public examinations.

This should not be taken to suggest that there is no longer a problem in relation to gender and science among Irish school-children. There is still a very serious problem in relation to differential take-up rates in science.

Junior and Leaving Certificates: Participation

At Junior Certificate level a lower proportion of girls than boys are entered for science. At Leaving Certificate level there are very marked variations in participation in science by gender. Indeed, overall, more girls than boys sit for the Leaving Certificate. Biology is the science subject most frequently taken by both boys and girls at Leaving Certificate. In terms of participation *rates*, though, it is predominantly a ‘female’ subject since two-thirds of the candidates are girls.

By contrast, in terms of participation rates, Physics is still very much a ‘male’ subject. Just under three-quarters of the Physics candidates are male. It is worthwhile noting that, although there is a great disparity in male and female take-up rates in Physics, there has been a marked increase in the proportion of females taking Physics since the early 1980s. This increase (albeit from a very low base) has been the result of a number of factors - one of these is the response of second-level schools (especially girls’ schools) to the findings of a major survey by the ESRI (Sex Roles and Schooling[2]) in the early 1980s. This study highlighted the extremely low proportion of girls taking Physics. Another factor is the growing awareness among girls of the importance of science for future careers. A further important component in the improvement in the take-up of Physics by girls is the impact of the various phases of the Intervention Projects in Physics and Chemistry. Evaluations of this programme have shown that it has had an important impact on the participation levels in Physics and Chemistry among girls in the target schools. This present handbook is the most recent example of the work of these worthwhile Intervention Projects. However, while it is important to note the increase in participation by girls, it is also a matter of serious concern that the imbalance in take-up rates between girls and boys in Physics is still so very great.

In summary, then, as regards achievement and participation in the physical sciences, it would appear that girls are capable of the highest levels of achievement. Indeed in terms of overall performance rates at Junior Certificate Science and in Leaving Certificate Physics and Chemistry girls now outperform boys. However, major problems still remain in relation to participation rates. While some of the variation in these rates is no doubt due to the attitudes and choices of girls, there is equally no doubt that they are significantly affected by school policy, particularly as it relates to the provision of the subjects and the allocation of pupils to them within the school.

School Policy

Provision

Whether or not a subject is provided in a school is clearly a matter of policy for that particular school. Obviously, there are constraining factors such as the availability of teachers with appropriate qualifications. This problem was the principal focus of the Intervention Projects in Physics and Chemistry. The efforts made in these Projects have met with some considerable success. Nevertheless, the variability in provision in Ireland, according to school type, indicates a very strong element of policy decisions in the provision of Physics and Chemistry.

Variations in provision according to school type

A survey in the early 1980s indicated a very considerable discrepancy in the provision of Physics and Chemistry to girls and boys. Since then provision of these subjects has improved, especially in girls' schools. However, the most recent analysis of provision indicates the persistence of the problem. Although provision for girls is now best in single-sex schools, girls' secondary schools are less likely to provide Physics to their pupils than are boys' secondary schools. In co-educational schools girls are proportionately less likely to be provided with the subject.

Given the differential provision in the various school types, the provision of Physics and Chemistry for girls has been linked with the debate on co-education. This is an important debate in an Irish context, in the light of the overall decline in pupil numbers, the resulting school amalgamations and the decline in the single-sex sector. As indicated above, for girls, the best provision in these two subjects is in girls' single-sex secondary schools. Provision for girls is less favourable in all other types of school. However, it is very important to realise that research has pointed to the close relationship of take-up of science and social class. Thus the weaker provision in vocational schools and community/comprehensive schools probably reflects their higher intake of working-class children rather than their co-educational structure. Nevertheless, this explanation, on its own, would not account for the variation between co-educational and single-sex secondary schools.

Concern with the effects of co-education on girls, especially with regard to take-up and performance in maths and science, is not confined to Ireland. For example, in Britain, it has been the focus of heated debate. Some have suggested that girls have more favourable attitudes to physical science in single-sex schools than in co-educational schools. It must be noted that the results on attitudes in Ireland, from a major Irish survey, are directly contrary to this. In the United States major controversies have arisen with the introduction of men to formerly all-women's colleges. In Australia also the issue is a major policy one. There also it has been suggested that the somewhat contradictory evidence must be assessed bearing in mind the higher ability intake in the majority of single-sex schools which are academically selective, and also the different social class intakes between types of school. It is not possible to reach a conclusion here on the relative merits of co-educational or single-sex schools. However, anywhere there is a lack of provision of key subjects such as Physics and Chemistry it should be a matter of concern to school authorities.

Allocation

Closely linked to the matter of *provision* of Physics and Chemistry is that of the *allocation policy* of the school. Research has shown that even where schools provide these subjects there tend to be considerable variations in access to them within the school. Allocation relates to a number of factors. In particular, it involves the academic prerequisites that the school demands before allowing pupils to choose particular subjects. At Senior Cycle it also connects to the timetabling and availability of different options.

This may be of particular relevance to girls. They may be less inclined to choose a ‘non-traditional’ option, such as Physics, if it is timetabled against a subject perceived as more ‘feminine’ such as Biology or Home Economics. The differential achievement levels apparent in Physics and Chemistry mentioned earlier, i.e. the greater likelihood of girls obtaining grades A - C and of boys obtaining Grades E - NG at Higher Level, and the proportionately greater number of awards to boys than to girls in the D, E, F, and NG grades at Ordinary level in Physics and Chemistry, suggest that schools tend to encourage only their ‘star’ female pupils to take these subjects, and thus reflect a more selective access of female pupils to these subjects at Leaving Certificate. Boys, on the other hand, appear to be allowed greater access irrespective of their ability levels.

Choice

As we have seen, schools need to critically evaluate their policies on the provision of Physics and Chemistry, and their internal practices of allocation within the school, in order to improve the access of girls. However, such improvements do not necessarily mean that girls will choose these subjects unless other barriers to participation are also addressed. For example, the ESRI study mentioned earlier found that even where schools offered Physics to pupils, over four times the proportion of boys to girls chose to do it. Analysis in the 1990s shows that, in spite of a rise in girls’ take-up rates in Physics, a marked differential is still apparent.

Before we turn to an assessment of why comparatively few girls choose to do Physics, even when it is available to them, let us consider briefly the concept of ‘choice’ itself. A great deal of educational research has shown that so-called ‘choices’, made by school-children in relation to subject options and careers, are themselves highly structured by the social situations within which they are made. When choosing options young people take account of the existing social context and the structure of opportunity available to their social class or their sex. Thus, the perceptions that young people have of the appropriateness of a particular option to their social class and their sex become an important element in their decision-making. Much of the international debate about girls and science has pointed to the very masculine image of the physical sciences. This masculine image, it has been suggested, contributes in an important way to the formulation of girls’ attitudes to the physical sciences.

Attitudes

‘Masculine’ Image of Science

The formation of attitudes is a highly complex process. When attitudes relate to issues as fundamental as gender roles the processes become even more complex. Such attitudes are deeply rooted in early socialisation within the family, in the school and via the media. The debate about girls and science suggests that there may be a mismatch between the ‘masculine’ image of science (especially Physics and Chemistry), and girls’ identification with the ‘feminine’ role at a critical period of adolescent development.

The first sense in which science can be regarded as ‘masculine’ is in the sense that men are numerically predominant. Perusal of any science textbook will suggest to the reader that the vast majority of scientific discoveries of any importance were made by men. To a very large degree this does represent a reality. However, this cannot be fully understood without the realisation that scientific discovery is itself as much a social process as a scientific one.

For example, at a time when the foundations of contemporary scientific enquiry were being laid, especially in the late nineteenth and early part of the twentieth century, women were not permitted to take degrees in many of the European universities at the forefront of scientific research, nor could they be members of the principal scientific societies. Even where women were involved in scientific discoveries it appears that they were allowed to carry out practical work but the named authors were mostly male.

Recent years have seen the publication of a number of accounts of the ways in which women’s scientific contributions have been rendered invisible through the operation of male power structures in scientific institutions and universities. One of the best documented cases is that of Rosalind Franklin whose crucial work on the analysis of DNA received scant recognition as a result of the difficulties experienced by her in a male-dominated institution. Cases such as these no doubt have had an impact on women’s self-image in the scientific community.

Kathleen Lonsdale[3] pinpointed the causes for the relative dearth of women scientists as the relative lack of women school teachers in ‘hard’ scientific subjects, girls opting for ‘general science’ rather than mathematics, pure Physics or Chemistry, more men than women continuing research after graduating and the small percentage of women appointed to responsible or creative academic posts. The ‘masculine’ image of science reflects unequal access to, and unequal relationships in, the scientific community. However, there are other ways in which this masculine image can be interpreted.

It has been argued that because science develops in relation to specific social and historical circumstances, in order to understand why girls choose Biology rather than Physics we need to consider the social role of science in general and the particular roles of the different sciences. It is suggested that, in advanced industrial societies, science has developed in relation to two major objectives: increasing the efficiency of production (economic) and the development of means of social control (military). The status of the different sciences will vary according to their perceived economic and military significance at any particular time. The higher their status, then the greater the exclusion of women in male-dominated societies, and the less relevant the subject matter is to issues of female concern. Therefore the variation in male domination between Physics and Biology follows from their different historical, economic and military significance.

Female and Male Roles and Behaviour

Let us turn now to examine the link between the image of the physical sciences, on the one hand, and male and female roles and behaviour, on the other. Physical science not only has a masculine image but also an impersonal image. Research among school-children shows that they think that science has to do with things rather than people. This image may be more off-putting to girls than to boys. Caring for people, both physically and emotionally, is an important part of the female role. A subject which appears to ignore people can seem irrelevant to girls’ concerns. Indeed, transnational research on the attitudes and work of women scientists indicates that the scientific interests of women are interrelated with a profound commitment to humanity and society.

Women have also been found to define themselves in terms of a network of relationships. Research has suggested that their positive view of themselves is linked to their judgement of their capacity for caring. Women tend to see the world as networks of relationships, men to see it in terms of hierarchies. Boys, research indicates, are concerned with making sense of the world through rules, and achieving an individual identity; they aspire to a position in a hierarchy. Girls' concerns centre on developing a network of close relationships with other people. These differences in self-image and interest have an impact on subject choice and career orientation.

Another factor of relevance in the formation of attitudes during adolescence is the difference in maturity between girls and boys. It has frequently been observed that girls tend to mature physically earlier than boys. At a period when important subject choices are being made in schools, girls - especially working class girls - are also becoming involved with a 'culture of femininity' which involves an ideology of romance, marriage, family life, fashion and beauty. Involvement with this culture, which places heavy emphasis on traditional female roles, may well make girls reluctant to select subjects which have a strong masculine image, such as Physics.

On the other hand Biology is very much a female dominated science. It can be argued that part of the reason for this is because of its image as a 'life' science - and because it is the only science subject which deals at all with the topic of sexuality which is so fascinating for adolescent girls. Sexuality is also fascinating for adolescent boys, of course. As we have already seen, more boys also select Biology than any other science subject, even if they are in a minority compared to girls. A further reason that girls may orient themselves to Biology in such disproportionate numbers is because of its perceived function as a prerequisite for certain 'traditional' female careers, such as nursing.

Research has also suggested that, apart from being perceived as masculine, Physics and Chemistry have another 'image problem' which affects attitudes. Young people, it has been found, perceive Physics and Chemistry as being very difficult, very mathematical, heavily content-loaded, very dull, and demanding passive reception rather than active involvement with the learning process. This perception of Physics and Chemistry as difficult may be more off-putting to girls than to boys, although girls are more successful when they enter for these subjects (linked, perhaps, to girls' more selective entry). Boys' higher entry to Physics may be linked to higher levels of self-confidence at that age. They may be more likely to 'have a go', irrespective of the level of difficulty. Again, it may be that traditional 'male' careers, such as engineering, exercise a greater attraction for boys thus making it easier, psychologically, for them to take on subjects perceived as difficult.

The twin images of Physics and Chemistry as both masculine and difficult, and the impact of these on the attitudes of girls, have significant implications. These revolve around the operation of school policy, the selection and presentation of the curriculum in both subjects, and teaching methodologies in the classroom and laboratory.

Strategies For Action I: School Policy

Provision

If the proportion of girls taking Physics and Chemistry is to be improved, one of the most obvious strategies for action for school authorities is to improve the provision of these subjects in schools. Although marked improvements in provision have taken place over the last decade, there still are considerable variations, especially in some of the co-educational schools. This issue needs to be addressed as a matter of priority.

Allocation

In addition to increasing the provision of these subjects to both sexes, but especially to girls, the policy with relation to allocation within the school must be addressed, both at junior cycle and at senior cycle. At junior cycle there is a strong argument for making science a 'core' subject. Although this is, in effect, the practice in the majority of schools, the evidence shows that girls are still less likely than boys to be entered for Junior

Certificate Science. This can only serve to perpetuate the notion that boys are somehow more 'suitable' for science.

At senior cycle the two key allocation factors appear to be a) the combination in which various subject options are offered and the way they are timetabled; and b) the degree of selectivity practised by the school for entry to Leaving Certificate Physics and Chemistry classes (e.g. the requirement of higher level Maths (Syllabus A) at Junior Certificate, or a high grade in higher level Junior Certificate Science). There is little hope of improving girls' participation in Physics, for example, if taking Physics eliminates the possibility of 'traditional' female options such as Biology or Home Economics, to which girls are likely to be very well predisposed. Furthermore, there is evidence to suggest that a high proportion of girls have less confidence in their abilities to do Physics and Chemistry than boys do. Girls require considerable encouragement from their teachers to take up these subjects, or related ones such as Higher Mathematics. These factors are important for all girls but more especially for working class girls who are the group least likely to orient themselves to Physics and Chemistry.

The Allocation of Teachers to Science Classes

The allocation of teachers to science classes can reflect schools' policies (and teachers' attitudes to science). Many science teachers, particularly in girls' schools, are Biology and/or Chemistry graduates. They may not feel very comfortable with Physics, and possibly Chemistry, at junior cycle. The Physics teachers may teach higher level mathematics, as well as Physics, and may not be allocated to Junior Science classes. This may lead to the perception among students that to do Physics you should be doing higher level mathematics, that subjects such as Physics and Chemistry are difficult. Secondly, it means that senior cycle Physics and Chemistry teachers may not know the junior cycle science pupils. This may affect take-up, given that girls may be more likely to link their choices in some way to their relationship with their teachers.

Whole School Approach

The allocation issues have implications for teachers of other subjects as well as for science subjects. This requires a holistic approach to science, as well as staff development in relation to general equality issues. The need for a whole school approach has been emphasised in evaluation of earlier phases of the Intervention Projects in Physics and Chemistry.

Careers Guidance

The whole school approach has implications not only for option choices and timetabling across the whole curriculum but also, very particularly, for careers guidance. Careers advice can be influential in encouraging girls in science. There is evidence that while both boys and girls benefit from careers advice on science, girls notice it and respond to it more than boys. Research indicates that where boys choose Chemistry, for instance, they say that they do so because they will need it in their careers when in fact the careers chosen have no such requirement (e.g. accountancy, banking, law). Conversely, the same research shows that girls often choose careers, such as nursing or catering, where Chemistry would be a useful qualification but do not link the choice to Chemistry. It seems that while careers guidance can encourage more girls to orient themselves to Physics and Chemistry, it can also discourage them if the guidance counsellor is not fully aware of the importance of these subjects for girls.

Parents

The school can also play a very positive role in raising parental awareness of the importance of subjects such as Physics and Chemistry for their daughters. In international comparisons, there is a statistically significant relationship between parental interest in science and pupil performance in science in many countries. Work on the earlier phases of the Intervention Projects in Physics and Chemistry has also indicated the importance of involving parents.

In sum, then, school policy has an important role to play in increasing the participation of girls in Physics and Chemistry through the provision and allocation of the subjects, through a whole school approach to staff development and through the involvement of parents.

Strategies For Action II: The Curriculum

Humanising Physics and Chemistry

We have seen that Physics and Chemistry developed as subject areas within a context of male domination in universities and research institutions. This, combined with the strong influence of economic and military interests in the generation of research in the physical sciences has given rise to their largely ‘masculine’ image. This, it has been argued, has been one barrier to the recruitment of girls and young women to science.

Many experts have suggested that, in order to attract more girls to Physics and Chemistry, it is essential to tackle the curriculum itself. To make science meaningful, science teachers must personalise and carefully contextualise science itself, whilst invoking and accepting the previous experiences and prior knowledge that girls bring to lessons. Students, especially girls, can be motivated by being helped to see the physical sciences (and mathematics) as a human creation, developed in a particular cultural and historical context, by individuals who were influenced by the needs and values of the society in which they lived. Although science has been dominated by men, it is also important to emphasise the areas (and there are many) where women have made significant discoveries and achievements.

As well as presenting Physics and Chemistry within historical and social contexts, research has shown that girls are more encouraged when examples are used which relate developments and materials to contexts in which females have dominated. Females have dominated in the domestic sphere, but of course in many other domains as well. This approach is particularly easy in Chemistry, but can be adopted within Physics. There is also evidence that girls’ interest in physical science is increased by stressing its relevance to human biology. If, for example, girls are uninterested in finding out how machines work, they may be introduced to moments and forces by studying how muscles work.

Transition Year

The introduction of Transition Year into schools provides an opportunity to encourage more girls into the physical sciences. There are issues both of school policy and of curriculum in the Transition Year that can affect the take-up of Physics and Chemistry in the senior cycle.

The structure of the science courses within the year, the allocation of teachers, the question of choice, can all be considered when setting up the Transition Year. The Transition Year science course(s) may be optional modules, or part of a core curriculum. It may be the separate sciences, or general science with no explicit Physics and/or Chemistry components. The course may be taught by one teacher, or by a number of teachers with a variety of science specialisms. Students who did not take science for the Junior Certificate may or may not be permitted to take up any of the science subjects at this stage. The effect that policy decisions on the structure and organisation of the Transition Year may have on the take-up of Physics and Chemistry in the senior cycle needs to be considered.

School policy decides and defines the structure of the courses taught in Transition Year. The courses taught in Transition Year are developed by the teachers in the school and often reflect their interests and ideas. It can be an ideal opportunity to develop girls’ confidence and competence in the Physical sciences before they begin the two year Leaving Certificate syllabuses. The contact with an interested and enthusiastic Physics/Chemistry teacher and the development of confidence, particularly in the ability to cope with the mathematics, may be what is needed to encourage some students to take the physical sciences. It is an opportunity for teachers both to humanise Physics and Chemistry and to develop ‘girl-friendly’ science.

‘Girl-Friendly’ Science

‘Girl-friendly’ science is an approach that attempts to place science in a context that appeals to both girls and boys, rather than to boys only. Traditionally, many areas in the physical sciences have focused on issues which have been predominantly of interest to boys rather than girls. Guidelines for a ‘girl-friendly science curriculum’, arising from an English intervention project, the ‘Girls Into Science and Technology’ (GIST) project, include the following.

(a) Set experiments in context by providing background information about the possible uses and applications of scientific principles. Do this, if possible, before the ideas are derived by experiment - tell the pupils where they are going and why.

(b) Link physical science principles to the human body.

(c) Stress safety precautions rather than dangers.

(d) Discuss scientific issues, e.g. the microprocessor revolution and unemployment, energy and the bomb, aiming at a balanced view of the benefits and disadvantages of scientific developments.

(e) Make aesthetically appealing exhibitions.

(f) Use imaginative writing as an aid to assimilating scientific principles and ideas.

Girl-friendly teaching is good teaching.

Strategies For Action III: Teaching Methods[4]

Teachers’ Perceptions of Pupils

There is evidence that, when it comes to girls participation in Physics and Chemistry, teachers are particularly important. Educational research shows that, across a range of areas, teachers’ expectations have an impact on pupil performance. Some studies have shown a clear tendency on the part of teachers to overrate the work of a boy compared with that of a girl. These results suggest that, even if there are differences between boys’ and girls’ interest in and attitudes towards science, teachers may be further magnifying these differences. There is some evidence that teachers believe science education to be of greater importance to boys than to girls. If teachers believe that boys are naturally better and more interested in scientific and technical subjects, this may become a ‘self-fulfilling prophecy’.

It is known also from various studies that girls, especially those in their early teenage years, have less confidence in their own ability than boys do. This is particularly the case in relation to traditionally male-dominated subjects such as Physics and Chemistry, and is especially manifested in the context of mixed classes. Since lack of self-confidence militates against achievement - and enjoyment - it is vitally important that girls’ confidence in their own ability be raised as much as possible.

The analysis of the Junior and Leaving Certificate examinations mentioned earlier shows that, while girls are participating less in Junior Certificate Science and in Physics, their level of achievement in these subjects, and in Chemistry, is, on average, better than that of boys. However, their level of confidence in these subjects may not be commensurate. Consequently, teachers can do much to improve participation by support, encouragement and high expectations. Girls need to be told they are capable, even if to the teacher this seems obvious. Teachers should strive to create a relaxed, supportive, non-competitive environment where pupils can gain and maintain confidence.

Encouraging Pupils in Single Sex and Mixed Classrooms

Pupils in the classroom interact in a variety of different ways with teachers. Different strategies are needed for girls-only classrooms, for boys-only classrooms and for mixed classrooms if pupils are to experience Physics and Chemistry in an inclusive way.

In girls-only classrooms, girls can be encouraged by teaching styles that develop their confidence and enable them to cope with the different ideas and skills that Physics and Chemistry demand. Girls often prefer to work in a co-operative way, helping each other. The team skills that girls prefer can be useful in a career that develops out of their studies of Physics or Chemistry. The use of social, personal and biological applications of Physics and Chemistry should help in developing a warm, non-threatening classroom atmosphere. It is important to praise girls, not just for their neatness and hard work, but for the excellence of their work. Practical work is essential and girls should develop their skills and competence in this area.

In boys-only classrooms, it is equally important that boys realise that Physics and Chemistry include men and women. The image of Physics and Chemistry presented should be inclusive of girls and women. Comments below about the layout and presentation of laboratories and of posters apply equally to boys' classrooms. Women and men should be shown working in Physics and Chemistry in non-stereotypical ways. Boys should be encouraged to work co-operatively and to share equipment and other resources. A range of applications should be taught including the social, personal and biological, not just the mechanical and technical. Physics and Chemistry are about people and boys need to realise this just as much as girls.

In mixed classrooms, there has been a considerable amount of research which shows that teachers interact differently with girls and boys in all subject areas. This is as much the case in science classrooms as in any other. Boys both demand and get more teacher attention. A significant amount of the attention boys get is in the form of disciplinary interventions. However, they also receive more praise from teachers. In some science classes teaching may be mainly directed to the boys with girls 'listening in'. However, if teachers find that for various reasons (perhaps disciplinary) they are unavoidably spending more time interacting with boys in the lesson, to compensate they can spend more time with the girls after class, or during practical sessions. Teachers should ensure that practical work is organised fairly for girls and boys. Among the considerations should be the organisation of working groups (mixed or single-sex), the allocation and issuing of equipment to the groups and the attention paid by the teacher during the practical sessions. Boys can tend to both hog the equipment and take the active roles in practical work. It is important that girls are as much expected to do the work as the boys. It may be possible to involve more girls in the lesson by gearing the work to their interests and aptitudes. A more humanistic approach to Physics and Chemistry could be tried which might also improve girls' attitudes to the social implications of these subject areas.

It has been suggested by research that the introduction of co-operative learning activities benefits female students. Teachers who use student-centred, 'problem-driven', enquiry methods in science have been found to be more effective in maintaining girls' liking for the subject. These methods involve co-operation among students and allow less opportunity for a competitive spirit to develop. Collaborative, problem-solving work allows girls to make effective use of their verbal abilities which can help to clarify their ideas and boost self-confidence.

Laboratory Organisation

The layout and presentation of the laboratory/classroom is an important consideration in encouraging students to take up Physics and Chemistry. A clean, bright room can be friendly and welcoming. Posters that reflect a range of applications, not just mechanical and technical, and that show that people (both women and men) are involved in Physics and Chemistry can encourage girls and give them the confidence to feel that they can belong in the world of the physical sciences.

Teaching Behaviour and Techniques for Encouraging Girls into Physics and Chemistry and Retaining Them

Research in the United States by Jane Kahle has summarised successful strategies for encouraging girls to pursue science. The teaching behaviour and techniques that are effective for retaining girls and women in science are as follows:

DO

- use laboratory and discussion activities
- provide career information
- directly involve girls in science activities
- provide informal academic counselling
- treat both sexes equally in the science classroom
- directly involve girls in science activities
- allocate and issue equipment fairly to all students

DON'T

- use sexist humour
- use stereotyped examples
- distribute sexist classroom material
- allow boys to dominate discussions or activities
- allow girls to passively resist

Conclusion

In conclusion, teachers can play a key role in increasing the participation of girls in Physics and Chemistry. They can do this through having high expectations of their female students, by giving them strong support and encouragement, by ensuring a fair, relaxed and hassle-free atmosphere in mixed classrooms, by using a good variety of teaching methods which are student-centred and problem-solving and by using group as well as individual work. Excellent science teaching must also be innovative and exciting. 'Science must be presented as not only basic but beautiful.'

Notes

1. The commentary on gender differences in uptake and performance in the sciences in public examinations is based on analysis of the 1993 Junior and Leaving Certificate Examination results. This detailed analysis is provided in Drudy, 1996.
2. In order to assist the flow of the text, the material is not referenced in the usual academic format. The bibliography gives a list of sources. Detailed referencing is to be found in Drudy, 1996.
3. Kathleen Lonsdale was born in Newbridge, Co. Kildare in 1903 – see module on Some Irish Contributions to Chemistry, p. 25.
4. I would like to gratefully acknowledge the contribution and assistance of Marian Palmer with this section and with the section on the Transition Year.

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MODULE 1

Atomic Structure and Trends in the Periodic Table of the Elements

CONTENTS

Chapter 1 Atomic Structure

Chapter 2 Periodic Classification of the Elements

Chapter 3 Trends in the Periodic Table

CHAPTER 1

ATOMIC STRUCTURE

1.1 Introduction

How can a study of atomic structure help us solve a wide range of problems in society, in agriculture, in medicine, in the environment, etc., as well as improving our understanding of theoretical chemistry?

Do you know how an understanding of atomic structure can:

(i) help solve crime, e.g. hit-and-run accidents or forgery;

(ii) analyse the soil for fertiliser requirements;

(iii) make fireworks displays colourful;

(iv) produce highly efficient, more economical, more environmentally friendly, lighting;

(v) monitor the environment for pollutants;

(vi) discover the composition of the sun and distant galaxies;

(vii) satisfy a basic psychological need?

A complete account of how atomic theory has developed from the first musings of the ancient Greeks to today's detailed picture would be very lengthy. For brevity and simplicity only the main contributors will be mentioned. They bring us from the Greek philosophers of the sixth century BC, past the dabblings of the alchemists, through the period when studies of wave mechanics and relativity revealed much about the nature of matter. We shall see how those problems and issues listed above are solved as we proceed.

1.2 Ideas from Ancient Greece[1]*

Earlier than the sixth century BC the Greek philosophers had begun to consider the nature of matter. As with most of their theories, their ideas were not based on experimentation – they considered any work of the hands demeaning – but on speculation and logical reasoning. Experimentation, when it was carried out, was always used to reinforce the existing theory rather than as a source of new theories. The ideas of the Greek philosophers in mathematics, medicine, and science in general, were very influential and their ideas continued to have an impact on the development of chemistry for nearly two thousand years afterwards.

If we trace our knowledge of the nature of matter back through history to this period we find that **Empedocles** (c.490–435 BC) was the originator of the idea of elements. Empedocles was not the first person to contemplate the nature of matter but his theory is the most ancient one to be still incorporated in some way in the modern picture of atomic structure. Prior to Empedocles there were other theories suggesting that water was the origin of all the cosmos or that fire was some sort of primal matter which gave rise to water and earth, etc. Indeed Empedocles based his theory on these earlier ideas and suggested that there were four elements, namely, fire, air, earth and water, each composed of minute unchanging particles, and that all visible matter is made up of these 'roots'. Empedocles further proposed that these roots could be combined together by Love and separated by Strife. So even in this 5th century BC theory are contained the ideas that

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**Numbers refer to the references on page 34.*

matter is composed of elements, these being composed of minute particles, and that the different elements combine according to some kind of law.

Experiments 1.1, 1.2a, 1.2b and 1.3, pp. 26–27, all illustrate the particulate nature of matter and its minute size; some are student experiments and some are more suitable as teacher demonstrations.

The ideas of Empedocles were developed further by **Democritus** (460–c.370 BC). Democritus suggested that the elements earth, fire, air and water were composed of individual particles of a particular geometric shape, e.g. he proposed that fire atoms were spherical, and that they were in continuous random motion in a vacuum. These individual particles were called ‘atomos’, meaning indivisible. Thus Democritus gave us the name for the atom and expressed for the first time a primitive kinetic theory of matter.

The ideas of Democritus were in turn developed by other Greek philosophers but unfortunately the idea that one element could be transmuted into the others was introduced. This idea became the focus for the alchemists and contributed to the neglect of the development of further understanding of atomic theory for quite some time as efforts were applied to attempts to convert base metals such as lead into precious metals like gold.

1.3 Alchemy

Alchemy was a combination of philosophy, mysticism and chemistry which had its origins in Greece and Egypt, in the Arab world and in China. Its various aims included the transmutation of base metals into gold, the prolonging of life and the pursuit of immortality. Alchemy was responsible for the discovery of some important techniques, apparatus and reagents, e.g. sand, dung or water baths were used for indirect heating of delicate reactions. Water baths (*bains-marie*) were invented by the famous alchemist **Mary the Jewess**[2] in the second century BC. Nitric, sulphuric and hydrochloric acids were discovered in the search for the ‘elixir of life’ to prolong life and the ‘philosopher’s stone’ which could change base metals into gold. However alchemy earned disapproval for making counterfeit gold and was held in suspicion and mistrust by the general population from its earliest times. By the 16th century two groups of alchemists could be recognised, those who concentrated on the mystical side and made no further contribution to chemistry and those who were interested in bringing about chemical change, especially to cure disease. It is the latter who advanced alchemy until it evolved into chemistry. Alchemy itself has never quite died out and it has become increasingly mystical and linked with the occult and astrology.

1.4 Later Developments Based on Observation (1650–1850)

Robert Boyle[3,4] (1627–1691), the seventh son of the Earl of Cork was born in Lismore, County Waterford but lived in England from an early age. He is chiefly remembered for his experiment which verified the relationship between the volume and pressure of a fixed mass of gas, now known as Boyle’s Law (1662) but he also made a very important contribution to the development of atomic theory. (See Experiments 1.4, 1.5 and 1.6, pp. 28–29.)

Boyle reverted to the theory of Democritus and described matter as being composed of small, solid, physically indivisible particles making up elements. **Robert Hooke** (1635–1703), who at one time was Boyle’s assistant, had invented the compound microscope about this time and it probably stimulated minds to accept the world of the infinitely small.

Otto von Guericke (1602–1686) invented the air pump in Magdeburg in the 1650s. In 1654, to demonstrate the power of the pump and to show the existence of a vacuum, von Guericke evacuated the space between two hollow metal hemispheres. Two teams of plough horses pulling in opposite directions were needed to pull the hemispheres apart. This spectacular demonstration showed the existence of a considerable atmospheric pressure and the efficiency of von Guericke's pump.

Back in England, Boyle learned of the air pump. Robert Hooke assisted Boyle in the construction of a similar air pump which helped Boyle to study the properties of air. Boyle argued that the fact that gases could be shown to be compressible was evidence in favour of the corpuscular theory of matter. If matter was continuous, gases could not be compressed. Boyle had not completely rejected the notion that one element could be transmuted into another by rearranging the constituent particles but he had completely dispensed with the alchemical notion of some metals being base. He insisted that there were mechanical and corpuscular explanations for all chemical phenomena and the behaviour of matter, e.g. his gas law described the mechanical behaviour of a gas at fixed temperature. He is sometimes called the 'Father of Modern Chemistry' because, by concentrating on mechanical and corpuscular explanations rather than mystical explanations and divine intervention for the behaviour of matter and chemical phenomena, he helped to separate finally chemistry from alchemy and to establish it as a study in its own right rather than as a subsection of medicine or physics.

Boyle 'begat a good understanding betwixt the chymists and the mechanical philosophers'. Previously there had been a tendency by natural philosophers (physicists) to consider chemistry irretrievably linked with the pseudo-science of alchemy and this "good understanding", we shall see, was of great importance in elucidating atomic structure in the early twentieth century.

Incidentally, in mainland Europe, Boyle's law is known as Mariotte's law after the Frenchman **Edmé Mariotte** (1620-1684) who made the same discovery independently in 1676.

The work of **John Dalton** (1766–1844) gave the first detailed physical picture of the appearance of atoms and, most significantly, for the first time a way of physically distinguishing atoms of one element from atoms of another. This was done by simple measurements which could be made in the laboratory despite the fact that individual atoms could not be seen or measured. (He is sometimes wrongly credited with being the first to describe matter as being composed of small individual particles but as we have seen that was actually a much earlier notion.)

In a publication of 1808 called 'A New System of Chemical Philosophy', Dalton described atoms as solid and indivisible spheres surrounded by an atmosphere of heat – the thickness of the heat atmosphere varied according to the state of the material, thin for solids, larger for liquids and largest for gases.

Dalton's atoms could not be created or destroyed (and thus not transmuted).

Matter made up of one type of matter only was called elementary matter and all atoms of elementary matter were taken to be identical.

Dalton assumed that atoms could combine in simple ratios to form compound matter which differed in its properties from its constituent elemental matter.

Atoms of different elements varied in size and mass. (Dalton, of course, referred to weight rather than mass.)

From these premises, Dalton introduced the concept of relative atomic mass with the purpose of distinguishing between atoms of different elements. He reasoned as follows: knowing that about 7 grams of oxygen combined with 1 gram of hydrogen to form about 8 grams of water and assuming that the atoms of hydrogen and oxygen combined in the ratio 1:1, then the mass of an oxygen atom was 7 times greater than the mass of a hydrogen atom. The alternative assumption, that the atoms of oxygen and hydrogen had equal masses but combined in the ratio of 7:1, was rejected by Dalton as less probable. Later it was discovered that oxygen and hydrogen actually combine in the volume ratio 1:2 and, with more accurate weighings, we now know that the mass of the oxygen atom is in fact approximately sixteen times greater than the mass of the hydrogen atom. Dalton's theory was flawed in several other respects also. However, the focussing on relative atomic mass as a means of identifying and distinguishing elements was a great advance, as was calculating relative atomic masses from combining masses of elements as in the example of hydrogen and oxygen above. Dalton's theory was adopted enthusiastically by **Jöns Jacob Berzelius** (1779–1848) who did much to improve the accuracy of the relative atomic mass calculations.

The combining masses of elements were one of the pieces of information needed to calculate a relative atomic mass. The other was the ratio in which the elements combined. Dalton assumed that hydrogen and oxygen combined in the ratio 1:1 and his calculations accordingly produced an incorrect result. The French chemist **Joseph Louis Gay-Lussac** (1778–1850) did not make assumptions about the combining ratios of elements. Rather he carried out experiments with gases and discovered a simple ratio in their combining volumes.

For example he showed that when hydrogen and oxygen combine to form water, they combine in the following proportions, all measurements made at the same pressure and temperature:

oxygen	+	hydrogen	=	water
1 volume		2 volumes		2 volumes

Similar experiments led him to formulate the law in 1808, now known as Gay-Lussac's law of combining volumes, which states that when gases combine chemically, the volumes of the reactants and products, if gaseous, bear simple relationships to each other, when measured under the same conditions of temperature and pressure. The work of Gay-Lussac was not accepted at all by Dalton or fully by Berzelius but was nevertheless adopted by Berzelius to the extent that made it possible for him to calculate accurately the relative atomic masses of the elements known at that time and publish a list of relative atomic masses in 1826 which agree quite closely with today's values for most elements.

The direct deduction which can be made from Gay-Lussac's law is that equal volumes of gases, at the same temperature and pressure, contain equal numbers of particles.

The equation above thus becomes:

oxygen	+	hydrogen	=	water
1 volume		2 volumes		2 volumes
n oxygen		2n hydrogen		2n water

and to make a single particle of water, therefore would require

1/2 oxygen	+	1 hydrogen	=	1 water

This was the reason why Dalton could not accept Gay-Lussac's work: he thought it implied that the atom was divisible. The explanation suggested by the Italian Count **Amadeo Avogadro** (1776–1856) was the first to distinguish between atoms and molecules. Avogadro accepted the work of Gay-Lussac, he deduced that this implied that equal volumes of gases at the same temperature and pressure contained equal numbers of particles, which statement became known as Avogadro's hypothesis. However, to avoid the notion of dividing atoms he suggested that molecules, consisting of pairs of hydrogen and oxygen atoms, existed and that to form water

1/2 oxygen molecule	+	1 hydrogen molecule	=	1 water molecule

or

1 oxygen atom	+	2 hydrogen atoms	=	1 water molecule.

Avogadro's idea of diatomic molecules was ridiculed thus: if pairs of gaseous hydrogen atoms can cling together, why don't they all cling together and condense to form a liquid? At this time there was no understanding of bonding to justify Avogadro's hypothesis and so his ideas were ignored for nearly fifty years. During this period relative atomic masses continued to be measured by a variety of methods all based on the ideas of combining masses and volumes and in some cases several different relative atomic masses were recorded for the same element. This tended to discredit Dalton's atomic theory somewhat until 1860 when the Italian chemist **Stanislao Cannizzaro** (1826–1910) resolved the problem at the first international chemical congress held in Karlsruhe by simply referring back to Avogadro. The apparent contradiction between relative atomic mass values from different experiments arose because relative atomic masses for an element were calculated in one experiment and relative molecular masses in another.

Atomic Masses[5]

In 1815 **William Prout** (1785–1850) had proposed that the atomic mass of hydrogen be taken arbitrarily as 1, since the atomic masses of all other elements could be expressed as integral multiples of the mass of a hydrogen atom. (Indeed part of his suggestion was that all atoms were composed of varying numbers of hydrogen atoms, which of course was at variance with Dalton's theory of solid indivisible atoms.) In fact, when measured accurately, only the lighter elements have relative masses which are near integer values. Later it was suggested that oxygen would make a better reference than hydrogen as it forms stable compounds with more elements. One sixteenth of the mass of an oxygen atom became the standard unit of atomic mass against which the masses of the atoms of other elements were compared.

This continued until as late as 1961 by which time chemists had adopted 16 to be the mass of naturally-occurring oxygen (i.e. a mixture of isotopes) while physicists and mass spectroscopists had taken 16 to be the mass of the most abundant naturally-occurring isotope of oxygen. At this stage most atomic mass determinations were carried out by mass spectroscopy and the principal isotope of carbon had a very convenient set of reference traces on a mass spectrograph. Adopting it, rather than an isotope of another element, as standard meant a small actual change in previously calculated data. So it was agreed by the International Union of Pure and Applied Physics in 1960 and by the International Union of Pure and Applied Chemistry in 1961 to change to the most abundant isotope of carbon as the standard and to define the atomic mass unit as one twelfth of the mass of the carbon-12 isotope.

Atomic Symbols

In 1814 Berzelius suggested that elements should be represented by the capital initial letter of their Latin name (and the second letter also in lower case if another element had already been assigned the initial letter). Dalton had already devised his own scheme to represent different elements, e.g. nitrogen ⦶, hydrogen ⊙, etc. Berzelius' symbols proved much more successful than Dalton's because of their simplicity and the fact that they could be printed by standard type face. In 1837 Berzelius' symbols were adopted by the British Association for the Advancement of Science. Dalton was extremely upset that Berzelius' "horrifying" symbols were preferred to his; he maintained that his symbols represented the structure of the atom more faithfully than those of Berzelius.

Thus in the early nineteenth century there was at last a picture of the atom which encompassed all relevant ideas to date and accounted for much observed chemical behaviour. We must imagine the picture of the atom of the early nineteenth century as a very small dense sphere of matter, differing in size and mass according to the element in question and surrounded by an atmosphere of heat which increased as the substance was heated.

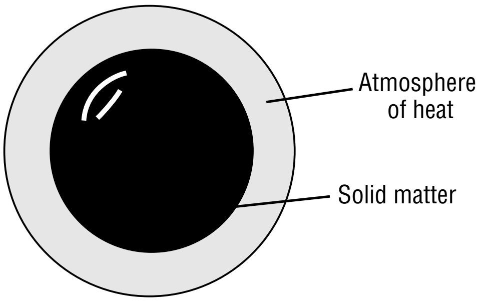

Fig. 1.1 *Dalton's atom, 1808*

1.5 The Architecture of the Atom

The next advance in understanding of atomic structure showed that the atom was not the solid indivisible structure described by Dalton but had its own internal architecture.

It was known since its discovery that electricity was somehow related to, and involved in, chemical behaviour but it was not until late in the nineteenth century that any clear connection between electricity and chemical behaviour was established.

Identification of the Electron

When electricity is passed through a gas at low pressure a stream of particles moves from the negative electrode (cathode) to the positive electrode (anode), Fig. 1.2. An electric current was first passed through an evacuated glass vessel as early as 1785 and produced a glow of light. In 1836 **Michael Faraday** (1791–1867) showed that the glow originated from the cathode. But it was not until 1865 when **Johann Heinrich Geissler** (1815–1879) invented a pump which made it possible to reduce the pressure inside a glass vessel to a few thousandths of atmospheric pressure that this phenomenon could be investigated fully. The reduced pressures allowed the radiation to be studied in isolation from its interaction with the gas through which it passed. The radiation was shown to be negatively charged and could be deflected in a magnetic field. The radiation became known as “cathode rays”. Cathode rays travelled in straight lines and **William Crookes** (1832-1919), while making a systematic study of their properties in 1874, discovered that they could exert forces on a small paddle wheel placed in their path, convincing him that they consisted of particles. In 1897 **Joseph John Thomson** (1856–1940), working in the Cavendish Laboratory at Cambridge, proved that the cathode rays consisted of negatively charged particles which were considerably lighter than the lightest known element, hydrogen. Then in 1897 Thomson calculated the specific charge, i.e. the ratio of the charge to mass (e/m), of these particles by equating the effects of the electrical and magnetic forces on the electrical beam produced by a cathode ray tube in an arrangement similar to that shown in Fig. 1.2. Since particles of the same charge to mass ratio could be produced by all metal electrodes, Thomson deduced that these particles, which had a very large specific charge, were constituents of all matter and were smaller than atoms. The term electron had been suggested in 1891 by **George Johnstone Stoney** (1826–1911)[6], an Irish physicist and astronomer, as the unit of electricity gained or lost when atoms became ions. In the few years after the 1897 experiment, the idea of the electron being a fundamental particle became widely accepted and the name ‘electron’ was adopted.

So, J. J. Thomson is usually credited with ‘discovering’ the electron in 1897, although it would be more correct to say that he identified it as a fundamental constituent of matter and recorded some of its properties, particularly its specific charge, in 1897. (See Experiment 1.7, page 29.)

J. J. Thomson went on to describe the atom as being composed of a matrix of positive material in which the small negative electrons were embedded. The atom was overall electrically neutral. This description of the atom became known as the ‘plum pudding’ model of the atom, Fig. 1.3, and successfully explained the origin of cathode rays and was used to explain bonding as an electrostatic attraction between atoms which had lost or gained electrons – essentially a description of ionic bonding.

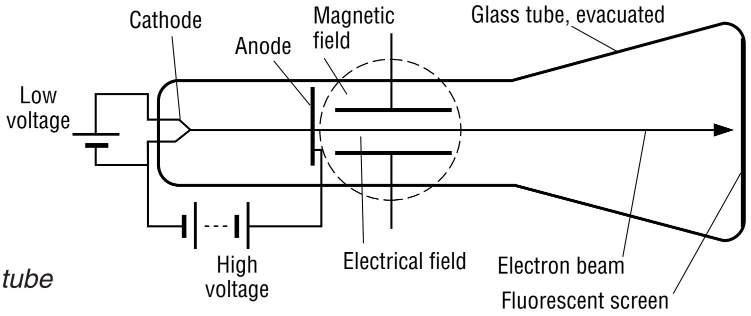

Fig. 1.2 *Cathode ray tube*

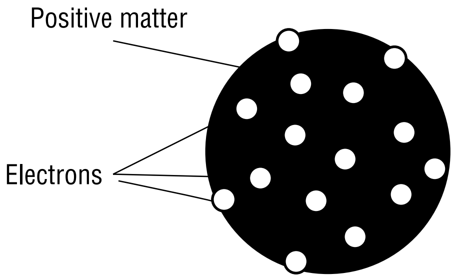

Fig. 1.3 *Thomson's 'plum pudding' atom, 1897*

In 1886 **Eugen Goldstein** (1850-1930) discovered what were referred to as "canal rays". These were streams of positively charged particles produced in a cathode ray tube, originating in the space between the cathode and the anode and travelling towards the cathode. If there was a hole in the cathode some of the positive particles passed through, giving rise to canal rays streaming away from the cathode but of course moving in the opposite direction to cathode rays. The specific charges of these particles were measured in 1897 by **Wilhelm Wien** (1864-1928) and found to be many thousands of times smaller than the specific charge of the electron. The actual value depended on the gas used in the cathode ray tube. He concluded that the canal rays consisted of atoms or molecules of the gas in the cathode ray tube which were given a positive charge when bombarded by the cathode rays as they accelerated along the cathode ray tube. The ions so formed were then attracted towards the cathode and gave rise to the canal ray phenomenon. Since different gases gave rise to different positive particles canal rays were not fundamental particles like electrons.

In 1911 the American **Robert Andrews Millikan** (1868-1953) calculated the quantity of charge on the electron in a series of experiments using the famous Oil Drop experiment. Millikan sprayed tiny droplets of 'the highest grade of clock oil' using an atomiser into the space between two metal plates to which a potential difference could be applied. The space between the plates was illuminated from one side and could be observed with a microscope. A radioactive source was used to ionise the air which in turn charged the droplets. In modern versions of the apparatus the droplets become charged by friction as they are atomised. With the electric field switched on the droplets were under the influence of four forces: (i) the gravitational force, (ii) the viscous drag of the air (friction), (iii) the buoyancy force, and (iv) the electrical force. The greater the charge they carried the greater the force of electrical attraction between the droplet and the oppositely charged metal plate. Millikan observed droplets moving at constant speed in the space between the plates. Using the fact that the four forces were in equilibrium when the droplets were moving at constant speed, Millikan was able to calculate the charge on each droplet he selected. After many measurements he was able to show that the charge on the droplets was always 1.592×10^{-19} coulomb or a whole-number multiple of that figure. This was the most accurate measurement of the electron charge for some time. The currently accepted value is 1.602×10^{-19} coulomb.

Radioactivity

In 1896 a French physicist, **Henri Becquerel** (1852-1908), was investigating whether various crystals could emit X-rays when exposed to sunlight. The crystals were placed next to photographic plates wrapped in dark paper with a copper grill sandwiched between the crystal and the photographic plate. The idea was that if X-rays were emitted from the crystal they could penetrate the dark paper and expose the photographic plate, except where they first struck the copper wires. Becquerel was expecting an image of the copper grill on the photographic plate as evidence of X-rays. One of the salts investigated by Becquerel was a uranium salt and during a break in his experiments due to lack of sunshine he discovered that an intense image of the copper mesh was formed on a photographic plate placed in a drawer with the uranium salt. Since there was no exposure to light a completely different phenomenon had been discovered by Becquerel other than the one his experiments were designed to investigate. Becquerel began to investigate the rays coming from the uranium which caused the exposure of the photographic plate and it soon became evident that other elements also emitted such rays.

About this time **Marie Curie** (1867–1934) and **Pierre Curie** (1859–1906) named the new phenomenon *radioactivity* and discovered two new elements, which were named polonium, after Marie Curie's native country, and radium, meaning 'giver of rays'. These elements were discovered through their radioactive properties, i.e. their nuclei were unstable and underwent spontaneous disintegrations to achieve more stable states.

Marie Curie is undoubtedly the most famous woman scientist. Here are some facts about her life which might help us to understand the reason for this.

Marie Sklodowska was born in Warsaw, Poland. Her father was a physics teacher and her mother was the principal of a girls' boarding school. Having finished school she became a governess but continued to study by herself. In 1891 she went to study in Paris where her elder sister was married. There she found big gaps in her knowledge and worked hard to improve. She was quite poor and struggled on her small allowance to pay her tuition fees and for food, fuel and lodgings. Her health suffered as a result of a poor diet and her sister and brother-in-law helped care for her.

In 1893 she obtained a degree in physics from the Sorbonne. She then began to work towards a degree in mathematics which she obtained in 1894.

In 1894 Marie met Pierre Curie (1859–1906), a physicist researching the electrical properties of crystals. They were married in 1895 and began to work as a team in Pierre's laboratory. Their first daughter, Irène, was born in September 1897. Marie Curie did not retire from her research to look after the baby which was very unusual at that time. Irène became a well-known scientist later on and also worked with a scientist husband, Frédéric Joliot.

Following the birth of her daughter, Marie began to investigate the nature of radioactivity. This phenomenon had been first reported by Henri Becquerel in 1896, but it was the Curies who first used the term 'radioactivity' in a paper in 1898.

Marie Curie investigated two uranium ores, pitchblende and chalcolite and noticed that they were far more radioactive than their uranium content alone could account for. She suggested that another radioactive element was present. Pierre abandoned his research into crystals to help her identify it.

The Curies announced that they had discovered two new elements, polonium and radium, in 1898. However the new elements had not yet been isolated. One of the difficulties was the price of pitchblende. The Curies solved this problem by obtaining a shed full of the waste residue left after the uranium had been extracted from the pitchblende. They used their savings to transport the waste directly from the mine in Bohemia, in what is now the Czech Republic, to Paris.

For the next four years the Curies worked in very spartan conditions and with great perseverance to finally isolate a tenth of a gram of radium chloride, proof that a new element had been discovered. This work was very tedious and was based on careful chemical separation techniques. It also involved quite a lot of heavy work, handling tonnes of pitchblende, most of which Marie did herself. And also during this time, Marie taught physics part time at a girls' school in Paris to help support her family.

Meanwhile the health of both Curies was deteriorating but they seemed not to make any connection between their general poor health and their work, although Pierre Curie wrote a paper about this time on the effects on mice of exposure to radioactivity. In 1903 a child, born prematurely, died. During the pregnancy Marie had been exposed to very high doses of radiation.

In this year also the Curies and Henri Becquerel were awarded the Nobel prize in physics for their work on radioactivity. The Curies were very ideological and refused to profit from their discoveries. They predicted the use of radium in the treatment of cancer about this time also.

In 1904 a second daughter, Eve, was born. Eve did not become a scientist but later accompanied her mother on lecture tours in America and Europe.

Pierre was made Professor of Physics at the Sorbonne in 1904. But in 1906 Pierre stepped into the pathway of a horse-drawn wagon and was killed. A month after his death Marie was back at work and took over Pierre’s position in the Sorbonne as assistant Professor. She was the first woman to become a professor in France.

Lord Kelvin had meanwhile questioned the whole concept of radioactivity on the grounds that it meant that atoms were subdivisible, which notion he rejected completely. He questioned whether radium and polonium were elements at all. Marie had not isolated polonium and had not separated radium from radium chloride. Thus, she began the tedious process of separating radium from pitchblende again and her health suffered the consequences.

In 1911, Marie Curie received the Nobel prize in chemistry for her work in isolating two new elements. She is one of the very few people to have been awarded two Nobel prizes in science.

During the First World War Marie Curie organised and raised finance for mobile radiological equipment on the battlefield. She and her daughter Irène visited the battlefields and trained other young women in the technique of using X-rays.

Her research resumed after the war but in the 1920s the health question loomed large. Workers in the radium industry, who painted numbers on clock dials with luminous radium-containing paint amongst other tasks, began to report sickness. Marie Curie was slow to accept that radium could kill as well as cure but eventually had to accept that this was the case. She helped raise money for further research into the properties of radium and its role in health by lecturing in America and Europe.

Marie Curie broke her wrist in a fall in her laboratory in 1932. It did not heal and was the beginning of the final deterioration of her health. Marie Curie died in July 1934 of leukaemia caused by exposure to radioactive materials.

Ernest Rutherford (1871–1937) was a physicist from New Zealand who had made radioactivity his area of special interest. Rutherford identified two types of radiation and named them α- and β-radiation. It was he who suggested in 1903 that radioactivity was the disintegration of atoms of an element by emitting small particles of matter, thus being transformed into atoms of another element. In 1906, α-particles were shown by Rutherford to be helium atoms with a dipositive charge; β-particles had been shown to be high speed electrons by Becquerel. In 1900 a third type of radiation had been observed by **Paul Villard** (1860–1934) and named γ-radiation. In 1914, Rutherford proved that γ-radiation was high-energy electromagnetic radiation.

The connection between radioactivity and the development of atomic structure was that it demonstrated that the atom was divisible, made up of smaller sub-atomic particles other than electrons, which were ejected from unstable radioactive atoms as they decayed. The study of radioactivity also revealed other information about atomic structure, e.g. the existence of a neutral sub-atomic particle and isotopy, and rapid progress on atomic architecture was made at the beginning of the 20th century. And most significantly, as Rutherford was continuing to investigate the properties of the particles emitted by radioactive elements he accidentally discovered information which led to a revision of J. J. Thomson’s model of the atom. (See Experiment 1.8, p. 30.)

Discovery of the Nucleus

In a very famous experiment, carried out by Rutherford’s assistants, **Hans Geiger** (1882–1945) and **Ernest Marsden** (1889–1970), a thin sheet of gold foil was bombarded with a beam of α-particles (which Rutherford had earlier shown were dipositive helium ions) from a radioactive source. An arrangement to detect the pathways followed by the α-particles upon striking the gold foil was used, see Fig.1.4. The detector consisted of a zinc sulphide screen on which a microscope was focussed. When the zinc sulphide screen was struck by an α-particle, a scintillation was observed.

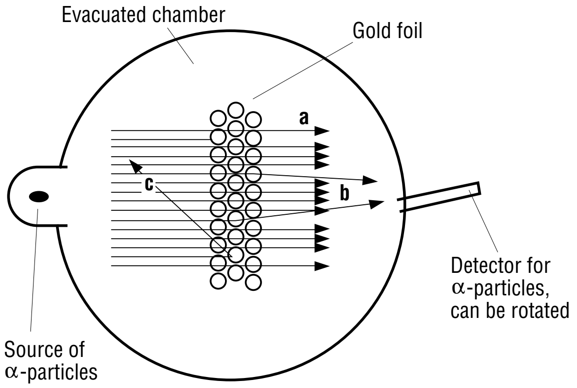

Fig. 1.4 *Bombarding gold foil with α-particles*

Rutherford and his assistants found that the majority of α-particles passed through the gold foil undeviated, some were deflected through large angles and a very few were reflected back along their original pathway.

Rutherford had analysed mathematically J. J. Thomson's plum-pudding model of a gold atom and anticipated the results of the experiment. He expected from his calculations that the α-particles would pass straight through gaps between the gold atoms (pathway a) or even be deflected through small angles from their original paths if they grazed atoms with positive charge uniformly distributed throughout them (pathway b). He was extremely surprised at the α-particles which were scattered through large angles (pathway c), as this only fitted in with an atom where the electrical field was concentrated within a small radius. He said, 'It was the most incredible event that ever happened to me in my life. It was almost as incredible as if you had fired a 15-inch shell at a piece of tissue paper and it came back and hit you.'

A series of similar experiments were carried out and the results were used to formulate a new description of the atom in 1910. Rutherford reasoned that the atom could not be solid but consisted of a very small dense central positive nucleus, which contained most of the mass of the atom, surrounded by an electron cloud which was largely empty space. This accounted for the fact that large numbers of the α-particles in his experiments passed through the gold foil undeviated, while some, if they grazed past the nucleus, were repelled by the positive nucleus through large angles and a very few were reflected back along their original pathways by colliding head-on with the nucleus. The fact that the electrons lay on the outside meant that they could be relatively easily removed and this accounted for electrical and electrochemical observations of the time. Electrical neutrality within the atom was maintained by having a certain total negative charge in the electron cloud and an equal positive charge in the nucleus. To account for the large angles of deflection as α-particles were repelled by the nucleus, Rutherford had to assume that the volume of the nucleus was very small in comparison to the volume of the whole atom.

Rutherford further calculated the quantity of charge in the nucleus and hence the number of electrons required to preserve neutrality. This number of electrons was equal to approximately half the relative atomic mass of the element.

Identification of the Proton

In a series of experiments carried out by Rutherford and his co-workers between 1911 and 1919, light atoms such as oxygen and nitrogen were bombarded with streams of fast α-particles in an evacuated chamber. In some of these experiments hydrogen nuclei were detected. The possibility that the hydrogen was present in small quantities at the beginning of the experiments was eliminated and it was established that the origin of the hydrogen nuclei was the break-up of the nuclei of the bombarded light atoms. This phenomenon had not been observed when gold or other heavy-metal elements were bombarded with α-particles because an atom with a large positive nuclear charge was capable of repelling the α-particles while a smaller nucleus was not. Thus, hydrogen nuclei were identified as fundamental particles of matter, present in the atoms of all elements. In 1920 Rutherford began to refer to the hydrogen nucleus as a proton[7] and this term crept into the literature from that time.

So, like the electron, the proton was not 'discovered' but rather identified as a fundamental particle of matter, shown to exist in all atoms. (See also section 1.13.)

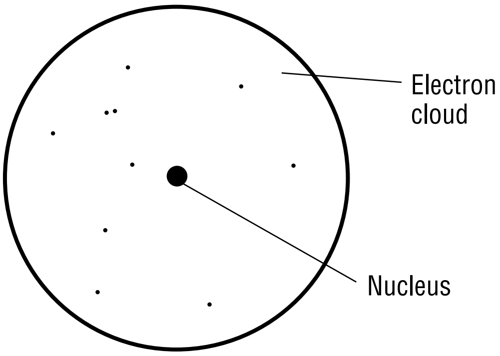

Fig. 1.5 *Rutherford's nuclear atom, 1910*

Rutherford's nuclear model of the atom had one major flaw – it could not obey the laws of classical physics. If the electrons in the electron cloud were motionless, then the electrostatic attraction between them and the nucleus would pull them into the nucleus. Or the electrons could be moving in circular orbits around the nucleus, like planets around the sun, where the electrostatic force was used to keep them from flying off at tangents from the atom. However, unlike a planet orbiting the sun, an accelerated charged particle should continuously lose energy, and thus speed, and the electrons should spiral into the nucleus. Either way, every atom in the universe would have long since collapsed – there was something wrong with the classical physics approach.

The Danish physicist **Niels Bohr** (1885–1962) proposed a model of the atom in 1913 which did not try to adhere strictly to the laws of classical physics. Niels Bohr was influenced by other physicists like **Max Planck** and **Albert Einstein** who had already departed from classical physics to account for other phenomena which were anomalous in terms of the older theories of light and mechanics.

1.6 Quantum Theory, Quantum Mechanics

Max Planck (1858–1947) had come up with an extraordinary new theory to explain black-body radiation. This is the emission of electromagnetic radiation from a perfect emitter/absorber at high temperature – in practice a small hole in the wall of a furnace. His new assumptions were that (i) only certain energies or multiples of these certain energies were permitted within the black body, and (ii) only radiation of certain energies or multiples of these certain energies could be emitted from the black body. In other words energy can only exist in these discrete packets or quanta and is not continuous. The concepts of continuous and discrete as applied to matter, energy, etc., can be difficult to communicate to Fifth Year pupils – the idea that money is used in quantum fashion might help, e.g. 21 pence is possible, 21.3 pence is not possible. Planck described his theory to the Berlin Physical Society on 14 December 1900, and a whole new realm of physics dates from then.

Albert Einstein (1879–1955) applied the new quantum theory to another phenomenon, the photoelectric effect – the emission of electrons from metals when electromagnetic radiation above a certain frequency is incident upon them. Again the experimental facts of photoelectric emission could only be explained by developing Max Planck's quantum theory further, and describing how energy was distributed in electromagnetic waves. In 1905 Einstein suggested that in electromagnetic radiation energy is not distributed in a continuous fashion but occurs in packets of energy of a certain size proportional to the frequency of the radiation. These packets of energy were called photons. A photon is a quantum of light energy. The energy, E, of the photon is given by

$$E = hf$$

where h is a very small constant number, Planck's constant, and f is the frequency of the particular electromagnetic radiation under consideration.

For example, the frequency of a beam of orange light may be 6×10^{14} Hz, the value for Planck's constant is 6.63×10^{-34} J s and so the energy of a photon of this light is only 3.98×10^{-19} J. The implication of this is that light consists of a stream of individual and separate photons travelling through space like a stream of particles rather than as had been previously believed as a classical wave with energy evenly distributed.

The quantum theory was further developed until it became quantum mechanics, a system of mechanics which proved useful in explaining the properties of atoms because of their small scale, and which is based on the idea that certain properties of a system, such as energy, angular momentum, charge, etc., cannot change by any amount but only by integral multiples of the relevant quantum for that property.

1.7 Atomic Spectra and the Bohr Model of the Atom

When an electric current is passed through a gas or if the gas is heated it emits electromagnetic radiation characteristic of that gas. This fact had long been known at the beginning of the 20th century and, as will be described later, it was the basis of a technique used to discover new elements and has many interesting modern applications. The visible light emitted by a sample of the gas was passed through a prism (or diffraction grating) in order to separate it into its constituent wavelengths. Infrared radiation and ultraviolet radiations were similarly analysed. The spectrum emitted by hydrogen atoms at low pressure (hydrogen gas, H_2, at low pressure separates or dissociates into neutral gaseous atoms at high temperature) was well documented. But it was not until Niels Bohr applied the new quantum mechanics to the hydrogen atom that a correspondence between atomic structure and the hydrogen spectrum was finally established.

The hydrogen spectrum consists of a number of series of lines. Each series consists of a set of lines becoming increasingly closer together until they end indistinguishably close at a definite wavelength. See Fig.1.6.

Only four lines lie in the visible part of the spectrum. These lines belong to the Balmer series. This series is named after a Swiss mathematics teacher who, in 1884, devised a formula to fit the positions of the lines on the spectrum[8]. The Lyman series, discovered in 1916, lies in the ultraviolet part of the electromagnetic spectrum; the Paschen, Brackett and Pfund series, discovered in 1908, 1922 and 1924, respectively, lie in the infrared region. These four series are named after those who originally reported their existence. The diagram only shows the first of these low frequency, low energy series; in theory there is no outer energy level so an infinity of series is possible.

Bohr accepted the Rutherford model of the atom, applying it particularly to hydrogen, and assuming that the single electron of hydrogen orbited the central nucleus in a simple circular orbit. He overcame the classical physics problem of the electron losing energy by assuming that its energy was quantised, i.e. that the electron could exist in certain stable states without losing energy. Each of these stable states was characterised by a quantum number, n, a positive integer. The lowest energy state, which had the smallest radius, was the $n = 1$ state, the next was the $n = 2$, etc. Calculation showed that the energy states

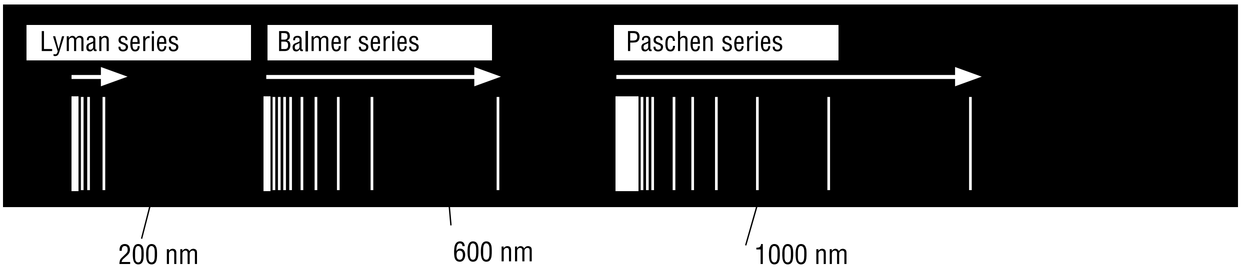

Fig. 1.6 *Spectrum of hydrogen*

became progressively closer to one another as the quantum numbers increased. The stable states can be termed energy levels, shells or orbits. The Bohr description of the atom is sometimes called the planetary model of the atom because it consists of a central body with a number of surrounding orbits of increasingly greater radius.

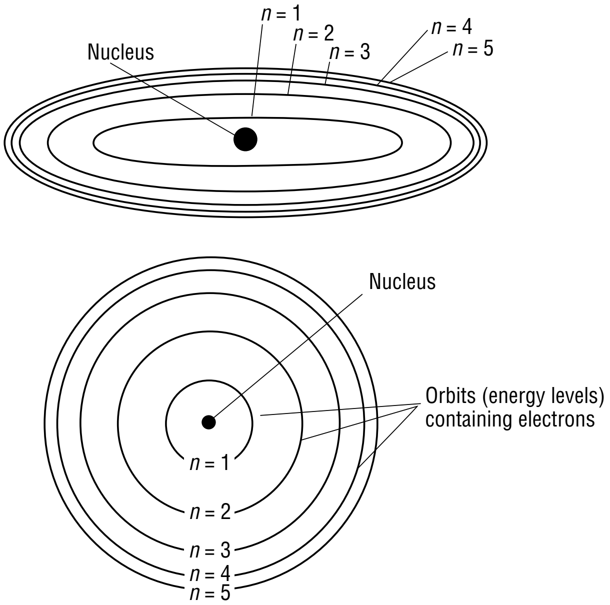

Fig. 1.7 *Bohr's planetary model of the atom, two views, 1913*

The lowest energy level is called the ground state. The electron in the hydrogen atom can move from the ground state to other higher energy states (sometimes called excited states) by gaining the exact quantum of energy corresponding to the energy difference between the higher and lower energy states. When an electron moves to a lower energy state it radiates a photon of electromagnetic energy again corresponding to the energy difference between the higher and lower energy states, i.e.

$$E_2 - E_1 = hf$$

where E_2 and E_1 are the energies of the higher and lower energy levels respectively, h is Planck's constant and f is the frequency of the emitted radiation.

Each individual line in the Balmer and Paschen series of the hydrogen spectrum could now be matched with an electron transition. Each series could be matched with a set of electron transitions from all possible higher energy states back to a particular state. Bohr predicted that there should be a series in the ultraviolet part of the spectrum corresponding to transitions of electrons from excited states back to the first energy level and this series was discovered by Lyman in 1916. Bohr also predicted the possibility that other lower energy series existed and this was shown to be correct[9], Fig. 1.8.

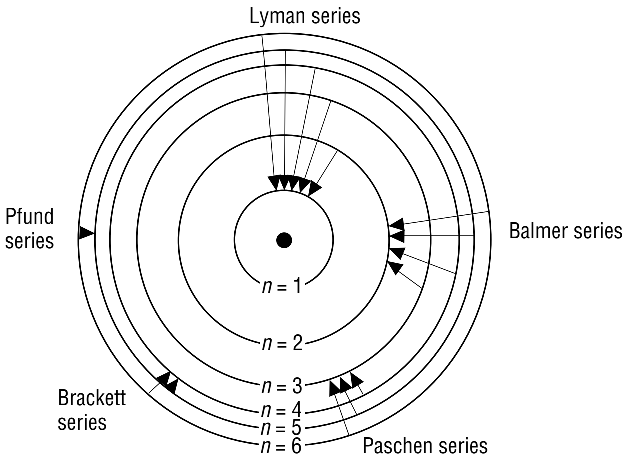

Fig. 1.8 *Origin of series of lines in the hydrogen spectrum*

The reason that all possible transitions are observed although hydrogen possesses only one electron is, of course, because in a sample of gas there is such a large number of hydrogen atoms that statistically there is a very high probability of all transitions being observed at once.

In 1890 a formula was devised by **Johannes Rydberg** (1854–1919), which was an adaptation of Balmer's formula for the visible lines in the hydrogen spectrum, to describe the exact positions of the lines on a spectrum. Neither Balmer's nor Rydberg's formula was based on any atomic model but simply described mathematically the position of the lines on the spectrum and could be considered a summary of experimental data. There was excellent agreement between the results obtained by Bohr based on mathematical analyses of his atomic model and the Rydberg equation for hydrogen. This correlation was good support for the Bohr theory.

However there were a number of faults with the Bohr theory and it needed much modification. The original theory was an important milestone in understanding atomic structure and was a good incentive to continue a wave-mechanical treatment to get a better-fitting model.

Flaws in Bohr Model

(i) It was only successful in explaining the hydrogen spectrum, and other one electron systems, e.g. He^+ and Li^{2+}. Even the next simplest case, helium, had a spectrum which was too complex for the theory.

(ii) Closer examination of the hydrogen spectrum with high resolution instruments revealed that some of the bright lines were actually double lines and triple lines very close together. These lines were not predicted by the Bohr model of the atom. The Zeeman effect, see below, could not be justified either.

(iii) The wave-particle nature of matter had not been discovered and the uncertainty principle had not been stated at the time of Bohr's theory. They had to be incorporated into any model of the atom.

See Experiments 1.9, 1.10, 1.11, pp. 31–33.

1.8 Bohr-Sommerfeld Model of the Atom

Bohr's theory was modified by the German physicist **Arnold Sommerfeld** (1868–1951) over the next number of years to make it more generally applicable. More quantum numbers were introduced in order to do this.

Extra Lines Seen at High Resolution

To account for the extra lines seen at high resolution in the hydrogen spectrum the idea of subsidiary energy levels of very similar energy within a given energy level (or subshells within shells) was introduced. Sommerfeld suggested, to account for the sublevels, that in addition to the original circular orbit there were also elliptical orbits – the set of ellipses and the original circular orbit comprised the energy level. To correspond to the doublets and triplets observed on the hydrogen spectrum it was necessary to assume that the $n = 1$ quantum level is not subdivided, but that the $n = 2$ level consists of two close-lying orbits, the $n = 3$ consists of three close-lying orbits, etc. These extra orbits give rise to the fine detail of the hydrogen spectrum. Sommerfeld was correct in assuming that there were subdivisions to main energy levels but his description of the sublevels had to be modified later.

A second quantum number was assigned to distinguish between the energy sublevels. For example an electron in the third energy level which consisted of one circular and two elliptical orbits could possess a subsidiary (or azimuthal) quantum number of $k = 3$, 2 or 1. A subsidiary quantum number equal to the main quantum number implied the electron was in a circular orbit, if the subsidiary quantum number was less than the main quantum number it meant the electron was in an elliptical orbit [10].

Extra Lines Seen in Presence of a Magnetic Field

The Zeeman effect was named after the German physicist **Pieter Zeeman** (1865–1943) who described it in 1896. This effect occurs when the sample of hydrogen whose spectrum is being viewed is placed in a very strong magnetic field. Some of the lines in the spectrum split up into more lines. The Zeeman effect was reviewed when Sommerfeld was refining the Bohr theory and to explain this observation the idea was introduced that some of the sublevels had different orientations in space and that in the absence of a magnetic field these different orientations had equal energies but in the presence of the magnetic field they had slightly different energies and therefore gave rise to a multiplicity of lines on the spectrum. Some orbits were unaffected by a magnetic field; others could adopt three, five or seven orientations, i.e. were tilted with respect to the magnetic field.

Sommerfeld assigned quantum numbers to describe electrons in the different orientations. He found that assigning a third quantum number, m, accounted for Zeeman's observations as follows:

that $m = k - 1, k - 2, ... 2, 1, 0, -1, -2 .... -(k - 2), -(k - 1)$. Thus for an electron with principal quantum number $n = 3$, i.e. in the third energy level, and subsidiary quantum number $k = 3$, there were five possible orientations in a magnetic field, labelled $m = -2, -1, 0, 1, 2$. If the electron had subsidiary quantum number $k = 2$, then there were three possible orientations in a magnetic field, $m = -1, 0, 1$ and if the electron had subsidiary quantum number $k = 1$, then it only had one orientation in an applied magnetic field, i.e. it was unaffected by a magnetic field, $m = 0$.

Further Fine Detail

It was found necessary to add a fourth quantum number to account for further spectral detail.

Accounts vary[10,11] as to whose idea it was originally. Certain fine structure doublets, not yet accounted for, implied yet further close-lying but distinct energy differences. These were taken into account by assigning a fourth quantum number, $j = +1/2$ or $-1/2$.

It was suggested in 1925 by **Samuel A. Uhlenbeck** (1900–1988) and **George E. Goudsmit** (1902–1979) that an electron in an atom possessed a property called spin which could be interpreted simply as the electron rotating either in a clockwise or anticlockwise direction about an imaginary axis. This interpretation was in keeping with the whole notion of a planetary model of the atom. There was a small energy difference between an electron spinning in a clockwise and an anticlockwise direction. This energy difference was taken into account by assigning the fourth quantum number. (See section 1.11, p. 18.)

So Bohr, Sommerfeld and others used quantum numbers to label an electron in an atom according to its energy and in doing so incorporated into Bohr's theory of atomic structure some information about subdivision of main energy levels, effects of magnetic fields and the property of electron spin. However, just as the finishing touches were put on the updated model of the atom, other developments rendered much of the theory invalid and in need of reconstruction.

1.9 Wave Mechanics

Wave mechanics is an improved version of quantum mechanics which developed as follows.

In 1924 **Prince Louis-Victor de Broglie** (1892–1987) suggested that if waves could behave like particles, as Planck and Einstein had indicated to explain black-body radiation and the photoelectric effect, then perhaps particles had wave properties. This is called wave-particle duality and was verified in 1927 by the American physicists **C. J. Davisson** (1881–1958) and **L. H. Germer** (1896–1971) by diffracting a beam of electrons, diffraction being behaviour considered typical of waves, (an application: the electron microscope). Note that the greater the momentum of the particle the shorter and more difficult to detect will be its wavelength and so the wave properties exhibited by an object like a tennis ball are unobservable.

But even before the verification of wave-particle duality was available the idea was taken up by the theoretical physicist **Erwin Schrödinger** (1887–1961). Schrödinger was born in Austria but became an Irish citizen in 1948[12]. He developed a set of highly complex mathematical formulae to describe the behaviour of an electron based on its wave-like properties. Using these wave equations to describe the behaviour of particles, like an electron, is termed **wave mechanics**. Just as any mathematical equation gives a set of points when solved, e.g. the solution to $x^2 + y^2 = 25$ is a set of points lying in a circle of radius 5, centre (0, 0), Schrödinger's wave equations when applied to an electron of a certain energy in an atom and solved, give a set of points where that electron has a high probability of being located. The sets of points map out three-dimensional spaces of particular shapes around the nucleus (all of Bohr's energy levels were 2-dimensional). It is not possible to determine absolutely the space occupied by an electron of a certain energy because of a principle called the Heisenberg uncertainty principle.

In 1927, **Werner Heisenberg** (1901–1976) proposed his uncertainty principle which states that it is not possible to determine simultaneously the momentum (hence velocity) and position of a moving particle with a high degree of accuracy. Consider an electron moving at a certain fixed velocity. To measure its position at some instant in time we beam electromagnetic radiation onto it. The photon of electromagnetic radiation which strikes the electron is absorbed, thus adding energy to the electron and in turn altering the kinetic energy of the electron. So the very act of measuring its position has changed its velocity and thus its momentum. In principle no method of measuring one of these quantities without disturbing the other can be devised. The statement, it can be shown, has no consequence in the macroscopic world of cars and tennis balls but it has extremely serious implications for discussion of the behaviour of the electrons in atoms.

1.10 Wave Mechanics Applied to the Atom

Schrödinger's wave equation for electrons of different energies in the hydrogen atom could only be satisfactorily solved for the energies predicted by the Bohr theory. As a mathematical necessity of the solution, quantum numbers similar to those used in the updated atomic model emerged with the solution, showing that the Bohr-Sommerfeld theory had some validity, although the shapes of the sublevels had to be completely revised. The solutions when plotted on three dimensional polar diagrams give a new and detailed picture of atomic structure. The solutions to Schrödinger's wave equations invalidated much of Bohr's original work because in the Bohr model of the atom it was assumed that the energy, position, etc., of the electron could be known exactly. Now we must accept that the exact position and momentum of any electron cannot ever be exactly stated and thus we cannot even say that an atom has an exact size, as in theory an electron may not reside inside any fixed boundary 100% of the time. This is the nature of wave mechanics and at first may be surprising and disturbing.

Four different types of solution to Scrödinger's wave equations emerged. Each of these is a three-dimensional space within which there is a greater than 99% probability of finding an electron of certain energy. Such a space was termed an **orbital** (the word being distinct from Bohr's word orbit but incorporating it just as this new wave-mechanical model of the atom incorporates Bohr's model).

One type of orbital is a spherical space, termed s, with the nucleus at its centre. Its size is determined by the energy level to which it belongs and is labelled accordingly.

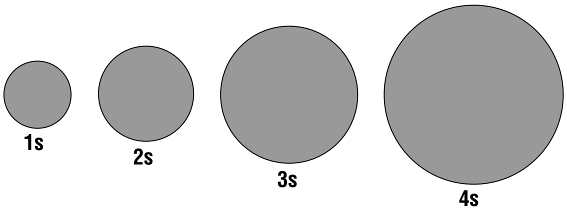

Fig. 1.9 *Set of s orbitals*

The next type of orbital, termed p, is dumb-bell shaped and is arranged about the central nucleus. For each principal quantum number except $n = 1$, three such dumb-bell-shaped orbitals exist at mutual right angles. The existence of three orbitals accounts for spectral observations in the presence of an applied magnetic field (the Zeeman effect). In the presence of an applied magnetic field all three orbitals have slightly different energies depending on their orientation with respect to the magnetic field; in the absence of a magnetic field they all have equal energies; the overall size is again determined by the energy level.

These p orbitals have a nodal point at the centre of the nucleus, i.e. there is zero probability of finding an electron at the centre of the nucleus. But then the question arises: how does an electron get from one side of the nucleus to the other?

This can be explained in two ways. Since the electron has wave properties, nodal points are points of zero amplitude but through which a wave can pass. Alternatively, the uncertainty principle makes it clear that an electron is not confined to an orbital; an orbital is only a region in which there is a high probabilty of finding an electron of certain energy.

Another feature of p orbitals is that they are anti-symmetric, i.e. the sign of the wave function (which may be thought of as the amplitude of the wave associated with the electron) changes on passing through the nucleus. This can be indicated on diagrams using plus and minus signs or using different colours. This change in sign is very significant when atomic orbitals combine to make bonds – only overlap of orbitals or parts of orbitals with the same sign can lead to bonding.

The third type of orbital, d, is even more complicated; there are two possible shapes and there are five different orientations in space. Four of these orientations are double dumb-bell-, or butterfly-, shaped orbitals and the fifth orbital is dumb-bell-shaped with a doughnut around its centre, Fig. 1.11. Nodal points exist in all of these orbitals and they are anti-symmetric.

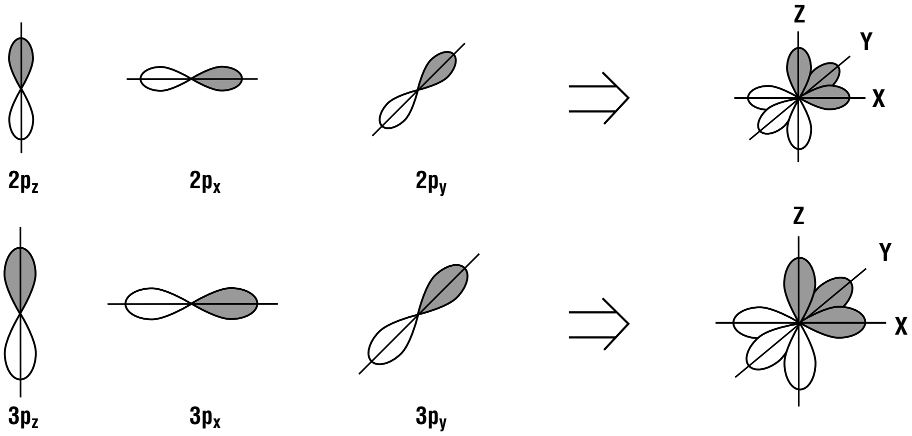

Fig. 1.10 *Sets of p orbitals*

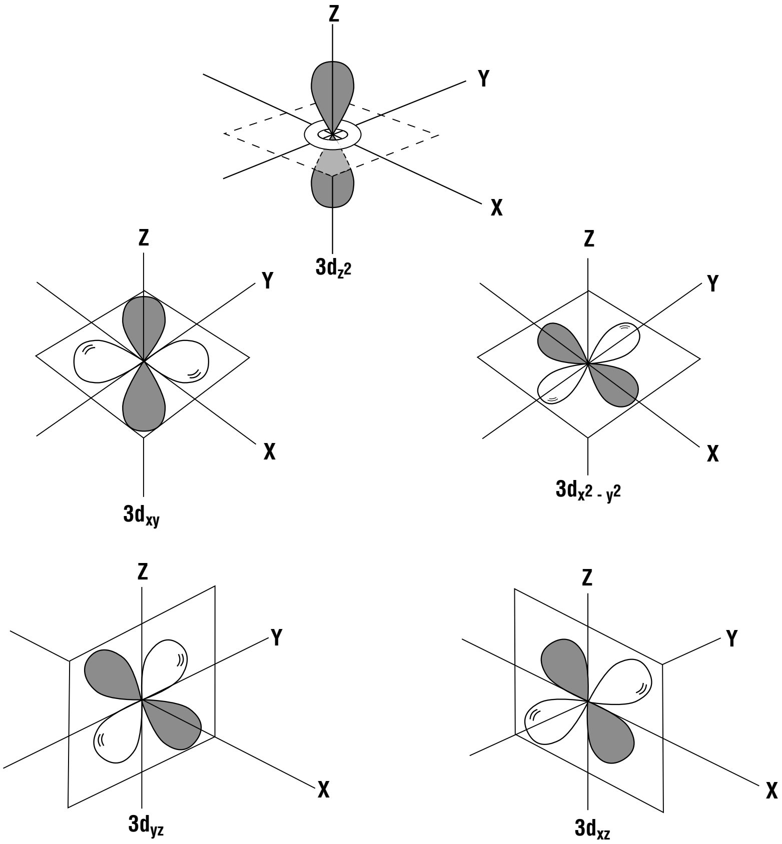

Fig. 1.11 *The 3d orbitals*

A fourth type of orbital, called an f orbital, is found to be made up of seven distinct parts but diagrams are almost meaningless when drawn in two dimensions without the aid of colour[13]. Again they have nodal points and are anti-symmetric.

The quantum numbers of the Schrödinger wave equations, which differ somewhat from the Bohr-Sommerfeld version, are as follows.

The principle quantum number, n, indicates the average distance between the electron and the nucleus. It can have any positive integral value.

The subsidiary (or azimuthal) quantum number, now denoted by l, determines which type of orbital is occupied by an electron. It can have any positive integral value less than n:

$$l \in \{(n-1) \ldots\ldots 0\}.$$

For an s sublevel, $l = 0$, for a p sublevel, $l = 1$, for a d sublevel, $l = 2$, etc.

Generally, l is not greater than 3, unless the atom is in an excited state.

The magnetic quantum number, m, determines which orientation in space is taken up by the orbital relative to an external magnetic field. For a given value of l, m can have values as follows:

$$m \in \{\pm l, \pm (l-1) \ldots\ldots 0\}.$$

Thus for an electron in a d sublevel, $l = 2$ and so there are five possible orientations in a magnetic field.

See Experiment 1.12, p. 34.

1.11 Relativity and the Atom

A fourth quantum number had been found necessary to completely account for spectral detail. This quantum number, called the spin quantum number, now denoted by s, does not emerge in the solution to Schrödinger's wave equations and while it was included to completely define the energy of an electron in an atom, spin is a property which is difficult to reconcile with wave mechanics, as spin on an axis is a particulate property. In 1928 **Paul Dirac** (1902-1984)[12] included the principles of relativity with wave mechanics and in the Dirac method of solving the wave equations, the fourth quantum number emerges as the consequence of the electron's relativistic speed. Spin can have the following values:

$$s \in \left\{\pm \tfrac{1}{2}\right\}.$$

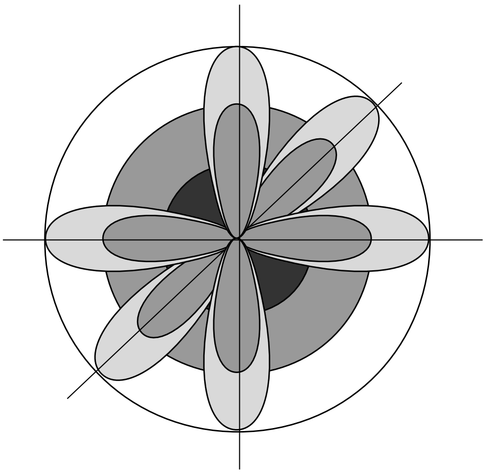

Fig. 1.12 *Schrödinger, Heisenberg, Dirac wave – mechanical model of atom, 1928*

1.12 Atomic Structure and Multi-Electron Atoms

The wave equations can only be solved absolutely for one-electron systems. However, sufficiently good approximations can be found for the more complex atoms, that we know that the atomic structure described for the hydrogen atom holds for larger atoms also. All that remains to be done is to describe some rules which apply to filling the electrons into such an atom.

As early as 1895 a study[14] of the periodic table had suggested that the elements occurred in groups of 2, 8, 8, 18, 32. In 1923, to fit in with his model of the atom which at that time had been modified by Sommerfeld to include energy sublevels, Bohr proposed[12] that electrons were distributed in shells according to a similar pattern, namely, 2, 8, 8, 18, 18, 32 electrons in each of the first, second, third, fourth, fifth and sixth shells, respectively.

Bohr approached the problem of electrons filling into atoms by considering a bare nucleus of charge +*z* and adding electrons in such a way that the previously bound electrons would be unaffected by the new electron added, i.e. electrons will occupy the set of lowest energy orbitals possible in an atom in its ground state. He called this approach the Aufbauprinzip (students of German will know that this means 'construction principle'. It is commonly called the **Aufbau Principle**[14]. Bohr did not actually know how many electrons could be accommodated in an s, p or d sublevel so was not able to assign electron configurations correctly. An electron configuration is the arrangement of electrons about the nucleus of an atom.

In order to account for spectral evidence of various elements, it must be assumed that no two electrons in the same atom have the same four quantum numbers. This means that an orbital can accommodate at most two electrons and then only if they have opposite spins. **Wolfgang Pauli** (1900–1958) deduced this generalisation in 1925 from a study of the spectra of elements other than hydrogen (to which it cannot apply, there being only one electron), and it is now known as the **Pauli exclusion principle** and stated thus: **no more than two electrons can occupy an orbital and this they can do only if the electrons have opposite spin.**

It follows that in the **first energy level** where $n = 1$, then $l = 0$ (i.e. there is one s sublevel), and $m = 0$ which means that there is one s orbital which we know holds a maximum of two electrons.

Similarly, in the **second energy level** where $n = 2$, then $l = 1, 0$ (i.e. there are two sublevels, a p and an s, respectively).

Where $l = 1$, $m = 1, 0, –1$, which means three p orbitals, each of which we now know can hold a maximum of two electrons.

Where $l = 0$, $m = 0$, which means again an s orbital, capable of accommodating at most two electrons.

Therefore in total the second energy level can hold eight electrons.

Similarly, in the **third energy level** where $n = 3$, then $l = 2, 1, 0$ (i.e. there are three sublevels, d, p and s, respectively).

Where $l = 2$, $m = 2, 1, 0, –1, –2$ which means five d orbitals each of which we now know can hold a maximum of two electrons.

Where $l = 1$, $m = 1, 0, –1$, which means three p orbitals each of which we now know can hold a maximum of two electrons.

Where $l = 0$, $m = 0$, which means again an s orbital, capable of accommodating at most two electrons.

Therefore in total the third energy level can hold eighteen electrons.

In this way[15] Pauli worked out a mathematical progression for the electron capacity of the energy levels within an atom:

$$\text{electron capacity} = \{2, 8, 18 \ldots\ldots 2n^2\}.$$

Hund's rule of maximum multiplicity, like the Pauli exclusion principle, is a generalisation deduced from the study of spectra of various elements. **Friederich Hund** (1896–) in 1927 observed that an orbital of highest spin and lowest magnetic quantum number is lowest in energy. The consequence of this is that whenever there is more than one orbital of equal energy (e.g. three 2p orbitals) available to electrons, the electrons will occupy them first singly (spin largest when orbital is singly occupied) before occupying them in pairs (spin total is zero when an orbital is occupied by two electrons of opposite spin).

It is now known that the orbitals in order of increasing energy are as follows:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s,
4f, 5d, 6p, 7s, 5f, 6d, 7p.............

The order of filling can be obtained by following the structure of the periodic table: there are two elements in the first period, corresponding to the 1s sublevel, eight in the second, corresponding to the 2s and 2p sublevels, eight in the third, corresponding to the 3s and 3p sublevels, eighteen in the fourth, corresponding to the 4s, 3d and 4p sublevels, etc. Following the arrows in Fig. 1.13, whose pattern is easily memorised, also gives the order of filling.

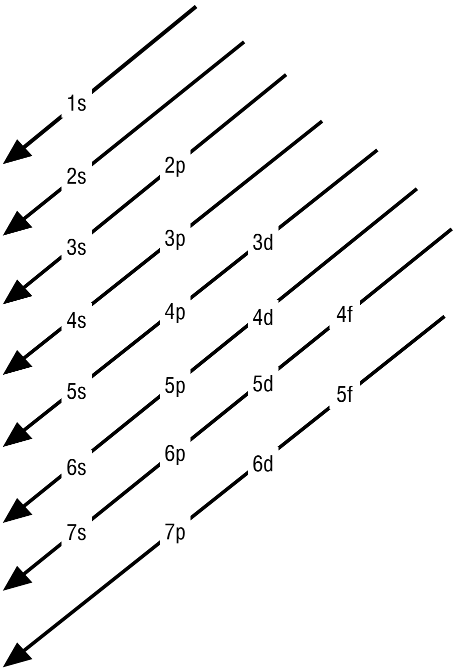

Fig. 1.13

Making use of the list of orbitals in order of least energy and the three rules given above, the electron configuration of an element is given as a list of occupied sublevels and the number of electrons in each. For the Leaving Certificate the highest energy p orbitals in the outer shell are listed separately. Some examples:

$$\mathrm{N = 1s^2,\ 2s^2,\ 2p_x^1,\ 2p_y^1,\ 2p_z^1;}$$

$$\mathrm{V = 1s^2,\ 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^3.}$$

There are occasional exceptions to these rules[17]. In chromium and copper the most stable electron configurations are found by experiment to be slightly different to those given by the rules above. The electron configurations for these two elements are listed below. It can be seen that in these cases the electron configuration with an exactly half-filled or filled d sublevel and a half filled 4s sublevel is more stable than the electron configuration with a completely filled 4s sublevel.

$$\mathrm{Cr = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^5}$$

rather than

$$\mathrm{Cr = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^4}$$

$$\mathrm{Cu = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^{10}}$$

rather than

$$\mathrm{Cu = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^9}$$

It is also important to note that when first row transition atoms lose electrons, they do so from the 4s sublevel first rather than from the 3d sublevel. This is because the 4s electrons are outside the 3d electrons. For example,

$$\mathrm{Ni = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^8}$$

becomes

$$\mathrm{Ni^{2+} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^8.}$$

It is usually during a discussion of electron configurations that a distinction is made between transition metals and d-block elements.

The d-block elements are those whose highest energy electron occupies a d sublevel. A transition metal may be defined as one which forms at least one ion with a partially filled d sublevel or one whose highest energy electron occupies an incomplete d sublevel. This allows a distinction to be made between the transition metals such as iron or manganese which exhibit variable valency and form coloured compounds and a metal such as zinc which has a fixed valency of 2 and only forms white or colourless compounds. Zinc, cadmium and mercury have a stable, complete d sublevel and have different chemical properties to the other d-block elements, because only their outer s electrons are involved in bonding.

Sometimes the elements scandium, yttrium, lanthanum and actinium are excluded from the transition metal group also. This is because these elements tend to have a fixed valency of 3, the result of the loss of their outer s electrons and the single d electron in the penultimate energy level.

1.13 Structure of the Nucleus

From the time of his discovery of the proton as a constituent of light nuclei, Rutherford began to describe the nucleus as consisting of a number of protons and 'nuclear' electrons. As mentioned earlier the nuclear charge had been calculated to be about half the relative atomic mass of an atom. Rutherford reasoned that a nitrogen atom, for example, should therefore consist of seven electrons located in the electron cloud, fourteen protons situated in the nucleus and, to preserve electrical neutrality, that the nucleus should also contain seven 'nuclear' electrons. Rutherford further suggested that the protons could probably combine with the nuclear electrons to give a neutral particle.

Discovery of the Neutron[18]

Thus, by 1920 Rutherford had predicted the existence and properties of the neutron but to him it was not a fundamental particle but actually composed of a proton and an electron. Because of its neutrality he predicted that such a particle could move easily through matter 'like an invisible man passing through Piccadilly Circus: his path can be traced only by the people he has pushed aside'.

In 1921, **Lise Meitner** (1878-1968) also thought it likely, to account for observations she made while studying radioactivity, that a neutral particle existed in the nucleus of an atom. She noticed that in many radioactive disintegrations the emission of an α-particle was followed by the emission of two β-particles and suggested that a neutral particle consisting of four protons and four electrons might exist in the nucleus.

The very neutrality of the neutron made it difficult to detect. In 1932, **James Chadwick** (1891–1974), who had been making 'a real search for the neutron' since 1924, found evidence for its existence. **Irène Joliot Curie** (1897–1956) (daughter of Pierre and Marie Curie) and her husband **Frédéric Joliot** (1900–1958) observed that when fast α-particles from a polonium source struck beryllium atoms, very penetrating radiation was produced. This penetrating radiation was powerful enough to knock protons out of hydrogen-rich compounds such as paraffin wax. The Joliot-Curies thought that the radiation was high-energy electromagnetic radiation. Chadwick, working in the famous Cavendish Laboratory, (cf. Rutherford's comment above about the invisible man pushing aside people in Piccadilly Circus) took up the study. He measured the recoil of the hydrogen atoms subjected to the penetrating radiation, and from the laws of conservation of momentum and energy, found results consistent with the radiation consisting of streams of neutrons having a relative mass of 1. Further experiments were carried out, bombarding atoms other than hydrogen with the penetrating radiation. The heavier the bombarded nucleus, the slower the recoil velocity, just as would be expected if the radiation consisted of particles of relative mass 1.

Chadwick, like Rutherford, thought that the neutrons were composed of a proton and an electron. Measurements of the mass of the neutron seemed to support this idea since the measured mass was less than the combined masses of a proton and an electron. This is exactly what Einstein's mass-energy relationship ($E = mc^2$) would suggest: the mass (energy) of a composite must be less than its constituents otherwise it would be unstable.

A more accurate measurement of the mass of the neutron helped to have this view of the neutron revised. In fact the neutron mass is larger than the combined mass of a proton and an electron suggesting that it is a fundamental particle. This description of the neutron was not immediately accepted because it meant that β-radiation became apparently inexplicable: if a neutron does not 'contain' an electron, how do β-particles arise? The answer came in a theory put forward by **Enrico Fermi** (1901–1954) in 1933. **George Gamow** (1904–1968), a Russian-American physicist, expressed it thus: the β-particle is no more in the nucleus until the instant it is emitted than a bubble exists until it is blown.

Discovery of Isotopes

Between 1911 and 1913 **Frederick Soddy** (1877–1956) put forward explanations for the disintegration of radioactive elements forming new elements. When the end products of the three radioactive series found in nature, the thorium, the uranium and the actinium series, were examined it was found that the same element, lead, was formed, but that it had a slightly different relative atomic mass in each case, $^{208}_{82}\mathrm{Pb}$, $^{206}_{82}\mathrm{Pb}$ and $^{207}_{82}\mathrm{Pb}$. Ordinary lead had an accepted relative atomic mass of 207.2 at the time. The name ‘isotope’, meaning the same place in Greek, was suggested by Frederick Soddy for different versions of the same atom. Soddy received the 1921 Nobel prize in chemistry for his work.

In 1920 J. J. Thomson began a search for isotopes among the lighter elements. He took a device similar to that used in his experiment to calculate e/m for the electron but with the polarity reversed and filled it with neon gas. Beams of positive ions were attracted along the tube and passed through a cylindrical cathode with a central hole less than a millimetre in diameter. The narrow beam of positively charged neon ions then passed through a magnetic field where they were deflected by different amounts according to their mass and finally fell upon a photographic plate where a number of traces confirmed neon ions of different masses and thus the existence of neon isotopes. That nearly all the elements possessed isotopes was quickly shown – in fact all the chemical elements possess several isotopes, many naturally occurring, others produced artificially in nuclear reactors or particle accelerators[10].

Francis William Aston (1877–1945) developed this apparatus further so that it was capable of measuring the masses of the different isotopes accurately[l8]. He received the Nobel prize in chemistry in 1922 for this work. The modified version became known as the **mass spectrometer** and became the definitive method for measuring atomic masses and finding out relative abundances of isotopes. Later it was developed for use in qualitative analysis of compounds which decay into fragments in a mass spectrometer in a characteristic fashion and can thus be identified.

All nuclei with the exception of the most abundant isotope of hydrogen contain neutrons. The electrostatic repulsive force between protons in a nucleus is balanced by the short-range strong nuclear force – the attractive force which acts between all nucleons (i.e. protons and neutrons). The strong force between the neutrons and between the neutrons and the protons increases the stability of the nucleus by increasing the total attractive force in the nucleus. The neutrons further help to stabilize the nucleus by increasing the distance between the protons and hence decreasing the repulsive forces between them. In stable isotopes, with the exception of the most abundant isotope of hydrogen and one isotope of helium, there are always at least as many neutrons as protons and more neutrons than protons in the heavier elements. Note that there is no stable isotope of any element above lead (Z = 82) but some elements, although radioactive, have such long half-lives that they are regarded as nearly stable[10,19].

The Mass Spectrometer

The mass spectrometer, first developed in 1920 by Francis Aston, has become a very important analytical tool. Its main use until about 1970 was in cataloguing the relative abundances of the isotopes of the elements. It was then modified to determine the molecular masses of unknown organic compounds and help determine their structures. This is now the principal use of the mass spectrometer.

The process of measuring atomic mass involves injecting the sample of the element to be analysed in the gaseous state into an evacuated chamber. The sample is bombarded by a stream of high-energy electrons which dislodge electrons from within the atoms of the sample to produce mostly monopositive ions.

$$\mathbf{M + e^- \longrightarrow M^+ + 2e^-}$$

The positive ions produced by electron impact in this way are directed into an electric field which accelerates the ions to a uniform kinetic energy.

The ions then enter a magnetic field where they are deflected into circular paths, the radii of which depend only on the masses of the ions (since they all have equal charges and kinetic energies). Ions of smaller mass suffer the greater deflection. A detector placed in the path of the ions records the relative number of ions of each mass. The detector may be a photographic plate in which case all the ions are detected simultaneously by the density of the images produced when ions of each different mass fall at different positions on the plate. In modern mass spectrometers, the mass spectrum is usually produced by scanning, i.e. detecting the isotopes one at a time starting from the smallest and working up or *vice versa.* This involves keeping the radius of the circular path the same for each ion and scanning from low to high magnetic field strength or *vice versa*. A slit is placed in the ion beam, in the pathway of the smallest ions, with the magnetic field set at a certain strength. The ions pass through the slit and fall on an electrical plate. The total charge accumulated on the electrical plate in a certain time gives the relative abundance of the ion. The procedure is repeated with the next heaviest ions in turn, which can be made to fall on the slit by increasing the magnetic field strength. Modern mass spectrometers are linked to a microprocessor so it is possible to obtain a graphical display of the relative abundances of the isotopes of the sample element. The diagram, Fig. 1.14 shows a representation of the different parts of a mass spectrometer.

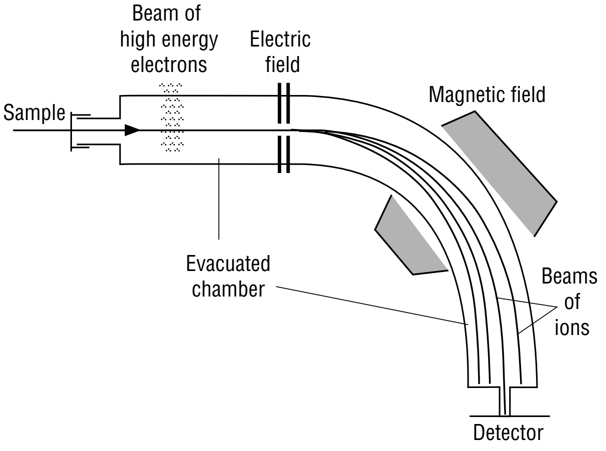

Fig. 1.14 *Representation of a mass spectrometer*

If an organic sample is to be analysed isotope abundances are not very important. The analysis concentrates on the compound composed of the isotopes of greatest abundance of its constituent atoms. Again the sample is injected into the evacuated chamber in the gaseous state where it is bombarded with the high speed electrons. An electron is knocked out of the organic compound and a positively charged ion results as described earlier. This ion is usually unstable and begins to fragment, forming smaller positively charged ions. An organic sample, having a very large number of molecules, will break up to produce a whole array of fragments all of which enter the electric field, where they are accelerated, and the magnetic field, where they are deflected according to their masses. A detector in the pathway records the relative abundance of each fragment. The ion of highest mass is the parent ion, whose mass is the molecular mass of the compound. Modern mass spectrometers used in organic analyses are linked to a microprocessor and a database of mass spectrograph analyses of thousands of organic compounds. It is therefore possible to see a display or obtain a printout of the array of fragments and their masses and identify an organic sample by its mass spectrograph if it matches a compound in the library of mass spectra.

The mass spectrum of the simple organic compound, propanone, is shown in Fig. 1.15. The peak at 58 corresponds to the compound propanone. The small peak at 59 is also the parent compound but it contains heavier isotopes. The peaks at 43 and 15 correspond to the

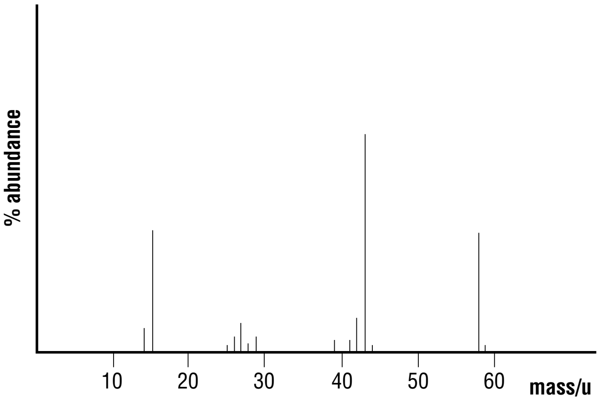

Fig. 1.15 *Mass spectrum of propanone*

fragments CH_3CO and CH_3 produced when the parent compound disintegrates. Analysis of the masses of the fragments can be useful in deducing the structure of an organic compound which must be identified.

Other Elementary Particles

In 1928, Paul Dirac predicted the existence of a new type of particle, an antimatter particle, the positron, identical to an electron but possessing the **opposite charge.** He predicted that annihilation of matter takes place when a positron and an electron collide. In 1932 the existence of the positron was confirmed. In 1930 W. Pauli predicted the existence of an even stranger entity, a massless, chargeless particle, the neutrino, (little neutral one), whose existence was confirmed in 1956. A whole zoo of elementary particles is now known to exist and a branch of physics is devoted to the search for order in this new chaos of muons, mesons, neutrinos, positrons, etc. In this world it is thought that the electron, a member of the lepton family, is truly elementary but that protons and neutrons, both of which are classed as hadrons, are themselves composed of more elementary particles called quarks.

Chemistry concerns itself only with interactions of the outer electrons of atoms which are involved in bonding, chemical changes, etc. The classification of elementary particles, the studies of nuclear reactions, the forces which bind the nucleons together and radioactivity were left to physicists. As Dirac said in 1929 ‘the underlying physical laws necessary for a large part of physics and the whole of chemistry are thus completely known’.

It may be a little dismaying for some chemistry students to find how large a role was played by physicists and mathematicians in discovering the internal structure of the atom while chemists appeared to take a back seat. The truth is that it was the skill of mathematicians and physicists who dared revise classical physics which allowed atomic structure to be described. However, chemists quickly applied this information to explain the properties of the elements, trends in the periodic table and bonding and thus to advance the subject of chemistry. That no resentment existed is clear from the fact that Nobel prizes were awarded to Rutherford and Aston and Marie Curie and later to Otto Hahn (nuclear fission) for their contributions to the advancement of chemistry.

1.14 Problem Solving

Just how are all those problems mentioned in the introduction solved as the result of an understanding of atomic structure?

Spectroscopy

According to an article called ‘The Centenary of the Bunsen Burner’ by Georg Lockemann published in the *Journal of Chem. Ed.,* 29, 281, 1952, **Robert Wilhelm Bunsen** (1811–1899) invented his famous burner to provide a steady, non-smoky, non-luminous flame of good heating power for his laboratory in Heidelberg.

This invention led to the invention of another important laboratory gadget, the spectrometer.

This was the subject of another article by T. H. Pearson and A. J. Ihde in the *Journal of Chem. Ed.,* 33, 20, 1956.

‘Bunsen had been making use, in qualitative analysis, of the flame colours imparted by different metallic salts to the colourless Bunsen burner flame. In order to distinguish between similar flames he had viewed them through coloured solutions or glasses.

Kirchhoff, at about this time, pointed out that one might better pass the light through a glass prism and view the spectrum. In acting upon the suggestion, the pair developed their instrument for viewing flame colours. The instrument represented no new principles or devices, but brought together on one stand the necessary collimating and viewing telescopes with the prism enclosed inside a blackened box.’

The inventor of the atomic absorption spectrometer is the Australian Alan Walsh. The principle of this instrument is to analyse for any one of about 67 of the elements by heating the sample to about 3000 °C so that it is atomised and then passing radiation from a special discharge tube containing the same element through the sample and examining the radiations absorbed. The idea is that if sodium is to be analysed a discharge tube containing sodium is heated to excite the sodium atoms and release the characteristic electromagnetic radiation of sodium. As this radiation passes through the sample any sodium atoms present will absorb the radiation as atoms absorb when in the ground state the same radiations as they emit when excited. The intensity of the light which passes through the sample is measured and since the amount of absorption is related to the number of sodium atoms in the sample, the concentration of sodium present can be calculated. Nowadays the process is highly sophisticated and several elements in trace quantities can be analysed simultaneously while a computer calculates the results and provides a printout of same.

See *Chemistry in Britain*, Vol. 22, 1986, starting page 116 for a number of articles on Atomic Absorption Spectroscopy.

Pyrotechnics

The colours of fireworks are produced by simply exciting the right atom for the right colour: sodium for yellow, strontium for red, magnesium for white, etc. See Experiment 10 on Flame Tests. Experiment 9 will demonstrate the link between atomic structure and lighting.

Emergency flares and photographic flash cubes also rely on exciting atoms.

See *The Magic of Chemistry*, B. Iddon, BDH Publication, 1985 for more information on this topic.

Astronomy

‘Astronomers have always wondered how the sun generates its enormous output of heat. At first, they thought it was literally burning, like a giant lump of coal. In the last century astronomers calculated how long a lump of coal the size of the sun would last before it burnt out. The answer was disappointingly short – only a few thousand years. An American astronomer put it in perspective by pointing out that the state of Pennsylvania contained enough coal to supply the United States for many centuries, yet it would not keep the sun shining for even a thousandth of a second.’ *The Stars from Superstition to Supernova*, H. Couper and N. Henbest, Pan Books, London 1988.

So what is the sun made of?

‘The atom “signs its name” in its spectrum. One of the great values of spectroscopy to the astronomer now becomes clear. He or she can identify atoms which compose a distant object by recording its spectrum and comparing it to the spectra of different elements produced in the laboratory. For example, some of the lines of calcium (Ca), iron (Fe), hydrogen (H), magnesium (Mg), sodium (Na) and argon (Ar) have been identified in the solar spectrum.’

Dynamic Astronomy, R. T. Dixon, Prentice-Hall International Editions, London, 1989.

Psychology

Why do scientists spend long hours in the laboratory, foregoing other activities and pleasures? Why do athletes endure months of training in preparation for competitions?

Abraham Maslow, an American psychologist, proposed an interesting way of classifying human motives. Maslow devised a hierarchy of needs ascending from the basic biological needs to the more complex psychological motives that become important only when the basic needs have been satisfied, Fig. 1.16.

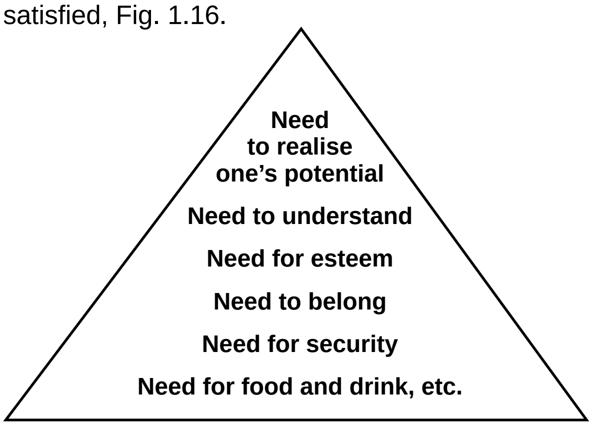

Fig. 1.16 *Maslow’s hierarchy of needs*

Pollution Control

'One of the trickiest trace elements to determine accurately is tellurium. It is rare in the Earth's crust, but because of the lack of sensitive analytical techniques, geochemists are not sure just how rare. Its concentration in seawater has simply never been reported. Researchers in the department of earth, atmospheric and planetary sciences at the Massachusetts Institute of Technology are studying the North Atlantic ocean basin with the aim of understanding what happens to transient elements. They hope to quantify the mechanisms by which reactive elements such as Al, Be, Bi and Te are removed, because these elements are analogues of reactive pollutants being introduced to the oceans and could be used to predict the effects of pollution.'

Chemistry in Britain, April 1985, Vol 21, page 330.

To do this the scientists at MIT have developed a technique based on detecting and monitoring tellurium levels by studying its spectrum.

1.15 Experiments

Experiment 1.1

To Demonstrate the Minute Size of Particles

Student experiment.

This gives practice at calculating factors of dilution and will emphasise the need for thorough rinsing in volumetric analysis when students meet it later. It also makes the concept of parts per million easier to understand.

Materials

Water
White paper
Crystalline $KMnO_4$
Graduated cylinders – 10 cm^3, 100 cm^3

Safety

Wear safety spectacles throughout.
$KMnO_4$ is harmful and oxidising.

Procedure

1. Select one small crystal of $KMnO_4$ and dissolve it in 1 cm^3 of water in a 10 cm^3 graduated cylinder. Note colour.
2. Fill the graduated cylinder with water to the 10 cm^3 level. Note dilution by a factor of ten. Note colour.
3. Transfer contents of the small graduated cylinder to a 100 cm^3 graduated cylinder. Rinse out small graduated cylinder a few times and add washings to 100 cm^3 cylinder. Fill to 100 cm^3 mark. Note dilution of the original solution by a factor of one hundred. Note colour.
4. Discard all but 10 cm^3 of this solution and again fill graduated cylinder up to 100 cm^3 with water. Note dilution. Note colour.
5. Repeat Step 4 until the colour of the potassium permanganate can no longer be seen against a white background.

Conclusion

What can be concluded from this experiment about (i) the size of particles and (ii) the number of particles in a small crystal?

Particle size must be very small and the number of particles in a crystal very large.

Experiment 1.2a

To Demonstrate the Particulate Nature of Matter by Diffusion of Hydrogen Chloride and Ammonia

Teacher demonstration.

Materials

Piece of glass tubing about 1 m in length and 2 cm in diameter
Sticky labels
2 rubber bungs to fit the tubing
Cotton wool, in pieces small enough to be inserted into ends of tubing
2 retort stands and clamps
0.88 ammonia solution
conc. hydrochloric acid (approx. 36% w/w)
forceps
glass rod

Safety

Wear safety spectacles throughout.
Fire polish ends of glass tubing.
Both HCl and ammonia are corrosive.
Ammonium chloride is harmful.
Use fume cupboard.

Procedure

1. Show effect of fumes of HCl coming into contact with fumes of ammonia by holding a glass rod dipped in HCl over the mouth of a beaker containing a little ammonia solution.
2. Clamp glass tube in a horizontal position. Label one end ammonia and the other HCl.
3. Dip a piece of cotton wool in ammonia solution and another in conc. HCl solution. Using forceps insert each piece of soaked cotton wool into the appropriately labelled end of the tubing and seal with the rubber bungs.
4. Observe.

Discussion

Has any bulk movement of matter, either gas or liquid been observed? No.

How can the appearance of a white ring along the tube be explained? Formation of ammonium chloride when ammonia gas and hydrogen chloride gas meet.

Is the ring nearer the end labelled ammonia or hydrochloric acid? Nearer the hydrochloric acid end.

Why is the ring formed nearer one end than the other? Ammonia diffuses faster than the hydrogen chloride.

Experiment 1.2b

To Demonstrate the Particulate Nature of Matter by Diffusion of Potassium Permanganate through Water

Student experiment.

Materials

Pipette
Solution of $KMnO_4$
Beaker
Water

Safety

Wear safety spectacles throughout.
$KMnO_4$ is harmful and oxidising.

Procedure

1. Using the pipette place a drop of $KMnO_4$ solution at the bottom of a beaker of water.
2. Observe.

Conclusion

The purple colour of the $KMnO_4$ spreading slowly through the water can be explained if the drop is composed of a large number of small particles which move through the water.

Experiment 1.3

Growing Crystals

Teacher demonstration.

Materials

Supersaturated solution of sodium ethanoate ($CH_3COONa\ 3H_2O$) in a conical flask which can be heated gently

Tight-fitting stopper for conical flask

Safety

Wear safety spectacles throughout.

Procedure

1. Prepare a supersaturated solution of sodium ethanoate by heating very gently about 200 g of sodium ethanoate in the conical flask. It dissolves in its own water of crystallisation. Allow to cool and a supersaturated solution of sodium ethanoate is formed.
2. Seed with a small crystal of sodium ethanoate and rapid crystallisation occurs.
3. Store conical flask and contents for re-use.

Conclusion

The growth of the crystals can be explained by the notion of small particles in the concentrated solution coming together in regular arrays to form the large crystalline mass.

Experiment 1.4
Boyle's Law

Teacher demonstration.
Can serve as graph drawing exercise for students.

Materials

Boyle's law apparatus, coloured oil type
Pump
Barometer
Graph paper and drawing equipment

Safety

Some versions of this apparatus have a plastic screen secured in front of the glass tube as a safety precaution in the event of a pressure burst. A free-standing plastic safety screen or safety spectacles for teacher and students should be used otherwise.

Procedure

1. Note atmospheric pressure, note pressure reading on Bourdon gauge of apparatus. The Bourdon gauge may only read the extra pressure applied during the experiment. If so atmospheric pressure read from the barometer must be added to each reading. Attach pump to tap of apparatus. Open valve.
2. Pump oil out of reservoir and up the glass tube by applying pressure with pump. Keep pumping until the volume of air in the glass tube is small or reading on pressure guage is maximum.
3. Note pressure reading on Bourdon gauge, add atmospheric pressure if necessary. Note volume of air.
4. Open tap a little to release some pressure. About seven points are needed to draw a graph, so the volume should be allowed increase in six increments. Some oil returns to the reservoir as the volume of air expands. Because of the viscosity of the oil and to allow the temperature to return to room temperature a little time must be allowed for the oil to reach its new level so that an accurate volume can be read.
5. Repeat Steps 3 and 4 until the pressure applied with the pump has been released.
6. Close tap and detach pump.
7. Plot a graph of pressure versus inverse of volume. A straight line through the origin verifies Boyle's law.

Notes

Students sometimes find it difficult to see the connection between the graph and the experiment. To get an appreciation for how graphs represent experimental data, the students can be shown, during the experiment and again on the graph, that when the pressure doubles the volume of gas halves.

Discussion

What do you think would happen to a gas when pressure was applied to it, if it was not made up of separate particles but was continuous?

Experiment 1.5
Kinetic Theory of Matter

Teacher demonstration.

Materials

Kinetic theory apparatus

Power supply

Safety

A free-standing plastic safety screen or safety spectacles for teacher and students should be used.

Procedure

1. Connect terminals of kinetic theory apparatus to d.c. power supply set to recommended voltage.
2. Switch on. The small plastic or metal spheres behave in a manner similar to the way we believe the particles of gas do, i.e. they exhibit rapid random motion. The 'lid' is free to move and can be seen to be bombarded by the moving particles.

3. The effect of increasing temperature can be demonstrated by increasing the applied voltage, i.e. supplying more energy. Note particles move faster and that they bombard the 'lid' more energetically than before and push it up so that they occupy greater volume – Charles's law.
4. The effect of increasing pressure can be demonstrated by increasing the mass of the 'lid' but keeping the same applied voltage. Note particles bombard the 'lid' as energetically as before but because of its greater mass, cannot push it up as much as before so that they occupy a smaller volume – Boyle's law.

Experiment 1.6
To Demonstrate Brownian Motion

Student experiment or teacher demonstration.

Brownian motion is the continuous random motion of tiny solid particles, about a micrometre in diameter, in a fluid medium. It was first observed in 1827 by botanist **Robert Brown** (1773-1858) when studying pollen particles although he was not able to explain it. Later it was recognised to be the result of collisions between the solid particles and moving particles of the fluid.

Materials

Microscope
Whitley Bay smoke cell
Cover slip
Smoke from a burning string
12 V power supply

or

Microscope slide
Suspension of Aquadag (colloidal graphite) in water
Microscope

Safety

Wear safety spectacles.

Procedure

1. Fill the smoke cell cavity with smoke from the burning string. Cover cavity with a cover slip.
2. Attach leads from the 12 V power suply to the smoke cell lamp terminals and switch on the power supply.
3. Position smoke cell on stage of microscope and focus microscope on cell.
4. Observe.

Alternative Procedure

1. Transfer a drop of the Aquadag suspension to the glass slide.
2. Examine with microscope.

Discussion

Describe the motion of the smoke – straight line motion or curving motion? It is often described as straight line, rapid, random motion.

Experiment 1.7
To Demonstrate Some Properties of Electrons

Teacher demonstration.

The student needs to know that electrons are emitted by a hot metal and will travel along an evacuated chamber towards a positively charged plate.

Materials

Cathode ray tube from the physics lab.; the Teltron range of cathode ray tubes is specially designed for demonstration purposes and safe handling by the students themselves. For this experiment the e/m tube is most suitable.

Power supplies, two 0–5 kV d.c., 6 V a.c.; one 12 V d.c.

Helmholtz coils

Universal holder

Safety

Wear safety spectacles.

Procedure

1. Fit the e/m cathode ray tube to the universal holder and connect the 6 V a.c. terminals of one 0–5 kV power supply to the heater of the tube and the high voltage terminals to the anode (positive) and cathode of the tube.
2. Switch on and allow a short time for the cathode ray tube to heat up.
3. Observe the beam of cathode rays (electrons) passing in a straight line along the front of the phosphorescent screen.
4. Switch off and connect the second 0–5 kV d.c. power supply set at approximately 2 kV to the metal plates above and below the phosphorescent screen so that the upper plate is connected to the positive of the power supply. (If a second 0–5 kV supply is not available the plates may be connected to the first supply.)
5. Switch on both power supplies and note the deflection of the stream of electrons. Switch off the second 0–5 kV power supply, reverse connections, switch on again. Note the deflection of the beam.
6. Switch off both power supplies and fit the Helmholtz coils to the universal stand. Connect the 12 V d.c. power supply to the coils. When switched on a magnetic field will be generated between the coils at right angles to the plane of the phosphorescent screen.
7. Switch on the first 0–5 kV power supply and the 12 V power supply to the Helmholtz coils. Note the deflection of the beam of electrons. Switch off the 12 V power supply, reverse connections, switch on again. Note the deflection of the beam.

Discussion

What two properties of the electron does this experiment demonstrate? That it travels in straight lines, unless deflected in an electric or magnetic field. The direction of deflection indicates that electrons are negatively charged.

Television uses three cathode ray guns to produce the full colour picture on the screen.

Experiment 1.8
Properties of α, β and γ-radiation

Teacher Demonstration.

Materials

Geiger-Müller (GM) tube and holder
Scaler/timer or ratemeter
Sealed radioactive sources:
α-emitter, e.g. americium-241, used in domestic smoke detectors
β-emitter, e.g. strontium-90, used to power small radio transmitters
γ-emitter, e.g. cobalt-60, used in cancer treatment
Source handling tool, e.g. forceps
Set of absorbers:
aluminium and lead sheets of thickness approx. 0.2 mm to 1.5 mm.
Lead, aluminium, steel, beechwood and polystyrene blocks of thickness approx. 30 mm.
Tissue paper in a plastic mount
Radioactivity bench to hold absorbers, sample.

Safety

Wear safety spectacles.
Do not handle sources directly, use forceps.
Do not eat or drink in the vicinity of radioactive materials.
Wash hands after the experiment.
Store sources in secure place.

Procedure

1. Assemble apparatus by attaching the Geiger-Müller tube to its holder and connecting the holder by cable to the scaler/timer or ratemeter. The Geiger-Müller tube holder is attached to one end of the radioactivity bench.

2. Remove GM tube window cover. Take a background count for 5 minutes. Calculate average background count over one minute.
3. Remove the α-source from its container and attach to the bench using the mounting peg located at the opposite end of the bench from the GM tube. Handle the source only with forceps.
4. Move the source closer to the GM tube in 5 cm intervals taking a one-minute count at each position. Replace α-source in its container using the forceps. Subtract background count from each reading. Draw a graph of count versus distance from GM tube window.
5. Repeat steps 3 and 4 with β-source and γ-source in turn.
6. Investigate the relative penetrating power of each type of radiation by placing each source in turn about 4 cm from the GM tube window and inserting sufficient absorbers between the GM tube window and the source to reduce the count to near the background count.

Notes

Although the experiment is low risk when the usual precautions are observed, it is stated in the chemistry syllabus that a video of this demonstration may be used.

Conclusion

The graphs show that, depending on the source used, the range of α-particles in air is a few cm, β-particles have a range of up to several m in air and γ-radiation is very penetrating.

The α-particles can be absorbed by paper, β-particles by a few millimetres of aluminium, γ-radiation only by several centimetres of the dense metal, lead.

Experiment 1.9
Observing Spectra

Student experiment.

Materials

Direct vision spectroscope or spectrometer

Some or all of the following light sources:

tungsten light source
indirect sunlight, e.g. bright sky
sodium lamp
sodium street lamp
neon lamp
fluorescent tube
CFL light source
mercury vapour lamp
mercury street lamp
cadmium lamp

Safety

Wear safety spectacles.
Do not look directly at the sun with the naked eye or through an optical instrument.

Procedure

1. Observe and describe the spectrum associated with a tungsten lamp filament as viewed using a direct vision spectroscope. This type of spectrum is associated with a hot metal. It is a continuous spectrum.
2. Observe and describe the spectrum of the sodium lamp or flame and the sodium street lamp viewed with the spectroscope. This type of spectrum is associated with excited atoms. It is a line spectrum.
3. Observe and describe the spectrum of the fluorescent tube viewed with the spectroscope. This type of spectrum is associated with excited molecules. It is a band spectrum. The line spectrum of the mercury vapour in the tube can be seen in the background.
4. Now view the other light sources using the direct vision spectroscope. Note the colours observed. Identify the type of spectrum in each case.

Conclusion

Is there any difference between the spectrum of the tungsten lamp filament and that of the indirect sunlight (bright sky)? Fraunhofer lines are obvious in spectrum of indirect sunlight. See Section 2.1.

Experiment 1.10
Flame Tests

Student experiment.

The chloride or nitrate salts are suitable for use in this experiment. There is no colour imparted to the flame by the elements chlorine, oxygen or nitrogen. This is related to the ionisation energies of the non-metallic elements which tend to be large, the atomic radii of these atoms being smaller and the nuclear charges bigger than metals of the same period. More energy must be supplied to excite electrons in these non-metallic ions and therefore there are no emissions of visible electromagnetic radiation. The sodium test should be carried out last because the yellow colour of sodium is very dominant and persistent.

Materials

A few grams of some or all of the following salts:

copper chloride or copper nitrate
strontium chloride or strontium nitrate
barium chloride or barium nitrate
lithium chloride or lithium nitrate
potassium chloride or potassium nitrate
sodium chloride or sodium nitrate

An unknown chloride or nitrate (or a mixture of two salts if the students have access to a spectroscope)
100 cm^3 beaker about one-third full of conc. HCl
Bunsen burner
Lighter
Flame test rod (platinum wire sealed in a glass rod is the recommended instrument but dissecting pins from the Biology lab. work well, as do lollipop sticks soaked overnight in water; nichrome wire may also be used but a fresh piece is required for each test)
Sheet of cobalt glass

For alternative procedure: one litre garden sprayers, one for each sample
Solutions of 1-3 g of each salt in approx. 30% ethanol in water

Safety

Wear safety spectacles.
Do not look directly at the sun with the naked eye or through an optical instrument.
Exercise care with Bunsen flame, tie back long hair, etc.
Concentrated HCl is corrosive and should be kept in the fume cupboard.
Barium chloride, barium nitrate, copper chloride, copper nitrate, lithium chloride, potassium chloride, sodium chloride, strontium chloride are harmful.
Calcium chloride is an irritant.
Lithium nitrate and potassium nitrate are oxidising.
Sodium nitrate is both harmful and oxidising.
Strontium nitrate is irritating and may cause fire on contact with combustible material.

Procedure

1. Light the Bunsen burner. Clean the flame test rod by dipping it in the beaker of conc. HCl and holding it in the Bunsen flame until the normal Bunsen flame colour can be seen again.
2. Dip the flame test rod in conc. HCl again and then in the salt to be tested. Some salt should adhere to the rod.
3. Hold the rod in the Bunsen flame. Make a note of any colour observed. View flame through cobalt glass and note any colour change observed.
4. View flame using the direct vision spectroscope. Identify the type of spectrum observed. Note the colours observed.

Alternative Procedure

1. Light the Bunsen burner.
2. Spray lightly a solution of the salt in ethanol into the Bunsen flame.

Notes

Flame tests for Li, Na, K, Ba, Sr and Cu only are specified on the syllabus.

A few grams of each salt in a sample bottle reserved specially for flame tests avoids the risk of contamination of a large quantity of a substance during this experiment. A work station for each sample could be set up, with the students rotating around to the samples. This avoids having to prepare several samples for each group.

This practical can be done in conjunction with tests for anions. Tests for the chloride, carbonate, nitrate, sulphate, phosphate, sulphite and hydrogencarbonate anions are specified on the syllabus.

Conclusion

copper	– shades of blue/green
strontium	– scarlet
barium	– green
lithium	– crimson
potassium	– lilac
sodium	– yellow

What metal(s) is (are) in the unknown chloride or nitrate?

The purpose of the cobalt glass is to absorb yellow light. Is the potassium chloride salt supplied contaminated with a sodium salt? Probably, nearly all salts are contaminated with trace quantities of sodium salts.

How is it possible to distinguish between metals which give similar flame colours? The wavelengths of the emitted light would have to be measured accurately. Then a distinction could be made using spectroscopic data for the two elements.

Experiment 1.11
Observing Emission Spectra Using Discharge Lamps

Teacher demonstration.

Materials

Direct vision spectroscope (a spectrometer and diffraction grating could also be used to view the spectra)

Some or all of the following discharge tubes:

- hydrogen discharge tube
- nitrogen discharge tube
- neon discharge tube
- argon discharge tube
- oxygen discharge tube
- sodium lamp or sodium flame pencil
- mercury vapour discharge tube

Holder for discharge tubes
Power supply, 3 kV, a.c.

Safety

Wear safety spectacles.
Do not look directly at the sun with the naked eye or through an optical instrument.

Procedure

1. Fit each one of the discharge tubes to the holder in turn and connect the power supply.
2. Switch on and allow a short time for the discharge tube to heat up.
3. The students can observe the colour of the discharge and view the spectrum with a direct vision spectroscope. The students should be able to identify each spectrum as either line or band emission spectrum.
4. Examine the spectrum produced by the sodium lamp which behaves as a sodium discharge tube.

Discussion

What type of spectrum is observed as the sodium lamp heats up? The spectrum of neon, the inert gas present in the bulb.

The line spectrum of the hydrogen atom, unfortunately, cannot be viewed in this manner. The spectrum of molecular rather than atomic hydrogen is obtained using school equipment because there is not sufficient energy to dissociate the molecular hydrogen.

Experiment 1.12
To Construct Models of Atomic Orbitals

Student experiment.

The use of models in chemistry is important to provide students with an idea of the three-dimensional nature of atoms, molecules, crystals, etc. Commercial models of atomic orbitals are available from the Aldrich Chemical Co., The Old Brickyard, New Road, Gillingham, Dorset SP8 4JL, but are expensive (the 1992–1993 sterling price was £115) but a model-making exercise is valuable in itself. The materials mentioned here are simple to use, readily available, cheap, re-usable and may suggest more ambitious modelling projects to students and teachers. Alternatively the six-coordinate frames from molecular model kits can be used to construct a set of x, y and z axes.

Materials

Modelling materials, e.g. plasticine for orbitals

Wire for axes

Safety

Wear safety spectacles.

Procedure

1. Construct a plasticine sphere to represent an s orbital and insert three wires at mutual right angles to meet at the centre of the sphere to represent the x, y and z axes. One wire can be clamped vertically.
2. Construct three sets of dumb-bell shapes centred on a piece of wire to represent three p orbitals. Arrange the wires at mutual right angles to represent a p sublevel.

Discussion

Define an orbital.

State two differences between a 2s orbital and a 3s orbital.

1.16 References

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CHAPTER 2

PERIODIC CLASSIFICATION OF THE ELEMENTS

2.1 The Elements

In ancient times nine elements were known, carbon (charcoal), sulphur (brimstone), gold, silver, iron, lead, copper, tin and mercury. All of these metals occurred free in nature or could be easily isolated from their ores.

Arsenic was known by 1200 AD and phosphorus was discovered by the alchemist **Hennig Brand** while investigating the golden colour of urine in 1669. Zinc and antimony were also discovered in the middle ages. By the end of the seventeenth century thirteen elements had been discovered.

But in fact at this time, although thirteen elements had been isolated, named and in use, scientists did not actually know what an element was. The Greek notion of the four elements, earth, air, fire and water had persisted. Another theory held that all the metals were composed of the 'principles' sulphur and mercury. **Paracelsus** (1493–1541), an alchemist interested in finding chemical remedies for illnesses, added a third element to sulphur and mercury, namely salt, which represented the body; thus there was the theory of the *Tria Prima*. **Jan Baptist van Helmont** (1577–1644) maintained that water was the basis of all substances and carried out many experiments to demonstrate the importance of water. He carried out one particular experiment with a willow tree over a five year period – the tree was planted in a weighed amount of earth and watered regularly for five years. At the end of this time the earth weighed the same as before but the tree had gained 74 kg. Van Helmont claimed that this proved that water had been converted into other substances and therefore was the origin of all chemical materials. In 1661 Boyle argued in the *Sceptical Chymist* that since chemists could not agree on whether there were one, two, three or four elements, that the idea of an element, as obtained at the time, should be abandoned altogether. He refused to accept, for instance, that gold could be separated into sulphur, mercury and salt 'till either experience or competent testimony hath convinced me of it'. The concept of elements was such a useful one that chemists held on to the idea despite Boyle's criticisms but were now open to the idea that not all the 'elements' had to be present in all substances. In 1686 **Nicolas Lémery** (1645–1715) defined a 'chemical principle' as a substance which is 'separated and divided, so far as we are capable of doing it with our imperfect powers' which of course is close to our modern idea of an element.

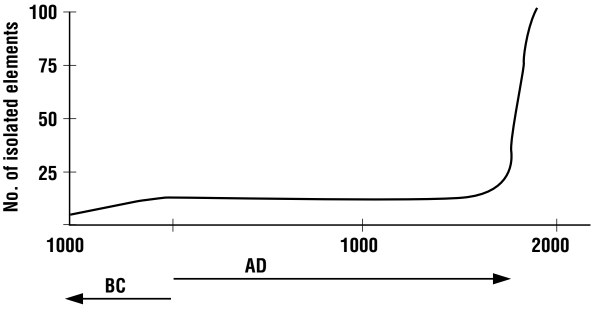

Fig. 2.1 *Discovery of the elements as a function of time*[1,2]

From 1740 onwards, as the graph (Fig. 2.1) shows, there was a dramatic increase in the number of elements which had been discovered. Some important metallic and gaseous elements were discovered around this time, e.g. platinum (1748), nickel (1751), hydrogen (1766), nitrogen and oxygen (1772), chlorine and manganese (1774), tellurium and tungsten (1783), molybdenum (1790), etc. It is worth noting that different sources quote different dates and discoverers for some of the elements.

In 1787 **Antoine-Laurent Lavoisier** (1743–1794) defined elements as substances which had not yet been decomposed in chemical reactions and listed thirty-three elements although he erroneously included light and heat as well as a few compounds in the list. This Lavoisier was the giant of eighteenth century chemistry. (‘Chemistry is a French science; it was founded by Lavoisier of immortal fame’ wrote **Adolph Wurtz**, a French chemist in 1869.) It was Lavoisier who clarified a number of important issues in chemistry. As well as providing a definition of an element, in 1773 he stated clearly that there were three states of matter and that a substance could exist in the three different states according as it had ‘a greater or lesser quantity of the matter of fire’. Fire was still thought to be a substance and all flammable materials were thought to contain phlogiston or fire which was ejected as the material burned. This is in complete contradiction to the observation that metals when burned become heavier by combining with oxygen and not lighter. The apparatus used by the eighteenth century chemists for heating was sometimes so powerful that they often evaporated some of the metal oxides formed and thus recorded a loss in mass. Organic compounds of course do appear to lose mass as they burn because the products are gaseous. In 1773 Lavoisier, after careful measurements, accounted for the increase in mass of metals upon burning by suggesting that air was added to metals during combustion. Later, in 1778, he revised his theory to propose that a single constituent of air, oxygen, was involved in the combustion process. The properties of hydrogen gas were described in 1766 by **Henry Cavendish** (1731–1810). Oxygen was discovered independently by **Carl Wilhelm Scheele** (1742–1786) and **Joseph Priestley** (1733–1804) between 1771 and 1774 and carbon dioxide had been isolated in 1756 by **Joseph Black** (1728–1799). These discoveries helped Lavoisier reach his conclusions and clarify the process of combustion.

Lavoisier was also the first influential western scientist to state formally the principle of conservation of matter in 1789. It had been given in the writings of the Russian scientist **Mikhail Vasil’evich Lomonosov** (1711–1765) in 1750 but his work was not well known. The idea that matter is neither created nor destroyed in chemical reactions had been assumed by most scientists since the time of van Helmont and Lavoisier also applied it effectively to chemistry and used it to write modern chemical equations.

Elements continued to be discovered, often serendipitously, by a variety of means, but there were a few notable methods of discovery which allowed a systematic search for elements to be made and in each case a number of other elements were discovered as a result.

Electrolysis

One of the next milestones in the discovery of the elements was the use of electrolysis to separate metals from their ores. Electrochemistry is a branch of chemistry which dates from 1800 when **Alessandro Volta** (1745–1827) constructed the electric pile, the forerunner of the modern battery. It was then discovered that the passage of an electric current through some compounds, e.g. water, caused decomposition or electrolysis. **Humphrey Davy** (1778–1829) investigated this new phenomenon and was able as a result to isolate for the first time in 1807 the elements sodium and potassium and in 1808 the elements calcium, magnesium, barium and strontium.

The ease of isolation of a metal from its ore is related to its position on the electrochemical series, i.e. a series which lists the elements in order of decreasing reactivity. The most stable metals are found free in nature or can be easily isolated from their ores by heating, e.g. copper which was consequently known in the oldest civilisations. The next most stable elements are those like iron or zinc whose ores are quite stable and can only be converted to metallic form by heating in the presence of a reducing agent. The third group of metals form such stable compounds that a supply of electrical energy is needed to bring about conversion to the metal.

Spectroscopy

Around 1860 **Robert Bunsen** (1811–1899) and **Gustav Kirchhoff** (1824–1887) discovered a new method of hunting for elements, namely spectroscopy. As described earlier, Bunsen first used the flame colour of elements as a method of qualitative elemental analysis and used coloured glass and solutions to distinguish between elements which emitted similar colours. Only minute traces of an element or its compound were required for this analysis. Kirchhoff suggested separating the emitted light into its component colours using a prism to allow the spectrum of each element to be analysed in more detail. In this way spectral lines inconsistent with any of the known elements were identified and led to the discovery by Bunsen and Kirchhoff of caesium in 1860 and rubidium in 1861. Also in 1861 the element thallium was discovered by **William Crookes** (1832–1919) using spectroscopic methods.

Indeed this new strategy for discovering elements led to the identification of the element helium in the sun before it was isolated on earth. When the solar spectrum is closely analysed it can be seen to be crossed by numerous black lines. These were named Fraunhofer lines after **Joseph Fraunhofer** (1787–1826), the optician who first investigated their positions and wavelengths. There are about 30 000 of them and they were later attributed by Kirchhoff to absorption by cool gases in the sun’s atmosphere of the light emitted by the hot gases in the sun’s core. When cool, elements absorb the same frequencies they emit when hot. Thus, many of the lines could be assigned to various elements known at the time. In 1868 **Norman Lockyer** (1836–1920) and others attributed a set of unassigned Fraunhofer lines to an element not known at the time on earth. Lockyer suggested the name helium (from the Greek for the sun, *helios*) for this element. Ramsay did not isolate helium on earth until 1894.

Inert Gases

The isolation of the first inert gas, argon, is another example of the discovery of one element leading to a general way of discovering a number of other elements. Argon was isolated as the result of collaboration between **Lord Rayleigh** (1842–1919), a physicist and **Sir William Ramsay** (1852–1916), a chemist. They found evidence that air contained a previously unidentified inert component and agreed that Rayleigh would investigate its physical properties while Ramsay investigated its chemical properties. They met with little encouragement because nitrogen is also unreactive and the gas in question could not be separated from nitrogen. Some suggested that the inert gas was an allotrope of nitrogen in the same way that ozone was an allotrope of oxygen. But the spectrum of the gas being investigated by the pair contained lines which did not occur in the spectrum of any known element, so they persisted. Ramsay could not bring about any chemical reaction of the gas and christened it argon, from the Greek *argos*, meaning idle or inactive. Then, making use of the fact that the rate of diffusion of a gas is inversely proportional to the square root of its density, Rayleigh was finally able to remove the nitrogen and isolate the argon by passing the mixture through porous earthenware and using various physical measurements, e.g. atomic mass, density, spectrum, specific heat capacity, etc., to distinguish between them. These measurements confirmed that a new element had been isolated and that, unlike other gaseous elements, it was monatomic.

Then Ramsay identified the gas given off by certain uranium-containing minerals as another monatomic gas and realised that it was helium, the element which had been identified by Lockyer and his co-workers in the sun in 1868. The search was then on for further inert gases. By liquefying air and fractionally distilling it in a very tedious separation process Ramsay and his co-workers isolated three more inert gases, neon, krypton and xenon (all in 1898).

Radioactivity

The discovery of radioactivity, like many other important scientific discoveries, was an accidental one while another phenomenon was under investigation. **Henri Becquerel** (1852–1908) was investigating the fluorescence (the emission of light from a source irradiated with electromagnetic radiation, usually of greater frequency than that emitted) from uranium salts as part of an investigation into the newly-discovered X-rays. The uranium salt when exposed to light fluoresced but also emitted radiation which penetrated black paper wrapping a photographic plate. This led Becquerel to suppose that the salt was emitting X-rays when exposed to light. But then he discovered that the salt emitted these rays even when left in the dark and thus began the study of this strange behaviour called radioactivity (see section 1.5).

The very famous Curie couple, Pierre and Marie, began to investigate the chemical properties of these radioactive materials. They began with a large supply of waste uranium ore, pitchblende, and from this isolated two new elements, polonium and radium. Another element, actinium, was found in pitchblende by **André Debierne** (1874–1949) in 1900. Studies of radioactivity also led to the identification of the element protactinium in 1925, independently by a British team led by **Frederick Soddy** (1877–1956) and by **Lise Meitner** (1878–1968) and **Otto Hahn** (1879–1968) in Germany. The radioactive element francium was discovered in 1939, and named after France, the native land of its discoverer, **Marguerite Perey** (1909–1975).

The first 92 elements are sometimes described as the 'naturally occurring' elements although it is now known that some elements of atomic number greater than 92 occur in nature[3]. In all, only 80 elements possess non-radioactive isotopes. The elements from bismuth to uranium are radioactive but some have isotopes with sufficiently long half-lives for them to be considered stable. The most stable isotope of uranium (mass number 238) has a half-life of 4.5×10^9 years.

The elements after uranium in the periodic table are called the transuranic elements[3]. Trace amounts of the first transuranic element, neptunium, occur in nature as the result of neutron capture by the uranium-238 isotope and the second transuranic element, plutonium, occurs in uranium ore. At present there are in all eighteen transuranic elements known, most of which can only be manufactured in nuclear reactions and some of which have ever only been made in minute quantities. However some elements are produced in sizable quantities and have practical uses, e.g. americium is used in household smoke alarms, plutonium is used to power heart pacemakers and as a nuclear fuel.

Naming the Elements

Sources: C.E. Jones in *The School Science Review*, 1970, **179,** p.326

D.W. Ball in *J. Chem. Ed.*, 1985, **62,** p.787.

Modern chemical nomenclature originated in a scheme devised in 1787 by Lavoisier and others, *Méthode d'une nomenclature chimique*. According to this scheme any newly discovered element was to be recognisable as a metal or a non-metal from its name by ending the name in -um if a metal and -on if a non-metal. This led to some misnomers e.g. 'selenium' and 'tellurium' were believed to be metals when found and 'helium' was assumed to be a metal when detected spectroscopically in the sun's atmosphere in 1868 and named by Lockyer.

It was generally accepted that the discoverer had the honour of naming the new element although Berzelius said 'I do not think that the author of the discovery ought to count for much' when A. G. Ekeberg isolated a new element and wished to call it columbium. Today it has the name that Berzelius suggested for it, tantalum. Again, when Reverend W. Gregor discovered a new element in the sands of his parish, Menachan, in Cornwall, and wished to name it after the place, Berzelius disliked its name also and the name the element eventually received was titanium, suggested by Klaproth, a German chemist. In most cases however the name was chosen by the discoverer.

Many of the names were based on Latin or Greek.

The alchemical symbols for the elements were replaced by Berzelius about 1814. He was the first to use one or two letters of the element's name to represent it. Where the names of several elements began with the same letter, the Latin name was sometimes used, with the exception of tungsten; the symbol W comes from the German, Wolfram. Although the names of the elements do vary from language to language, the symbols generally form an international language for chemists.

Ten elements are named after heavenly bodies (cerium, helium, mercury, neptunium, palladium, phosphorus, plutonium, selenium, tellurium, uranium), nine have names from European mythology (titanium, vanadium, cobalt, nickel, niobium, promethium, tantalum, mercury, thorium), ten after their own colour or the colours of their compounds (bismuth, chlorine, chromium, gold, iodine, iridium, praseodymium, rhodium, silver, zirconium), four take their names from the colours of their spectra (caesium, indium, rubidium, thallium), others are named after their physical properties, e.g. osmium comes from the Greek 'to smell' and bromine from the Greek 'bad smell'. Many elements are named after places or countries. France is the only country which has had two elements named in its honour (francium and gallium) and the small town Ytterby in Sweden has been the origin of the names of no fewer than four elements, yttrium (Y), erbium (Er), terbium (Tb), and ytterbium (Yb). Many unusual minerals originated from a quarry in Ytterby and these elements were extracted from the minerals. Many of the more recently discovered elements have been named after prominent people of Science: they include, amongst others, nobelium (No), curium (Cm), einsteinium (Es), and of course mendelevium (Md).

Elements that never were

In The School Science Review, 1987, **224**, p. 507, R. A. Schibeci refers to 'ghostly' elements or elements that never were:

'. . . the isolation of 'virginium' was reported in an American chemistry journal [J. of Amer. Chem. Soc., 1932, **54**, p. 613–5]. Subsequent experiments showed that this 'new' substance was not in fact an element.'

'These reports of the discovery of new "elements" can be used in chemistry teaching to illustrate the important idea that chemists are human; they sometimes see what they want to see.'

The Naming of Elements 104 to 109

In recent years there has been considerable debate among scientists regarding the names to be assigned to elements 104–109. Traditionally the discoverer of a new element has had the honour of naming the new element. However, problems have arisen with regard to elements 104–109 because different groups claimed first discovery. Claims for the discovery of new elements are adjudicated by the Commission on the Nomenclature of Inorganic Compounds of IUPAC. This committee also approves the name of the element and the symbol, which must be unique and have no more than two letters.

While conflicting claims were being adjudicated, the IUPAC commission assigned the following interim names and symbols to the elements (Table 2.1).

Atomic Number	*Name*	*Symbol*
104	*Unnilquadium*	*Unq*
105	*Unnilpentium*	*Unp*
106	*Unnilhexium*	*Unh*
107	*Unnilseptium*	*Uns*
108	*Unniloctium*	*Uno*
109	*Unnilennium*	*Unn*

Table 2.1

In 1992 a committee called the Transfermium Working Group reported on its investigation into the competing claims for the discovery of the elements. The committee made decisions on the discovery of the elements and names were assigned to the elements. However, these decisions were disputed and this has led to some confusion about the names.

Element 104, for which Russia and America share the credit, was called rutherfordium, Rf, (after Ernest Rutherford) by scientists in the USA and kurchatovium, Ku, (after Igor Kurchatov) by scientists in Russia. Element 105, for which again the credit is shared, was called hahnium, Hn, (after Otto Hahn) by scientists in the USA and nielsbohrium, Ns, (after Niels Bohr) by scientists in Russia. Element 106, discovered by the Americans alone, was assigned no name at that time. Element 107 was called nielsbohrium, Ns, (after Niels Bohr) by the Germans who discovered it. Element 108 was called hassium, Hs, after the Latin name Hassia for the state of Hesse where the German research group credited with its discovery was located. Element 109, discovered by the Germans, was called meitnerium, Mt, after the Austrian Lise Meitner.

In March 1994 element number 106 received the name of seaborgium, symbol Sg, (after Glenn Seaborg) at the meeting of the American Chemical Society in San Diego. Thus, by 1994 the names and symbols assigned to elements 104–109 were as shown in Table 2.2.

Atomic Number	*Name*	*Symbol*
104	*Rutherfordium*	*Rf*
105	*Hahnium*	*Hn*
106	*Seaborgium*	*Sg*
107	*Nielsbohrium*	*Ns*
108	*Hassium*	*Hs*
109	*Meitnerium*	*Mt*

Table 2.2

However, a few months after element 106 was named in honour of Glenn Seaborg by the American Chemical Society, the Commission on the Nomenclature of Inorganic Compounds announced that element number 106 cannot be named after him because he is still alive! Instead it decided that element number 106 will be called rutherfordium, symbol Rf. After dealing with disputes, claims and counter-claims over what groups discovered the elements, the IUPAC nomenclature committee at its meeting in August 1994 finally revealed its suggestions for naming elements 104–109.

Element number 104 was named dubnium, symbol Db, after the Dubna institute where the Russian team credited with its discovery works. Changing the name of this element from rutherfordium has caused confusion as rutherfordium is now element number 106!

Element number 105 was named joliotium, symbol Jl, after Frédéric Joliot-Curie. Element number 106 is now named rutherfordium, symbol Rf, and element number 107 is named bohrium, symbol Bh, after Niels Bohr. The name hahnium, symbol Hn, was previously given to element number 105 but is now assigned to element number 108. Finally, the name meitnerium, symbol Mt, after Lise Meitner, has been retained for element number 109.

The new proposed names and symbols are therefore as shown in Table 2.3.

Number	*Name*	*Symbol*
104	*Dubnium*	*Db*
105	*Joliotium*	*Jl*
106	*Rutherfordium*	*Rf*
107	*Bohrium*	*Bh*
108	*Hahnium*	*Hn*
109	*Meitnerium*	*Mt*

Table 2.3

The above names were ratified by the IUPAC's General Council at their meeting in August 1995. However, the American Chemical Society has announced that it will not accept the new proposals. Thus, the situation for the future is still not clear and this may mean that the same element could have a different name and different symbol depending on the naming system adopted. Teachers will find it useful to read the articles associated with the naming of these elements in *"Chemistry In Action!"*, 1992, 38, 24 and 1994, 42, 11 and 1994, 44, 19.

As an example of the lack of clarity with regard to the names of these elements, in the following recent article in New Scientist, element number 106 is referred to as seaborgium.

Superheavy elements could soon be made, John Emsley in *New Scientist* 13 August 1994.

'Physicists may be on the verge of creating "superheavy" elements, surprisingly stable nuclei with atomic numbers greater than 112. Currently, the heaviest known element is meitnerium (Mt), which has an atomic number of 109, but hopes have been raised by a group of Russian and American physicists who have made heavy isotopes of seaborgium (Sg), element 106, and found that they live much longer than expected.

Atoms of elements with atomic numbers greater than uranium, element 92, are not found naturally on Earth. This is because their half-lives – the time taken for half the atoms in a sample to decay – are much shorter than the age of the Earth. However, in the past 40 years, heavier elements have been made artificially by bombarding heavy nuclei with smaller ones.

Physicists have found that elements become less and less stable as their atomic number increases.

Elements up to fermium, which has atomic number 100, have half-lives long enough for chemists to carry out experiments and determine their chemical properties. With post-fermium elements it has proved impossible to make more than a few atoms of each element, and none of the elements has a half-life longer than a few months.

A team of physicists … (have) made isotopes of seaborgium with atomic masses of 265 and 266.

In a paper in Physical Review Letters (vol. 73, p. 624), the physicists announce that the half-lives of these isotopes are much longer than anyone expected. Seaborgium-265 decays by emitting an alpha particle with a half-life of between 2 and 10 seconds. Seaborgium-266 has a half-life of between 10 and 30 seconds; it emits an alpha particle of energy 8.63 MeV, then fissions spontaneously.... '

2.2 Döbereiner's Triads

Johann Döbereiner (1780-1849) observed that when trios of elements of similar chemical properties were arranged in order of increasing relative atomic mass, the relative atomic mass of the middle one was the average of the relative atomic masses of the other two. He observed this first in 1817 when 49 elements were known, in the case of calcium, strontium and barium and later, shortly after the discovery of bromine in 1826, in the case of chlorine, bromine and iodine. Such groups of elements were named triads and other chemists went on to point out further triads and other mathematical patterns in relative atomic masses up to 1860.

In 1860, Cannizzaro pointed out the difference between atoms and molecules (see section 1.4 page 4) and the emphasis shifted away from triads and arithmetic relationships to simply listing all the known elements in order of increasing relative atomic mass. Up until then, this task was not possible because, as explained earlier, the relative atomic mass quoted for an element depended on assumptions about valency and the assumption that many gases were monatomic while they were in fact diatomic or polyatomic.

Once the distinction between relative atomic mass and relative molecular mass or combining mass was accepted, each element was assigned a single value for its relative atomic mass and progress in arranging the elements was made quickly. Three chemists would appear to have independently developed the notion of the periodic law about this time.

2.3 Newlands' Octaves[4]

In 1864 **John Newlands** (1837-1898) published the first list of the elements known at that time in correct order of increasing relative atomic mass. Furthermore, in 1865, he attempted to show periodicity in chemical behaviour within this list. He proposed the Law of Octaves taking the term 'octave' from music. He wrote in 1865: 'The eighth element starting from a given one is a kind of repetition of the first. This peculiar relationship I propose to provisionally term the *Law of Octaves.*' He listed, in 1865, the known elements in a table of eight vertical columns, seven elements in each. The elements in each column were listed in order of increasing relative atomic mass. We know that none of the inert gases was known at the time. The important ideas introduced by Newlands for the first time are that of periodically repeating chemical behaviour and attempting to arrange the elements so that groups of elements with similar properties occurred in rows together.

Newlands developed his ideas further and presented his ideas and an improved table at a meeting of the Chemical Society in London in 1866. The arrangement of the elements in his 1866 table is shown in Fig. 2.2.

H	F	Cl	Co, Ni	Br	Pd	I	Pt, Ir
Li	Na	K	Cu	Rb	Ag	Cs	Os
G	Mg	Ca	Zn	Sr	Cd	Ba, V	Hg
Bo	Al	Cr	Y	Ce, La	U	Ta	Tl
C	Si	Ti	In	Zr	Sn	W	Pb
N	P	Mn	As	Di, Mo	Sb	Nb	Bi
O	S	Fe	Se	Rh, Ru	Te	Au	Th

***Fig. 2.2** Newlands' periodic table, 1866*

The elements are listed in order of increasing relative atomic mass in a vertical array, a new column commencing every eighth element so that elements of similar properties fall into horizontal rows together. The element beryllium was called glucinium (from the sweet taste of its salts) and given the symbol G in the original table. Boron was given the symbol Bo and Di was later shown to consist of two rare-earth elements, praseodymium and neodymium. Where elements had very similar relative atomic masses, Newlands placed them together in the table. It compares well (especially when rows and columns are transposed, Fig. 2.3) with the modern periodic table of the elements for the first eighteen elements but as was pointed out at the meeting there is as little chemical similarity between the metals in the last vertical column as between the elements of any horizontal row.

						H
Li	G	Bo	C	N	O	F
Na	Mg	Al	Si	P	S	Cl
K	Ca	Cr	Ti	Mn	Fe	Co, Ni
Cu	Zn	Y	In	As	Se	Br
Rb	Sr	Ce, La	Zr	Di, Mo	Rh Ru	Pd
Ag	Cd	U	Sn	Sb	Te	I
Cs	Ba, V	Ta	W	Nb	Au	Pt, Ir
Os	Hg	Tl	Pb	Bi	Th	

***Fig. 2.3** Newlands' 1866 table, rows and columns transposed*

Newlands' proposal of periodic behaviour of the elements was not readily accepted by the meeting. He was asked 'humorously' by one member of the Chemical Society whether he had considered examining the elements according to their initial letters. That member felt that any arrangement of the elements would show occasional coincidental periodicity in chemical behaviour. Another serious point of criticism was that Newlands' table, as presented to the meeting, could not accommodate any new elements which might be discovered unless they were heavier than any of the known elements. Later Newlands tried to point out that the 'octaves' were merely provisional units and that the repeating unit might involve 7, 8, 9, 10, 20, elements as new elements were found and fitted into the pattern.

Thus the use of the term 'octave' by Newlands was unfortunate because despite his claim that the size of the repeating unit was arbitrary the name he gave his law seemed to restrict the horizontal rows to seven elements. For the rest of his life Newlands tried to put forward his claim to being the first person to discover the periodic law. A fair assessment of the situation would appear to be that Newlands was in the process of developing and perfecting his ideas on the periodic law when Mendeleev meanwhile presented a more completely thought out table and his daring predictions were quickly realised. Newlands' claim was at least partially accepted because he was awarded the Davy Medal of the Royal Society in 1887, five years after Mendeleev was honoured.

2.4 Meyer's Curves

Lothar Meyer (1830-1895) attended the famous meeting at Karlsruhe, where Cannizzarro distinguished between relative atomic, molecular and combining masses of the elements. Influenced by this and the earlier work on triads he constructed, about 1868, a sixteen column table with elements of the same chemical properties appearing in groups. He too left gaps for elements not yet known. It formed part of a textbook he was revising and was not published until 1872, by which time Mendeleev (see below) had established a prior claim to discovering this type of pattern. Also, Meyer had published an article in 1870, acknowledging Mendeleev's work and providing evidence in support of it. He is now remembered for this work done in support of the periodic law. He plotted graphs of atomic volume versus relative atomic mass and the shapes of the graphs provided visual support in favour of the periodicity of chemical behaviour. (Atomic volume was taken as the ratio of relative atomic mass to the specific gravity (relative density) of an element.)

Although Meyer did not publish his findings until after Mendeleev, most of Newlands' work had been published in Britain before Mendeleev developed his ideas on the periodic law. However, Mendeleev, working in Germany and Russia, was unaware of it and developed his ideas independently.

2.5 Mendeleev's Periodic Law and Periodic Table of the Elements

Dimitri Mendeleev (1834-1907) had been writing a text on organic chemistry when it occurred to him that the properties of organic compounds were related to their relative molecular masses. He wondered whether the properties of the elements might not also be related to their relative atomic masses. He began to consider the known elements, first in small groups, e.g. H, C, N and O, the alkali metals, the halogens, the transition metals and made notes about their valencies, chemical behaviour, etc., and listed the elements in each group in order of increasing relative atomic mass. Then he placed all 62 elements known at the time together in a larger array and by 1869 he deduced that 'elements placed according to the value of their (relative) atomic weights (masses) present a clear periodicity of properties'. This relationship between relative atomic mass and periodically recurring chemical and physical properties became known as the **Periodic Law**.

Mendeleev had such faith in the existence of this periodically repeating chemical behaviour that, where there was no known element with the required properties for a particular place in his table, he left a gap and predicted that elements would be later discovered to fill these gaps. He predicted the chemical and physical properties of these yet to be discovered elements, e.g. eka-aluminium and eka-silicon were the names given to some of the elements Mendeleev predicted would be discovered to fit into spaces in the table below aluminium and silicon respectively. When gallium was discovered in 1875, it was shown to correspond to Mendeleev's eka-aluminium. Also, germanium, discovered in 1886 was shown to be eka-silicon. The revelation that the properties of these newly discovered elements had been so accurately predicted by Mendeleev's system had far greater impact in the scientific world than Mendeleev's original publications. It is probably the result of Mendeleev's courage in this matter that it is he who is chiefly remembered for laying the foundations of the modern periodic table rather than Meyer or Newlands.

Another example of Mendeleev's own faith in the periodic law was his reversal of the order of a few pairs of elements so that they fell into the correct places according to their chemical properties. For example, in the case of iodine and tellurium, iodine should appear before tellurium according to relative atomic masses but Mendeleev reversed this so that iodine would fall into the same group as fluorine, chlorine and bromine which had similar chemical properties. He reasoned that their relative atomic masses must have been inaccurately determined but he was in fact not correct in this, as we shall see.

Mendeleev produced a number of versions of his periodic table, some with chemically similar groups listed vertically, others horizontally. Figure 2.4(a) shows Mendeleev's 1869 table with the element yttrium given the symbol Yt. Figure 2.4(b) shows part of Mendeleev's 1872 table and how the first 49 elements were arranged. The 'element' listed as Di in both tables was subsequently shown to consist of two rare-earth elements, praseodymium and neodymium.

Note that in the 1869 table, the elements are listed in order of increasing relative atomic mass and elements of similar properties occur in horizontal rows of differing lengths. In the 1872 table, the elements are listed horizontally in order of increasing relative atomic mass and elements of similar chemical properties appear in vertical columns. The latter type of periodic table is called a short table because it has few vertical columns – the elements of the long periods are arranged in two horizontal series – e.g. Series 4 and 5 of this table contain the same elements as the 4th period of the long tables. Bearing this in mind it is clear that both tables are essentially equivalent and that they are the forerunners of our modern tables. When Mendeleev came to certain positions on the tables he left gaps for unknown elements whose relative atomic mases he predicted were 44, 68, 72 and 100.

These tables are clearly more advanced than Newlands' work because they show periods of differing length while all of Newlands' periods consisted of seven elements. Furthermore, they very deliberately contain gaps for the discovery of new elements as well as having iodine and tellurium and cobalt and nickel in their correct groups. There are no pairs of elements.

Yet, Mendeleev's tables are still only primitive versions of our modern table:

they do not include the noble gases which were undiscovered at the time;

			K	Rb	Cs		
			Ca	Sr	Ba		
				Yt	Di	Er	
			Ti	Zr	Ce	La	Th
			V	Nb		Ta	
			Cr	Mo		W	U
			Mn				
			Fe	Ru		Os	
			Co	Rh		Ir	
			Ni	Pd		Pt	
H	Li	Na	Cu	Ag		Au	
	Be	Mg	Zn	Cd		Hg	
	B	Al		In		Tl	
	C	Si		Sn		Pb	
	N	P	As	Sb		Bi	
	O	S	Se	Te			
	F	Cl	Br	I			

Fig. 2.4(a) *Mendeleev's 1869 table*

there are gaps for germanium, scandium, gallium, and technetium, etc., which had not been isolated at that time;

the transuranic elements were unknown at the time;

there is no correlation between atomic structure and the splitting of the long periods;

they list the elements in order of increasing relative atomic mass with a few exceptions like tellurium and iodine and cobalt and nickel.

Series	Group I R_2O	Group II RO	Group III R_2O_3	Group IV RO_2	Group V R_2O_5	Group VI RO_3	Group VII R_2O_7	Group VIII RO_4
1	H 1							
2	Li 7	Be 9	B 11	C 12	N 14	O 16	F 19	
3	Na 23	Mg 24	Al 27	Si 28	P 31	S 33	Cl 35.5	
4	K 39	Ca 40	– *44*	Ti 48	V 51	Cr 52	Mn 55	Fe 56 Co 59 Ni 59 Cu 63
5	(Cu) 63	Zn 65	– *68*	– *72*	As 75	Se 78	Br 80	
6	Rb 85	Sr 87	Y 88	Zr 90	Nb 94	Mo 96	– *100*	Ru 104 Rh 104 Pd 106 Ag 108
7	(Ag) 108	Cd 112	In 113	Sn 118	Sb 122	Te 128	I 127	
8	Cs 133	Ba 137	Di 138	Ce 140				

Fig. 2.4(b) *Mendeleev's 1872 table*

2.6 Moseley, Soddy and the Modern Version of the Periodic Table

Other chemists continued to work on the periodic table and it had evolved into its present day form by 1945.

In 1903 **Alfred Werner** (1866–1919) produced the first chart which included the newly discovered noble gases on the right of the halogens and which has a split in the second and third periods, although he placed the split between the alkali and alkali-earth metals rather than after the alkali-earth elements. By this time scandium, gallium and germanium had also been discovered but there were still gaps for technetium and some of the other rare-earths. In 1885 it had been shown that didymium was in fact the two elements praseodymium and neodymium. The first part of Werner's table, Fig. 2.5, shows how its layout is essentially that of the modern periodic table.

The discovery of the significance of atomic numbers by **Henry Moseley** (1887–1915) in 1913 allowed the elements to be arranged in the periodic table according to this fundamental property rather than according to relative atomic masses.

Moseley observed that when cathode rays struck a metal, X-rays of a frequency characteristic of the metal of which the target was made, were produced. The highest frequency, *f*, of the X-rays produced in any case could be represented by

$$f = A(N - b)^2$$

where *A* and *b* are constants and *N* is an integer characteristic of the metal. *N* was found to increase uniformly as one passed from one element to the next on the periodic table. Moseley called *N* the atomic number of the element and suggested that it was the positive charge of the nucleus. It was further suggested that it was a more fundamental quantity associated with an atom than relative atomic mass which varied in an arbitrary fashion from one element to the next and that the elements should be listed on the periodic table according to atomic number. There was then no need to reverse the order of any elements in order to have them appear in a group of elements of similar properties. Also, atomic numbers allowed chemists to say for the first time how many elements there were. For example, chemists for some time had been working on the isolation of the rare-earth elements or lanthanides, those elements which occur between lanthanum and hafnium in the modern periodic table. In nature the rare-earth elements occur in mixtures and have very similar chemical and physical properties. Chemists had succeeded in separating some but, until the work of Moseley, had no idea how many elements existed between lanthanum and tantalum (hafnium was not discovered until 1923). Calculation now showed that there were fourteen rare-earth elements. The discovery of rhenium in 1925 by the Berlin husband and wife, **Walter Noddack** and **Ide Tacke**, was also based on this information and on the use of emissions in the X-ray part of the spectrum rather than visible emissions to identify the new element.

Moseley's discovery of atomic numbers in 1913 allowed the rare-earth elements to be fitted into the table in the correct place after lanthanum and before hafnium. It was a suggestion of Niels Bohr that the rare-earth elements be listed apart from the other elements of the periodic table in a horizontal row called the lanthanide series.

H																	He
Li											Be	B	C	N	O	F	Ne
Na											Mg	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo		Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba			Ta	W		Os	Ir	Pt	Au	Hg	Tl	Pb	Bi			
	Ra																

Fig. 2.5 *Werner's arrangement of the elements, 1903*

But how many elements exist in total? In 1939 the first transuranic element, atomic number 93, was made at the University of California at Berkeley. It was named neptunium because the planet Neptune occurs beyond Uranus in the solar system while neptunium fitted beyond uranium in the periodic table. Its chemical properties were similar to uranium and not rhenium. Soon after, a second transuranic element, atomic number 94, was manufactured and named plutonium. Again its chemistry was like that of uranium and neptunium. It was evident to **G. T. Seaborg** (1912–), one of the manufacturers of plutonium, americium and curium, where these elements belonged in the periodic table. They formed part of another series of fourteen elements, like the lanthanides, which fitted into the table after actinium and under the lanthanides. This series was called the actinide series. In 1945 Seaborg published the first periodic table with the actinides and lanthanides in their now familiar positions.

Nowadays the most usual form of presentation of the periodic table is the eighteen column form where the lanthanides and actinides are arranged under the other elements and their points of insertion marked. This avoids having a very wide table and the accompanying printing difficulties. The main groups were labelled with Roman numerals and capital letters A and B but unfortunately in the United States the main groups were labelled IA to VIIIA and the first five groups of transition elements were labelled IIIB to VIIB, the next three columns of transition elements together were Group VIIIB and then the last two transition groups were IB and IIB respectively while in Europe the letters A and B were assigned differently. This obviously has led to confusion in chemical publications. In the Mathematics Tables used in Irish state examinations and published by the Government Publications Office, the United States system is followed. The latest recommendation of IUPAC (1989) is to label the groups from 1–18 continuously across the table[6,7]. All three notations are shown in the table in Fig. 2.6 (below).

Most modern versions of the periodic table include the atomic numbers and the relative atomic masses of the elements approved by IUPAC. The discovery of isotopes in 1922 by Frederick Soddy and the development of the mass spectrometer which allowed very accurate atomic mass measurements (see section 1.12) as well as the agreement on the definition of the atomic mass unit in 1960-61 have influenced the actual values for relative atomic masses included on periodic tables. The table given on p. 50 has the masses most recently approved by IUPAC (1983), numbers in parentheses are mass numbers of the most stable isotope of that element.

IUPAC	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Eur.	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA			IB	IIB	IIIB	IVB	VB	VIB	VIIB	VIIIB
US	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
	H																	He
	Li	Be											B	C	N	O	F	Ne
	Na	Mg											Al	Si	P	S	Cl	Ar
	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
	Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
	Fr	Ra	Ac◻	Db	Jl	Rf	Bh	Hn	Mt									

*Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
◻Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Fig. 2.6 *Arrangement of the elements, 1994*

Periodic tables in the format described above but with additional information about physical properties and uses of the elements are available. Wall chart and wallet-sized versions are also available. Some chemical manufacturing companies use the periodic table as a business card in the same way other companies issue calendars. It has been printed on shopping bags, t-shirts and ties.

Different versions of the periodic table have appeared over the years[8,9]. Various tree-shaped patterns, and versions which have a separate line for each subshell have been presented. Spiral arrangements are well known, starting with hydrogen at the centre and placing elements of increasingly higher atomic number on the curves of a flat spiral so that elements with the same chemical properties appear in a line. Three-dimensional periodic tables have also been produced, e.g. where the elements are arranged on a cylindrical helix or like a three-dimensional bar chart. Whilst some of these present the periodic law perfectly well, none has presented any serious challenge to the popularity of the 'short form' with which we have all become accustomed as it hangs on the school laboratory wall.

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THE PERIODIC TABLE

KEY

Atomic number
Symbol
Name
Relative atomic mass

I 1	II 2	3	4	5	6	7	8	9	10	11	12	III 13	IV 14	V 15	VI 16	VII 17	O 18
1 **H** Hydrogen 1.0079																	2 **He** Helium 4.00260
3 **Li** Lithium 6.941	4 **Be** Beryllium 9.01218											5 **B** Boron 10.81	6 **C** Carbon 12.011	7 **N** Nitrogen 14.0067	8 **O** Oxygen 15.9994	9 **F** Fluorine 18.9994	10 **Ne** Neon 20.179
11 **Na** Sodium 22.9898	12 **Mg** Magnesium 24.305											13 **Al** Aluminium 26.9815	14 **Si** Silicon 28.0855	15 **P** Phosphorus 30.9738	16 **S** Sulphur 32.06	17 **Cl** Chlorine 35.453	18 **Ar** Argon 39.948
19 **K** Potassium 39.0983	20 **Ca** Calcium 40.08	21 **Sc** Scandium 44.9559	22 **Ti** Titanium 47.88	23 **V** Vanadium 50.9415	24 **Cr** Chromium 51.996	25 **Mn** Manganese 54.9380	26 **Fe** Iron 55.847	27 **Co** Cobalt 58.9332	28 **Ni** Nickel 58.69	29 **Cu** Copper 63.546	30 **Zn** Zinc 65.39	31 **Ga** Gallium 69.72	32 **Ge** Germanium 72.59	33 **As** Arsenic 74.9216	34 **Se** Selenium 78.96	35 **Br** Bromine 79.904	36 **Kr** Krypton 83.80
37 **Rb** Rubidium 85.4678	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.9059	40 **Zr** Zirconium 91.224	41 **Nb** Niobium 92.9064	42 **Mo** Molybdenum 95.94	43 **Tc** Technetium (98)	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.906	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.868	48 **Cd** Cadmium 112.41	49 **In** Indium 114.82	50 **Sn** Tin 118.71	51 **Sb** Antimony 121.75	52 **Te** Tellurium 127.60	53 **I** Iodine 126.905	54 **Xe** Xenon 131.29
55 **Cs** Caesium 132.905	56 **Ba** Barium 137.33	57 **La**► Lanthanum 138.906	72 **Hf** Hafnium 178.49	73 **Ta** Tantalum 180.948	74 **W** Tungsten 183.85	75 **Re** Rhenium 186.207	76 **Os** Osmium 190.2	77 **Ir** Iridium 192.22	78 **Pt** Platinum 195.08	79 **Au** Gold 196.967	80 **Hg** Mercury 200.59	81 **Tl** Thallium 204.383	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.980	84 **Po** Polonium (209)	85 **At** Astatine (210)	86 **Rn** Radon (222)
87 **Fr** Francium (223)	88 **Ra** Radium 226.025	89 **Ac**►► Actinium 227.028	104 **Db** Dubnium (261)	105 **Jl** Joliotium (262)	106 **Rf** Rutherfordium (263)	107 **Bh** Bohrium (262)	108 **Hn** Hahnium (265)	109 **Mt** Meitnerium (264)									

► Lanthanide elements	58 **Ce** Cerium 140.12	59 **Pr** Praseodymium 140.908	60 **Nd** Neodymium 144.24	61 **Pm** Promethium (145)	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.96	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.925	66 **Dy** Dysprosium 162.50	67 **Ho** Holmium 164.930	68 **Er** Erbium 167.26	69 **Tm** Thulium 168.934	70 **Yb** Ytterbium 173.04	71 **Lu** Lutetium 174.967
►► Actinide elements	90 **Th** Thorium 232.038	91 **Pa** Protactinium 231.036	92 **U** Uranium 238.029	93 **Np** Neptunium 237.048	94 **Pu** Plutonium (244)	95 **Am** Americium (243)	96 **Cm** Curium (247)	97 **Bk** Berkelium (247)	98 **Cf** Californium (251)	99 **Es** Einsteinium (252)	100 **Fm** Fermium (257)	101 **Md** Mendelevium (258)	102 **No** Nobelium (259)	103 **Lr** Lawrencium (260)

Fig. 2.7 *Periodic table of the elements. The relative atomic masses are based on the* $^{12}_{6}C = 12$ *scale. A value in brackets denotes the mass number of the most stable isotope.*

CHAPTER 3

TRENDS IN THE PERIODIC TABLE

3.1 Atomic Radius

Idea of Atomic Radius

In theory there is no boundary to the electron cloud of an atom. According to the Heisenberg uncertainty principle it is not possible to specify precisely at any instant in time the position and momentum of the electrons as they move about inside the electron cloud. However, using quantum mechanics it is possible to calculate the probability of finding an electron of given energy in a particular region in an atom. Thus the regions with high probability of containing an electron of given energy are the **atomic orbitals**.

In the case of the hydrogen atom, for example, the single electron has a very high probability of being contained within a spherical space of radius 0.1 nm around the nucleus and has the greatest probability of being located within a distance of 0.0529 nm from the centre of the atom[1]. There are two ways of visualising this situation:

(a) using an electron density sketch, where the regions with high probability of containing the electron are shaded darker than the regions of lower probability;

(b) using a graph of probability of locating the electron versus distance from the nucleus.

Both are illustrated for the hydrogen atom in Fig. 3.1.

Definition of Atomic Radius

Atomic radius is defined as half the distance between the centres of two atoms of the same element when bonded by a single covalent bond[2].

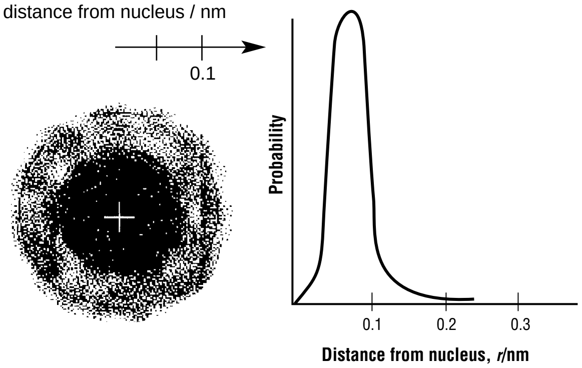

Fig. 3.1

Metallic Bonding

Metals consist of an orderly array of positively charged ions in a ‘sea’ of electrons (or more technically a delocalised electron cloud). The attraction of the positive ions for the electrons overcomes the repulsion of the positive ions for one another. The outer electrons are free to move through the arrangement and are not associated with any particular atoms. The electrons move in a random way ensuring overall neutrality in the solid. If an electrical potential difference is applied to the two ends of a piece of metal the electrons will move from low to high potential, constituting an electric current: thus metals conduct electricity.

No values for the atomic radii of the noble gases can be given since atoms of these elements do not form any chemical bonds together. It is possible to find the packing radius (van der Waals radius) of the noble gases, i.e. half the distance between centres when the elements are in the solid state. However, this value is larger than the atomic radius since atoms lie closer together when metallically or covalently bonded than when packed together but not bonded. See Fig. 3.2.

This diagram represents a non-metallic element with diatomic molecules in the solid state. The bonded atoms lie closer than the non-bonded atoms.

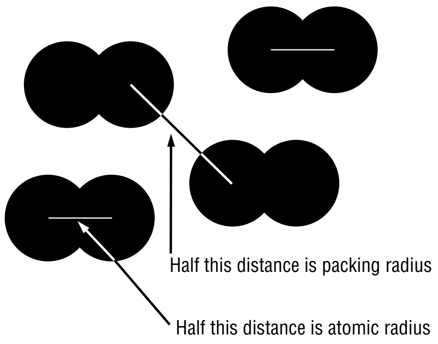

Fig. 3.2

The measurements of atomic radii are obtained using the technique of X-ray crystallography. This involves X-raying a crystal of a metallic element or a crystal of the covalent compound, frozen if necessary. The measurements are taken from the X-ray photographs produced.

Trends in Atomic Radius

Fig. 3.3 shows the trends in atomic radius (single-bond covalent radii).

Three general trends are obvious:

(i) shrinkage in atomic size from left to right;

(ii) expansion in atomic size from top to bottom;

(iii) similarity in atomic size from left to right across a period of transition metal elements.

(i) Shrinkage in atomic size from left to right

It often comes as a surprise to students to see that atoms actually get smaller as the atomic number and atomic mass increase across a period. Intuitively one expects atoms to become progressively larger as they become progressively heavier. (The *nuclei* of atoms do get larger across a period since the attractive forces in the nuclei are short-range, unlike the electrostatic forces which are long-range.) However, the main influencing factor on atomic size across a period is *increasing nuclear charge.* Nuclear charge obviously increases across a period and each electron in the outer shell of an atom comes under the electrostatic attraction of an increasingly larger cluster of protons and is thus pulled increasingly nearer the nucleus across a period. The number of electrons in the outer shell also increases and these electrons exert repulsive electrostatic forces on one another but the attractive force of the cluster of protons in the nucleus is much greater than the repulsive force of the neighbouring electrons ('four pulling four is

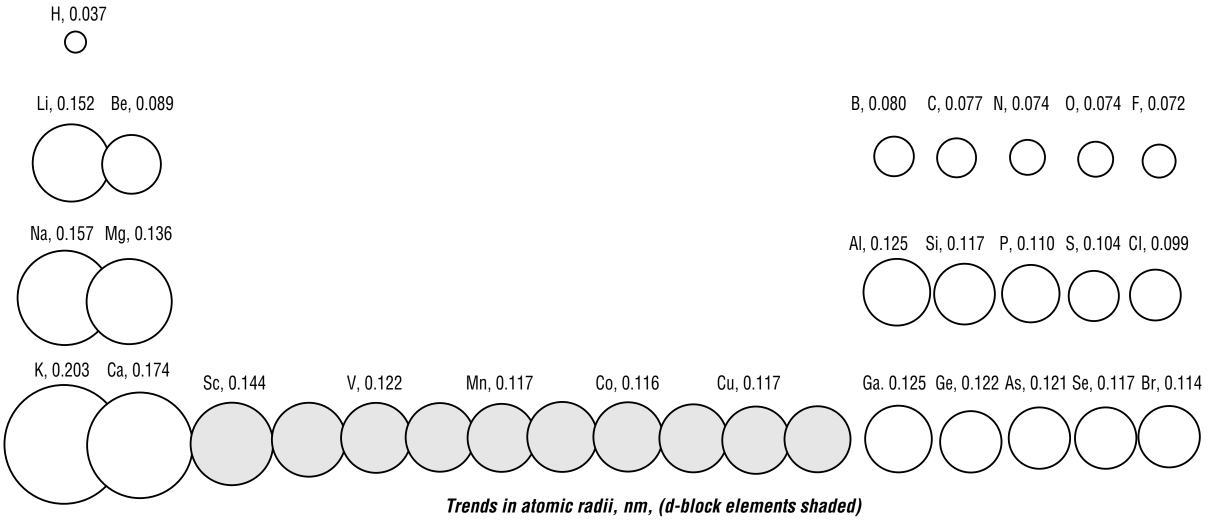

Fig. 3.3 *Covalent radii of some atoms*

more effective than three pulling three'). Thus the outer shell of electrons in the element fluorine is actually closer to the nucleus than that of lithium.

The atoms of all the elements in a period have the *same number of shells* and the same number of *electrons in inner shells* so size differences between them cannot be influenced by either of these factors.

Another way of explaining the decrease in atomic radius across a period is to refer to effective nuclear charge.

Effective nuclear charge = nuclear charge – no. of electrons in inner shells.

Therefore effective nuclear charge increases across a period and the outer electrons are held more closely to the nucleus.

(ii) Expansion in atomic size from top to bottom

Atoms do increase in size down a group. The main influence here is that an *extra outer shell* of electrons is added as one proceeds from one element to the next down a group and thus the atoms increase in size down a group.

There are two additional influences to be mentioned also. The nuclear charge also increases as one proceeds from one element to the next down a group and we have seen that this should have the effect of drawing in the outer electrons more and more closely. However remember that as one proceeds from one element to the next down a group there is an additional inner shell of electrons which have the effect of screening the outer electrons from the electrostatic attraction of the nucleus. Therefore the shielding effect of electrons in inner shells helps to offset the effect of increasing nuclear charge.

Q. Which element has the lightest atoms?
Hydrogen.

Q. Which element has the largest atoms?
Francium.

(iii) Similarity in atomic size from left to right across a period of transition metal elements

The transition metal elements of the same period do not show much variation in size. The reason for the similarity in size is understood by examining the electronic structures of neighbouring elements. It can then be seen that the difference in their electron configuration occurs in the penultimate shell rather than in the outer shell. Obviously a slight difference in internal structure has little influence on overall size whereas a slight difference in the external structure would be expected to have a more significant impact on size.

For example the electron configurations of iron, cobalt and nickel are:

$$\text{Fe} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^6;$$
$$\text{Co} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^7;$$
$$\text{Ni} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^8.$$

The difference in their electron structures occurs in the 3d sublevel. This increased shielding effect cancels out the increase in nuclear charge. Their sizes are therefore very similar, 0.116 nm, 0.116 nm and 0.115 nm, respectively.

Ionic radii

(i) Positive ions are smaller than their parent neutral atoms

If an electron is removed from an atom the result may be to reduce the size of the atom by removing the outer shell. This happens in the case of the ionisation of sodium. No electrons occupy the third shell in a sodium ion and thus the ion, Na^+, is smaller than the neutral atom.

$$\text{Na} = 1s^2, 2s^2, 2p^6, 3s^1.$$
$$\text{Na}^+ = 1s^2, 2s^2, 2p^6.$$

Sometimes however the outer shell is not completely emptied by removing a single electron. In this case the positive ion is still smaller than the corresponding neutral atom. There will be less repulsion between the remaining electrons in the outer shell and thus they will be drawn closer to the nucleus than in the neutral atom.

$$N = 1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1.$$

$$N^+ = 1s^2, 2s^2, 2p_x^1, 2p_y^1.$$

Also, if a sublevel is emptied in the process of removing an electron, the resultant ion undergoes a decrease in size as the region of higher energy sublevels extends outside the lower energy sublevels.

$$Al = 1s^2, 2s^2, 2p^6, 3s^2, 3p_x^1.$$

$$Al^+ = 1s^2, 2s^2, 2p^6, 3s^2.$$

Thus Al^+ is smaller than Al.

(ii) Negative ions are larger than their parent neutral atoms

Electrons added to an atom obey the Aufbau principle and occupy the next lowest energy orbital available. Usually the outer shell is not completely full before adding the electron or electrons to make the negative ion. There will now be more repulsion between the electrons in the outer shell than before whilst the effective nuclear charge has remained constant. Thus they cannot be drawn as close to the nucleus as they are in the neutral atom so the outer shell of electrons expands.

$$F = 1s^2, 2s^2, 2p^5.$$

$$F^- = 1s^2, 2s^2, 2p^6.$$

Thus the fluoride ion is larger than the fluorine atom.

Atomic radii of isoelectronic species

Isoelectronic species have the same electronic structures, e.g. Na^+, Mg^{++}, Ne, F^-, O^{--} all have the same electron configuration:

$$1s^2, 2s^2, 2p^6.$$

Since Mg^{++} has a nuclear charge of +12, the electrons in this ion are more closely drawn to the nucleus than in any of the other species and so Mg^{++} is the smallest and conversely O^{--} with a nuclear charge of only +8 must be the largest.

In all of the species there is equal shielding from the 1s electrons and equal repulsion between the electrons in the outer shells so size differences cannot be attributed to either of these effects.

3.2 Ionisation Energies

Definition of First Ionisation Energy (or First Ionisation Potential)

First ionisation energy is the energy required to remove to infinity the most loosely bound electron from an isolated atom of an element in its ground state.

Since energy is required, ionisation energies have, by convention, positive values. The values are usually given in kilojoules per mole of atoms.

The term ‘isolated atom’ means that any bonds joining the atoms of the element together have been broken; the atoms are in the gaseous state. The term ‘infinity’ effectively means outside the atomic radius of the atom.

The Idea of First Ionisation Energy

The process of ionisation can be represented by a simple equation:

$$X + \text{energy} \longrightarrow X^+ + e^-$$

The idea of ionisation of an isolated atom can be illustrated as follows for lithium:

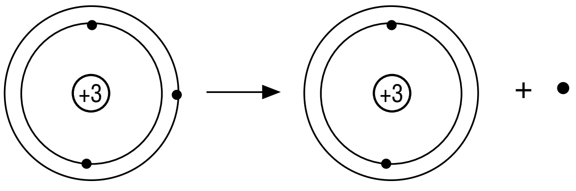

Fig. 3.4 *First ionisation of an isolated atom of lithium*

How are First Ionisation Energies Measured?

First ionisation energies can be measured spectroscopically. Taking hydrogen as an example, the highest energy series of lines in the atomic spectrum of hydrogen, the Lyman series, corresponds to electron transitions from all higher energy levels to the first level. See Fig. 1.8, p. 13. The higher the frequency of the emission, the higher the energy difference between the excited state and the ground state which, in the case of the Lyman series, is the first energy level. The lines become closer together at higher frequencies as the outer energy levels lie closer together until they merge into a continuum where separate energy levels are indistinguishably close and then stop completely. This limit of the Lyman series corresponds to the removal of an electron from the first energy level to outside the atom altogether, i.e. infinitely far from the nucleus, and thus also corresponds to ionising the atom of hydrogen. The energy corresponding to this transition can be easily calculated from the maximum frequency and Planck's constant using the formula $E = hf$.

See Experiment 3.1, p. 63.

Trends in First Ionisation Energies

The graph, Fig. 3.5, is useful to show the trends in first ionisation energies**.** Tables of values can also be obtained from chemical data books[3,4].

There are three trends to notice:

(i) increase in ionisation energy from left to right;

(ii) decrease in ionisation energy from top to bottom;

(iii) particularly high ionisation energy values in Groups II and V.

(i) Increase in first ionisation energy from left to right

It becomes increasingly difficult to remove the most loosely bound electron from an atom of an element as one moves across a period. This is because the *atomic radius decreases* across a period. Then the most loosely bound electron lies increasingly closer to the positive nucleus which obviously makes it increasingly more difficult to remove. In addition the *nuclear charge increases* across a period so the nucleus has an increasingly stronger electrostatic attraction for the most loosely bound electron across the period and for this reason also it becomes progressively more difficult to detach.

The atoms of each element across a period have the same number of electrons in inner shells and so the *screening effects of these electrons in inner shells are equal* and this factor cannot contribute to the increase in first ionisation energy across the period.

See Experiment 3.2, p. 63.

(ii) Decrease in first ionisation energy from top to bottom

First ionisation energies decrease from the top to the bottom of the periodic table and therefore it becomes increasingly easier to remove the most loosely bound electron down a group. Down a group *atomic radius increases* and the *shielding effects of electrons in inner shells also increase* because a new shell of electrons is involved as

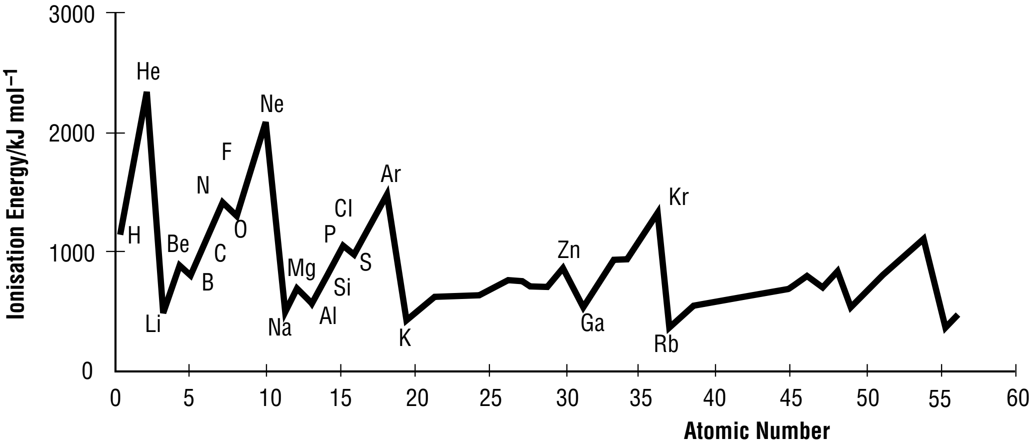

Fig. 3.5 *First ionisation energy*

one passes from one element to the next. Both of these effects account for the increasingly weaker electrostatic attraction between the nucleus and the most loosely bound electron down a group.

However, down a group the *nuclear charge is increasing* and it would be expected that this should result in an increasing attraction for an outer electron. This is true but the increasing attraction for the outer electron due to increasing nuclear charge is *more* than offset by the decreasing attraction due to increased atomic radius and increased shielding from inner electrons. Thus first ionisation energies do decrease from top to bottom of the periodic table.

(iii) Particularly high first ionisation energy values in Groups II and V

The graph of first ionisation energy versus atomic number shows that there is a gradual increase in first ionisation energy across the periods except for elements in Group II and Group V, which have particularly large values. The conclusion is that it is particularly difficult to remove the most loosely bound electron from atoms of elements in these groups or, in other words, atoms of these elements are relatively stable, see Fig. 3.6.

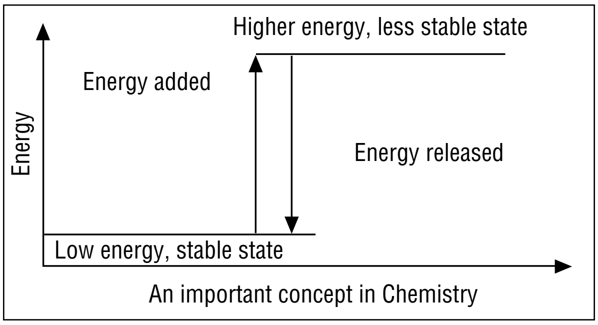

Fig. 3.6

The first three Group II elements have the following electron configurations:

$Be = 1s^2, 2s^2;$

$Mg = 1s^2, 2s^2, 2p^6, 3s^2;$

$Ca = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2.$

These elements and their congeners* have a stable set of filled sublevels and removal of the most loosely bound s electron is relatively difficult because it results in a half-filled outer s sublevel which is a less stable configuration. Energy must be added to convert a stable state into a less stable state. In addition to the energy needed to overcome the nuclear attraction for the most loosely bound electron, energy must be supplied also to move from a stable to a less stable electron configuration in Group II ionisations.

The first three Group V elements have the following electron configurations:

$N = 1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1;$

$P = 1s^2, 2s^2, 2p^6, 3s^2, 3p_x^1, 3p_y^1, 3p_z^1;$

$As = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p_x^1, 4p_y^1, 4p_z^1.$

These elements also have a stable set of filled sublevels and an exactly half-filled outer sublevel. Removal of the most loosely bound p electron is relatively difficult because it results in an outer p sublevel with two electrons which is a less stable configuration than an exactly half-filled p sublevel. Energy must be added to convert a stable state into a less stable state. In addition to the energy needed to overcome the nuclear attraction for the most loosely bound electron, energy must be supplied also to move from a stable to a less stable electron configuration in Group V ionisations also.

Successive Ionisation Energies – Evidence for Existence of Energy Levels

It is possible to define second, third, fourth, etc. ionisation energies until all the electrons in an atom have been removed.

The second ionisation energy of an element is the energy required to remove to infinity the most loosely bound electron from an isolated mono-positive ion of that element in its ground state.

Third, fourth, etc., ionisation energies are similarly defined.

Successive ionisation energies show a gradual increase. When an electron is removed from a neutral atom a monopositive ion results and as the electron is removed to infinity a species of

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*Congeners are members of the same group in the periodic table.

overall charge +1 develops. When a second electron is then removed from the monopositive ion, a dipositive ion results. It requires more energy to detach an electron and remove it to infinity from a monopositive ion than from a neutral atom. We saw earlier that positive ions are smaller than the corresponding neutral atoms and therefore the most loosely bound electron of the positive ion is closer to, and more strongly bound to, the nucleus than the most loosely bound electron in the parent neutral atom. Similarly the third ionisation energy is greater than the second, etc.

However, a series of successive ionisation energies does not increase in a linear fashion. A series of successive ionisation energies mirrors the electron structure of an atom and provides evidence for the existence of energy levels. There are small differences between ionisation energies for electrons belonging to the same shell but large differences if electrons are removed from different shells. The successive ionisation energies are relatively close when the electrons are removed from the same shell because these electrons all lie at approximately the same distance from the nucleus and experience similar shielding from electrons in inner shells. But even when electrons are removed successively from the same shell, some electrons seem to be more difficult to remove than others. More energy will be observed to be required to remove an electron from a species of stable electron configuration, e.g. from a half-filled p sublevel or a full s sublevel. Large differences between successive ionisation energies will be observed if the electrons are removed from different shells because the electron in the inner shell will be significantly closer to the nucleus and will experience less shielding from electrons in inner shells.

A graph of $\log_{10}$ of successive ionisation energies versus number of electrons removed from oxygen[4] is given below. There is a relatively small difference between the second and third ionisation energies, 3390 and 5320 kJ mol^{-1} respectively, a difference of 1930 kJ mol^{-1}, but a much larger difference between the sixth and seventh ionisation energies, 13300 and 71000 kJ mol^{-1} respectively, a difference of 57700 kJ mol^{-1}. The small increase between the second and third ionisation energies is accounted for by the increase in overall charge of the ions involved from +1 to +2 and as explained above it becomes more difficult to remove an electron from a species as its positive charge increases but as both electrons are removed from the same shell the increase is small. Note the greater difference between the fourth and fifth ionisation energies however; a difference of 3550 kJ mol^{-1} is recorded. This is because, although the fifth electron removed is still in the same shell, it must be detached from a filled stable s sublevel. The large increase in ionisation energy when the seventh electron is removed is because the seventh electron lies in an inner shell, closer to the nucleus, not shielded from the nucleus by any electrons in inner shells and thus significantly more strongly attracted to the nucleus than the first six electrons and thus significantly more difficult to remove.

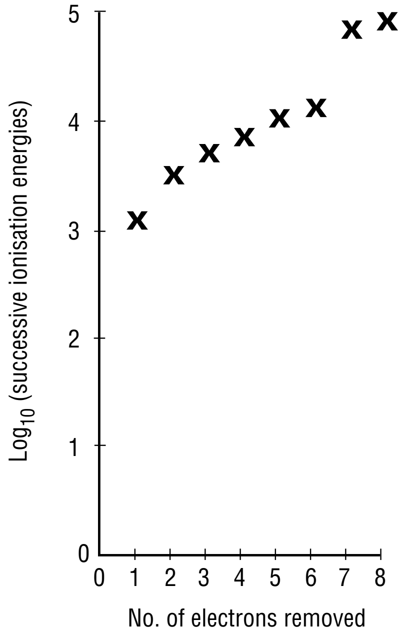

Fig. 3.7

3.3 Electron Affinities

Definition of Electron Affinity

Electron affinity of an element is the energy released when an electron is added from infinity to an isolated atom of that element.

By convention it is given a negative value in kilojoules per mole of atoms. However it is not possible to add an electron to every atom with the release of energy. Sometimes energy must be supplied to ‘force’ an atom to accept an electron. Referring to Fig. 3.6 on p. 56, we can conclude that the addition of an electron in these cases is destabilising.

The term ‘isolated atom’ means that any bonds joining the atoms of the element together have been broken. The term ‘infinity’ in effect means outside the atomic radius of the atom.

The Idea of Electron Affinity

The process of adding an electron to a neutral gaseous atom can be represented by a simple equation:

$$\text{X} + e^- \rightarrow \text{X}^- + \text{energy.}$$

Alternatively, the idea of electron affinity can be illustrated as follows for lithium:

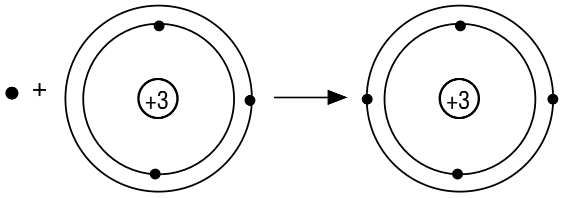

Fig. 3.8 *Addition of an electron to an isolated atom of lithium*

Trends in Electron Affinity

The table, Fig. 3.9, gives electron affinity values (in kJ mol^{-1}) for some of the main group elements[4,5]. The values are difficult to determine and are only approximate. Different sources quote different values but the same general trends occur in each.

H –72							He 20
Li –52	Be 66	B –29	C –120	N –3	O –142	F –348	Ne 30
Na –71			Si –180	P –70	S –200	Cl –364	Ar 35
						Br –342	
						I –314	

Fig. 3.9 *Electron affinity values*

Important trends are:

- (i) the *general* decrease from left to right across a period, i.e. becoming more negative;
- (ii) positive values for Group II elements and Group 0 elements.

(i) More energy is released as an electron is added to an element on the right of the periodic table because these elements possess smaller atomic radii and larger nuclear charges than those on the left and thus have a greater attraction for the incoming electron. The halogens release exceptionally large quantities of energy upon gaining an electron as in each case addition of an electron completes the filling of a p sublevel and thus the ion formed has the very stable electron configuration of the noble gas element lying next to the parent halogen on the periodic table. Exceptions to the general trend of decreasing electron affinity across a period can be explained in terms of electron configuration, e.g. see (ii) below.

(ii) The Group II and Group 0 elements do not release energy as an electron is added. The electron configurations of these elements are stable. Addition of an electron brings about a change to a less stable configuration and so energy must be supplied. For example, beryllium has a set of full stable sublevels. Addition of an electron produces a beryllium anion, which has a less stable electron configuration having a 2p sublevel containing a single electron.

$Be = 1s^2, 2s^2.$

$Be^- = 1s^2, 2s^2, 2p^1.$

3.4 Electronegativity

Idea of Electronegativity

A pair of atoms can join together chemically in two ways. The first involves the **transfer** of an electron from one to the other, creating in the process a positive and a negative ion which are then electrostatically attracted to one another and constitute an ionic bond. The second involves the atoms **sharing** a pair of electrons in order that each atom achieves a more stable electron configuration. The mutual attraction the atoms have for the shared pair of electrons constitutes a covalent bond.

In this second type of bonding, if two atoms of the same element join together, the electron pair is shared equally since both atoms have identical electrostatic attraction for it, having the same nuclear charge, the same atomic radius, and the same degree of screening from electrons in inner shells. Such covalent bonding is called pure covalent bonding.

However, if two atoms of different elements are joined together by their attraction for a shared pair of electrons, there may be unequal sharing of the electron pair as different electrostatic attractions for the pair of electrons may arise in the two atoms due to differences in nuclear charge or in atomic radius or in the degree of screening from electrons in inner shells or combinations of these effects. The result is that the electron pair is transferred towards the atom with the greater electrostatic attraction for it, i.e. the probability of locating the electron pair is greater nearer the atom with the bigger electrostatic attraction for an electron pair. Such unequal sharing of an electron pair in a covalent bond gives rise to a dipole along the bond, i.e. a partially positively charged atom and a partially negatively charged atom. This kind of bonding is called **polar covalent bonding**. The extreme case of polar bonding is when one atom has such a greater electrostatic attraction for the shared pair compared with the second that the electron pair is completely transferred to the first atom. This of course is ionic bonding as described above.

Note that in chemical compounds a whole continuum of bonding types occurs from pure covalent to slightly polar covalent to quite polar covalent to pure ionic bonding.

Definition of Electronegativity

The electronegativity of an element is the relative attraction an atom of that element has for the shared pair of electrons in a covalent bond.

Since they are comparisons of attractions, electronegativity values have no units.

Measurement of Electronegativities

Several different methods for calculating and measuring experimentally electronegativity values have been devised. The best known system is that of Linus Pauling.

The bond energy of a single covalent bond joining two atoms of different elements, represented by X and Y, is greater than the average of the X–X and Y–Y bond energies. The excess energy can be attributed to an electrostatic attraction between the two atoms caused by unequal sharing of the electron pair. **Linus Pauling** (1901–1994) drew up a table of electronegativity values for the elements based on this thermochemical observation[6]. His values have since been corrected as more accurate thermochemical measurements were made but his method for assigning values gives rise to the most commonly used set of electronegativity data.

Linus Pauling is not only a big name in twentieth century chemistry but, according to *The Sunday Times*, is one of the '1000 Makers of the Twentieth Century'. *The Sunday Times* compilation '1000 Makers of the Twentieth Century' published in 1991 has the following entry for him.

Linus Pauling

'U.S., born 1901, chemist

Lord Rutherford showed that an atom looks a bit like a miniature solar system, having a central nucleus with electrons orbiting it. It was known that these electrons formed the bonds by which atoms joined to form compounds. These two ideas led to a paradox: for years chemists had drawn pictures of chemical compounds with straight lines representing bonds between the atoms, yet these fixed bonds had to be made of whirling electrons. It was Linus Pauling's triumph to resolve this paradox. His theory was explained in his book, *The Nature of the Chemical Bond,* which was for decades the bible of Chemists. Pauling showed by brilliant mathematical theory that electron waves between two electrons would interact to hold the atoms together. He extended the idea of bonds formed from waves to show how it explained the properties of a wide range of chemical compounds. Pauling was awarded a Nobel Prize for this and for research into 'molecular illness', diseases produced when the body genetically manufactures a defective compound. Some people manufacture a defective haemoglobin which cannot take up sufficient oxygen for health. Because of the shape the defective haemoglobin molecule forces on the blood cells, the disease is known as sickle-cell anemia. In 1962 Pauling received the Nobel Prize for peace for his campaign against nuclear armament, taking him into the tiny group of people who have won two Nobel Prizes.' Pauling's Nobel prize for chemistry was awarded in 1954. He laid the foundations for the method which led to the description of the DNA molecule by Watson and Crick in 1953. He proposed the theory of hybridization. Linus Pauling led an active life and continued research up until his death in the summer of 1994.

Two other methods[6] for calculating electronegativity values are as follows.

One method, put forward by **R. S. Mulliken** (1896–1986), was based on calculating the electronegativity value of an element from the first ionisation energy and the electron affinity values of the element. A second method, due to A. L. Allred and Rochow, calculates the electronegativity values of the atoms in a molecule by applying Coulomb's law of electrostatic attraction to work out the electrostatic attraction of each nucleus for an electron at half the internuclear distance from each atom in turn. The nuclear charge is modified to allow for shielding effects of electrons in inner shells.

All three methods are based on different theoretical approaches so do not produce identical values but show trends which agree well.

H																	He
2.1																	–
Li	Be											B	C	N	O	F	Ne
1.0	1.5											2.0	2.5	3.0	3.5	4.0	–
Na	Mg											Al	Si	P	S	Cl	Ar
0.9	1.2											1.5	1.8	2.1	2.5	3.0	–
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
0.8	1.0	1.3	1.5	1.6	1.6	1.5	1.8	1.8	1.8	1.9	1.6	1.6	1.8	2.0	2.4	2.8	–
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
0.8	1.0	1.2	1.4	1.6	1.8	1.9	2.2	2.2	2.2	1.9	1.7	1.7	1.8	1.9	2.1	2.5	–
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
0.7	0.9	1.1	1.3	1.5	1.7	1.9	2.2	2.2	2.2	2.4	1.9	1.8	1.8	1.9	2.0	2.2	–
Fr	Ra	Ac															
0.7	0.9	1.1															

Fig. 3.10 *Table of electronegativity values (Pauling)*

Trends in Electronegativity

A table of Pauling electronegativity values is given in Fig. 3.10, p. 60.

Electronegativity values:

(i) increase across a period;
(ii) generally decrease down a group;
(iii) are not given for the noble gases.

(i) Increase in electronegativity across a period

The increase in electronegativity across a period is easily explained. As the *atomic radius decreases* in size across a period, the nucleus of the atoms will approach increasingly closer to the shared pair of electrons. In addition, the *nuclear charge is increasing* thus increasing the attraction between the nucleus of the atom and the shared pair. All atoms of a period have the same number of electrons in *inner shells so the screening effects* of these electrons is a constant and cannot explain changes in electronegativity across a period.

Elements on the left of the table whose atoms have relatively large atomic radii and relatively small nuclear charges compared with other elements of the same period are termed 'electro-positive'.

Elements on the right of the table which have atoms with relatively small atomic radii and relatively large nuclear charges compared with other elements in the same period are called 'electro-negative'.

(ii) Decrease in electronegativity down a group

Electronegativity values become increasingly smaller down a group of elements in the periodic table. This is because the *atomic radii of the atoms down a group become larger*, increasing the distance between the nucleus and a shared pair of electrons in a covalent bond. Electrostatic attractions diminish over distance so the atoms down a group of the periodic table have increasingly smaller electronegativity values. However, *nuclear charge increases* down a group, suggesting that the electrostatic attraction of the nucleus for the shared pair of electrons in a covalent bond might be increasing, but this is more than offset by the effects of the increasing separation between the nucleus and these electrons and the *increasing screening effects* of electrons in inner shells.

(iii) No electronegativity values for the noble gases

Since the noble gases have no tendency to form bonds the definition of electronegativity does not apply to them and no values can be assigned.

Electronegativity Values and Bonding

A study of electronegativity is useful for predicting the type of bonding in a compound.

If elements of a compound have equal electronegativities then atoms of these elements have equal attraction for a shared pair of electrons in a covalent bond so the bonding can be described as pure covalent bonding. The bonding in PH_3 is non-polar covalent as the two elements, phosphorus and hydrogen, both have electronegativity values of 2.1.

The electronegativity value of hydrogen is 2.1 and that of chlorine is 3.0. This indicates that chlorine has a greater attraction for the shared pair of electrons in the H–Cl bond than hydrogen. Consequently the chlorine atom is partially negatively charged while the hydrogen atom is partially positively charged since the electron of the hydrogen atom is more likely to be found near the chlorine nucleus. An electrostatic attraction then arises between these two oppositely charged species. This electrostatic attraction is in addition to the original attraction both atoms have for the shared pair of electrons and so it strengthens the bond between them. This extra bond energy is referred to as Extra Ionic Resonance Energy (EIRE) and this type of bonding is called polar covalent bonding. The partial negative charge on the electronegative atom is indicated by δ^- and the partial positive charge on the electropositive atom is indicated by δ^+, see Fig. 3.11.

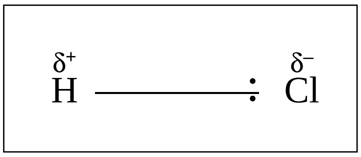

Fig. 3.11

The electronegativity values of sodium and chlorine are 0.9 and 3.0, respectively. Unequal sharing of an electron pair will therefore result. However, since chlorine is a highly electronegative element and sodium is a highly electropositive element there is a very high probability of locating the electron pair near the chlorine nucleus. The electron which originated in the sodium atom is effectively completely transferred to the chlorine atom making the chlorine atom a negative ion and the sodium atom a positive ion. A strong electrostatic attraction is then set up between the two fully charged species. This is an ionic bond. The ease of transfer of an electron from one atom to another and the percentage ionic character of the resultant bond is related to the size of the electronegativity difference between their elements. Thus the strongest ionic bond should be that formed between francium and fluorine, the elements with the smallest and largest electronegativity values, respectively.

As a rule of thumb, if the electronegativity difference between two elements is 0.4 or less, the bond formed between atoms of these elements is essentially non-polar covalent. If the electronegativity difference between two elements is greater than 0.4 and less than 1.7, the bond formed is polar covalent, the degree of polarity increasing as the difference between electronegativity values increases. Where the electronegativity difference between the two elements is 1.7 or greater the transfer of the shared pair of electrons towards the electronegative atom is significant and the bond may be predicted to be ionic[2]. However, the electronegativity difference between the elements in a compound is not the only factor which influences the nature of the compound, and the rule of thumb given here is useful for predicting the type of bonding which *might* be expected in a given compound. (See Dipole Moments.)

Dipole Moments

A polar covalent bond like that in HCl, consisting of two oppositely charged species separated by the bond length, can be described as a dipole. A dipole has a dipole moment equal to the product of the size of one of the charges, q, and the separation between them, d, i.e. dipole moment = qd. The dipole moment by convention is taken as pointing in the direction of the negative end of the bond. The dipole moment is indicated by an arrow in Fig. 3.12.

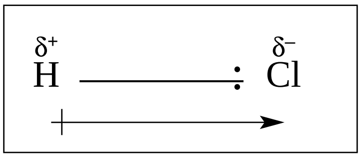

Fig. 3.12

In simple diatomic molecules like HCl only a single dipole exists but in polyatomic molecules such as ammonia or tetrachloromethane, a dipole moment exists along each bond. The dipole moment of the molecule is the vector sum of all these individual dipole moments. In ammonia, electronegativity values indicate that there are three dipole moments in the molecule lying along the N—H bonds in the direction of the nitrogen atom. When these are added vectorially the resultant dipole moment of ammonia points away from the hydrogen atoms to give the resultant dipole moment marked 'Net dipole moment' in Fig. 3.13.

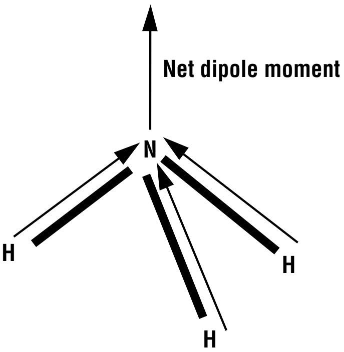

Fig. 3.13

The sum of bond dipole moments may be zero even when each bond is appreciably polar. For example, the electronegativity difference between carbon and oxygen is 1.0 and using the rule of thumb given above we would predict that the compound carbon dioxide should be polar. However a look at the geometry of the carbon dioxide molecule shows that this cannot be so. The carbon dioxide molecule is linear and a double bond joins the carbon atom to each oxygen atom. The dipole moments lie along the direction of these bonds both pointing away from the carbon atom towards the more electronegative oxygen atoms. Vectorially they cancel each other out and carbon dioxide is non-polar. Thus we must distinguish between polar bonds and polar molecules.

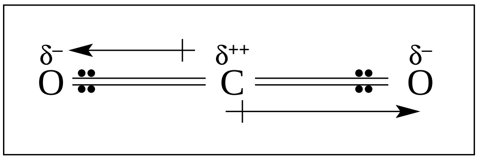

Fig. 3.14

3.5 Experiments

Experiment 3.1
To Calculate the First Ionisation Energy of Hydrogen from the Atomic Spectrum of Hydrogen

Student Experiment.

Materials

Data on Lyman Series of hydrogen spectrum[4]
Planck's constant, h
Avogadro's constant, L

Procedure

1. Take frequency value of transition of an electron from infinity to first level of hydrogen atom from a spectrum or data book.
2. Calculate corresponding energy using the formula: $E = hf$ (result in joules).
3. Calculate the energy for electrons in a mole of atoms undergoing this transition, $E = LE = Lhf$ (result in joules/mole).
4. Convert from joules/mole to kilojoules/mole.
5. Compare with value given on a table of ionisation energies.

Conclusion

$f = 3.290 \times 10^{15}$ Hz
$h = 6.626 \times 10^{-34}$ J s
$E = hf = 2.180 \times 10^{-18}$ J
$L = 6.022 \times 10^{23}$
$E/\text{mol} = EL = 1.313 \times 10^{6}$ J mol^{-1}
$= 1313$ kJ mol^{-1}

Compare with value in Mathematics Tables.

Experiment 3.2
To Plot a graph to Show Trends in First Ionisation Energy Values across Second Period

Student Experiment.

Materials

Graph paper and drawing instruments
Data on ionisation energy values

Procedure

1. Plot a graph of ionisation energy value versus atomic number.

Conclusion

Note and explain the general trend and comment on the values corresponding to the elements beryllium and nitrogen.

3.6 References

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APPENDIX A

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APPENDIX B RESOURCE MATERIAL

1. John Davis's Classroom Video, Darby House, Bletchingley Road, Merstham, Redhill, Surrey RH1 3DN, England offers the following video titles on this subject matter for second level chemistry students.

The Nature of Matter (Atomic Structure) (16–18 years)

The Mole (11-14 years)

Millikan's Oil Drop Experiment (16-18 years)

Nuclear Physics (16-18 years)

3rd Row Elements Periodic Table (16-18 years)

Catalogue available

2. Philip Harris Education, through their Irish agent Alkem Chemicals Limited, Industrial Estate, Little Island, Co. Cork and Alkem Chemicals Limited, Unit 4C, Ballymount Industrial Estate, Dublin 12, offer the following video titles in their Catalogue for Education.

Nuclear Physics

The Periodic Table and Periodicity

Elements, Compounds and Mixtures

Matter – Building Blocks of the Universe

Chemical Bonding & Atomic Structure

Chemical Changes All About Us

3. Philip Harris Education, through their Irish agent Alkem Chemicals Limited, Industrial Estate, Litttle Island, Co. Cork and Alkem Chemicals Limited, Unit 4C, Ballymount Industrial Estate, Dublin 12, also offer the following software titles in their Catalogue for Education.

Periodic Table (BBC, Nimbus)

Elements and Compounds

4. Irish Science Teachers' Association.

Famous Irish Scientists Posters – Robert Boyle

5. SICICI Video Library, University of Limerick, Plassey, Limerick. Catalogue of approximately 350 titles available, including films on atoms and atomic structure. See also SICICI Directory of Resources for Teaching Chemistry, 2nd Edition, 1994.

MODULE 2

Hydrocarbons

CONTENTS

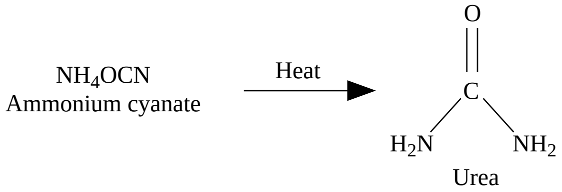
CHAPTER 1

INTRODUCING ORGANIC CHEMISTRY

1.1 History and Development

Historically all chemical compounds fell into two distinct classes. This simple division was based purely on the source of the compound in question. Those compounds derived from living organisms or organisms which once lived (plants, animals, coal or oil) were called '**organic**' while those derived from mineral sources were called '**inorganic**'. It was also believed that those compounds which burned were organic and those which melted were inorganic. Indeed, many notable scientists of the day believed that these organic compounds could only be manufactured by living organisms and even bestowed on them a mystical 'vital force' which only they could contain. So to synthesise them in a laboratory situation was tantamount to playing God!

Nevertheless, through experimentation much was learned about organic compounds. **Antoine Lavoisier** (1743-1794) analysed organic compounds and found them to contain the elements carbon, hydrogen and oxygen primarily, and to a lesser extent nitrogen, sulphur and phosphorus. **Jon Jacob Berzelius** (1779–1848), a Swedish chemist, confirmed that carbon was indeed the essential element in organic compounds. Then in 1828 **Friedrich Wohler** (1800–1882), a young German student of Berzelius, performed what was at that time understood to be the impossible. Starting with an aqueous solution of a known inorganic compound, ammonium cyanate, NH_4OCN, Wohler proceeded to heat the solution, evaporating it to dryness and, by what we now know to be isomerisation, the organic compound urea was formed. Wohler's reaction is as follows, Equation 1.1.



Equation 1.1

This was the end for the 'vital force' theory. Soon organic compounds were being synthesised on a regular basis in laboratories. Organic chemistry now became the chemistry of carbon compounds, and the name 'organic' continued to be used.

Some carbon compounds not listed as being organic were carbon monoxide, carbon dioxide, carbonic acid and its salts – the carbonates and bicarbonates (hydrogencarbonates). These were already in widespread use and classified as inorganic.

In 1832 Wohler moved to Giessen in Germany to work with another famous scientist, **Justus von Liebig** (1803–1873), where they improved and developed much of the experimental procedures and apparatus used in modern laboratories today. It was also in Giessen that another German, **Friedrich August Kekulé** (1829–1896), drawn by the fame of the chemistry professors, turned from a career in architecture to one in chemistry. He decided to abandon the structures of buildings and concentrate instead on the structure of organic compounds. He discovered that carbon was tetravalent and was capable of forming long chained molecules. Perhaps his best known discovery was during a dream in which he saw the structure of benzene in the shape of a six-membered ring.

Around this time the industrial revolution was beginning to gather momentum. So it was that industrialists began to cash in on the new discoveries in the chemical world. In 1856 **W. H. Perkin** (1838–1907), a student working in London trying to prepare the drug quinine from aniline, accidentally discovered the purple dye ‘mauve’. This was the forerunner to many of the synthetic dyes called ‘azo-dyes’. The synthetic dyestuffs industry was born and was dominated up to the 1870s by England after which Germany took her place. Unfortunately this led to the collapse of the Indian dye trade where many of the naturally-occurring dyes were found but it meant prosperity for Manchester and Mannheim. German chemists began to diversify into pharmaceuticals, and in 1899 Bayer applied for a patent to synthesise ‘aspirin’. Another giant German chemical company BASF also had its origins in the dye industry. The initials stand for *Badische Anilin und Soda Fabrik* (The Badische Aniline and Soda Factory).

The organic chemical industry is much more dynamic than its inorganic counterpart. This is mostly due to the large numbers of possible organic compounds and the various routes by which they can be synthesised. Rapid growth in recent years has been shown in the

SOME IMPORTANT DATES IN ORGANIC CHEMISTRY

1784	Karl Wilhelm Scheele isolates uric acid, tartaric acid, citric acid, lactic acid, formic acid and glycerine.
1807	Berzelius suggests that anything that melts when heated is ‘inorganic’ while anything that burns is ‘organic’.
1815	Berzelius advances the ‘vital force’ theory.
1815	Sir Humphry Davy perfects the miner’s safety lamp.
1821	Johann Loschmidt introduces single and double lines to represent single and double bonds.
1824	Justus Von Liebig and Friedrich Wohler discover different organic compounds having the same empirical formula.
1825	Michael Faraday isolates benzene from whale oil.
1828	Friedrich Wohler manufactures urea.
1830	Berzelius gives the name ‘isomer’ to different compounds having the same molecular formula.
1830	Baptiste Dulong perfects a method for determining the percentage of carbon and hydrogen in organic compounds.
1839	Charles Goodyear discovers the vulcanisation of rubber.
1848	Louis Pasteur discovers that the two forms of tartaric acid affect polarised light differently due to the arrangement of their atoms.
1848	Adolph Kolbe manufactures ethanoic acid (acetic acid) from inorganic sources.
1855	Charles Wurtz develops a method of making long-chain hydrocarbons.
1856	W. H. Perkin discovers the dye mauve.
1865	Kekulé proposes a structure for benzene.
1874	Jacobus Van’t Hoff and Joseph le Bel suggest the tetrahedral arrangement of bonds around carbon.
1897	Bayer synthesises aspirin.
1928	Alexander Fleming discovers penicillin.
1933	Polythene is discovered at ICI.
1936	Wallace Hume Caruthers discovers nylon.
1951	Rosalind Franklin discovers the helical structure of DNA.
1953	Watson and Crick unravel the mystery of the DNA molecule.
1964	Dorothy Hodgkin determines the structure of the vitamin B_{12} molecule.

petrochemical industry and its spin-off industries of polymers and pharmaceuticals. Ireland itself has shown a phenomenal growth in pharmaceutical industries over the last thirty years and can be found in the top ten of the pharmaceutical exporting countries of the world. It would seem the future of the organic chemist is assured for the foreseeable future.

1.2 Extent of Organic Chemistry

Organic compounds are as diverse as life itself. They vastly outnumber inorganic by 32 to 1 with almost 4 million known compounds. It is now possible to manufacture an organic compound containing any of the elements with the exception of the noble gases and some recently-discovered metals. For example, haemoglobin is a naturally-occurring organic compound of iron; chlorophyll contains magnesium; some synthetic compounds include trinitrotoluene, TNT, $C_7H_5(NO_2)_3$, aspirin $C_9H_8O_4$ and indigo (dye) $C_{16}H_{10}N_2O_2$. Organic chemistry is also the chemistry of the food we eat and the clothes we wear. The following brief list shows more clearly the extent and range of organically-based substances.

Fuels:	Coal, Natural Gas, Petrol, Wood.
Drugs:	Aspirin, Quinine, Morphine, Cocaine.
Explosives:	Dynamite, Nitroglycerine, TNT, Cordite.
Poisons:	Cyanide, Strychnine.
Dyes:	Indigo.
Synthetics:	Nylon, Terylene, Acrylics.
Plastics:	Polythene, Bakelite, PVC, Polystyrene.
Household:	Paper, Cotton wool, Glycerine, Olive oil, Vaseline, Soap, Turpentine.

To illustrate this point even further consider the following extract from a book published in 1930 called **An Introduction to Organic Chemistry**, by E J Holmyard (Arnold). Most of what is written is still true today and yet so many more examples could be added.

‘Let us follow a man through a day of his life. Emerging from between the sheets (made of the organic compound ***cellulose****), he uses* ***soap*** *to wash, cleans his teeth with a tooth-paste containing* ***carbolic acid****, puts on various garments (all organic) and proceeds to eat a hearty breakfast practically all of which consists of compounds of carbon, except the water and the salt.*

He then takes the ‘bus (driven by ***petrol*** *and shod with* ***rubber*** *tyres) to the office, first over* ***tarred*** *roads and then over streets paved with* ***wood*** *blocks soaked in* ***creosote****. Feeling a little stuffy in his nose, he uses his* ***artificial silk*** *handkerchief (made of cellulose, dyed with an organic dye), upon which he has taken the precaution to sprinkle a few drops of* ***eucalyptus oil****. Wrapping his scarf around his neck, he notices with annoyance that it has moth holes in it, and decides to take back some moth balls (made of the organic compound* ***naphthalene****) when he returns home. After a morning’s work at an organic table, writing with organic ink on organic paper, he remembers that he has an appointment with the dentist during lunch-hour. This is less of an ordeal than he expected, as the dentist gives him an injection of* ***cocaine*** *and he therefore experiences no inconvenience when the tooth is extracted.*

Returning to the office after lunch, he finds one of his clerks suffering from a severe headache, which passes off, however, after a dose of ***aspirin****. He then rings for the office boy, whom he wishes to send for a bottle of* ***paste****, but the boy cannot be found for some time. At length he is tracked down by a strong smell of* ***acetylene*** *proceeding from the yard at the back, where he is filling his new bicycle-lamp with* ***calcium carbide****. Sent off for the paste, he is away for more than an hour, having met a companion who tells him of a daring robbery at a neighbouring bank. The criminal had* ***chloroformed*** *the caretaker and blown open the safe with* ***nitroglycerine****, after which he had escaped with £2,000 in Bank of England notes (organic). The police were still at work* ***photographing*** *the scene of the crime.*

As he has now finished his day’s business, the employer sets off homeward, calling in at a perfumer’s on the way to buy his wife a bottle of ***scent****. Seeing a friend filling up his car with*

***benzol**, he begs a lift, and finally arrives home to a savoury dinner, washed down with an organic beer and followed by an organic cigar. Poking the organic fire and reading the organic evening paper, he spends the rest of the evening in placid comfort, till the organic sheets claim him once more.'*

1.3 What's So Special About Carbon?

To understand the uniqueness of carbon, let us consider its ability to form bonds.

(a) Carbon bonds by sharing four electrons in covalent bonds to gain an outer octet of electrons. All of its outer electrons are involved in this bonding and there are no 'lone pairs', Fig. 1.1. In addition, unlike silicon also in Group IV which has empty low-energy d orbitals, carbon has no low-energy empty orbitals. Thus carbon compounds are far more stable than those of silicon.

Carbon – $1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^0$,

Methane – CH_4

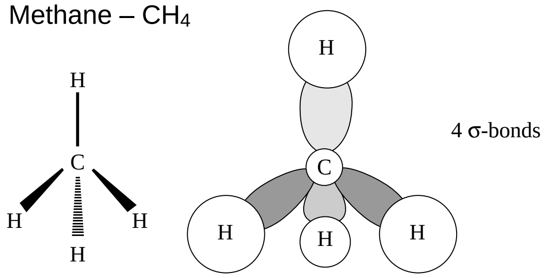


Fig. 1.1

(b) Carbon can bond with other carbon atoms, forming stable single, double and even triple bonds, Fig. 1.2.

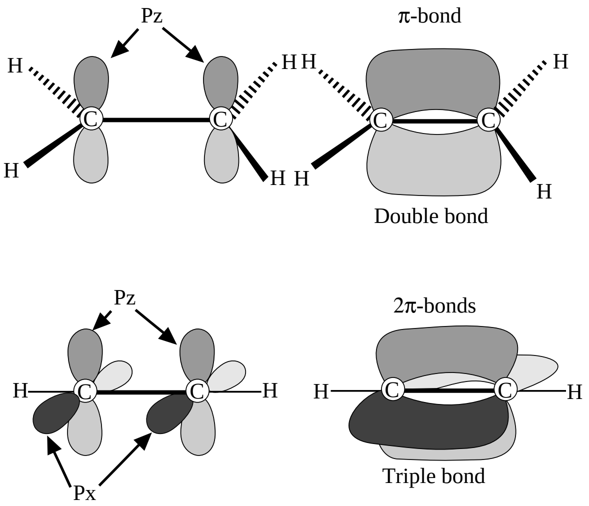


Fig. 1.2

(c) Carbon can form long chains with other carbon atoms (catenation) and still be relatively stable. These chains can be branched, giving complex structures, Fig. 1.3, and may contain many thousands of atoms (polymers).

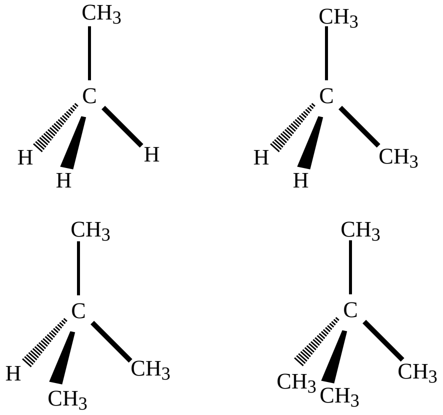


Fig. 1.3

(d) Carbon can form ring structures with itself and still have electrons available to link up with other carbon chains, Fig. 1.4.

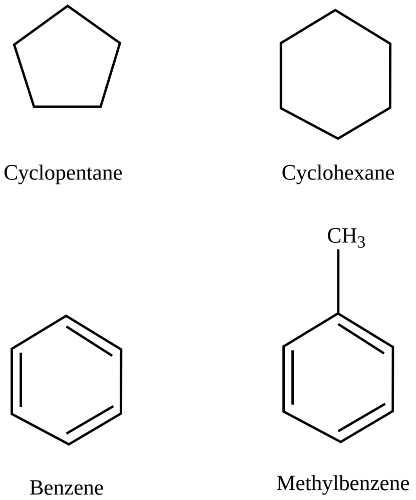


Fig. 1.4

As well as the above, carbon can also form single, double and triple bonds with other elements. However, more importantly, the C—C bond of the chain remains strong even when carbon is bonded to other elements, including fluorine and oxygen.

Some other elements come close to these properties but none can lay claim to them all. The ability to form double or triple bonds depends on the 'side-on' overlap by parallel orbitals of adjacent atoms. Elements beyond the second period cannot do this as the repulsion of the electrons in the lower levels and the increased length of the sigma bond will not allow the orbitals to come close enough for efficient 'side-on' overlap. This rules out the lower members of carbon's group, e.g. silicon, which can only form chains of single bonds. Even these chains are unstable as the Si—Si bond (226 kJ mol^{-1}) is much weaker than the Si—H bond (318 kJ mol^{-1}) or Si—O bond (464 kJ mol^{-1}), unlike carbon where the C—C bond (346 kJ mol^{-1}) is close to the C—O bond (360 kJ mol^{-1}) and the C—H bond (413 kJ mol^{-1}).

Boron can also form boron–boron chains but these are found to be electron-deficient, i.e. three atoms being held together by only two electrons, Fig. 1.5. This is referred to as 'electron deficient multicentred bonding'. Boron chains also tend to close in on themselves as they get longer and the geometrical arrangement of the atoms makes it impossible for the orbital overlap needed for double bonding.

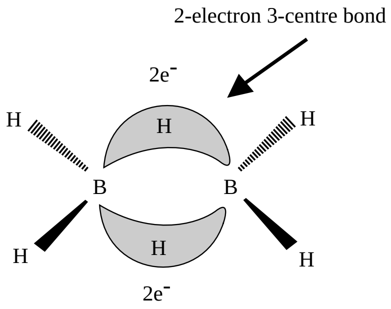


Fig. 1.5 *Boron hydride, B_2H_6*

Nitrogen can form single, double and triple bonds with itself and other elements, Fig. 1.6, but, in contrast to boron, it has excess electrons. As a result the N—N single bond is weakened by the repulsion of lone pairs on adjacent atoms.

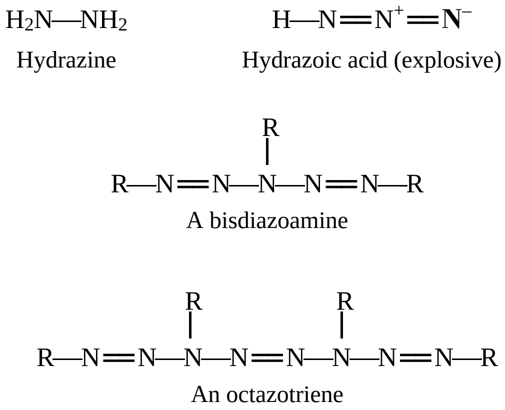


Fig. 1.6

The N≡N triple bond is almost six times as strong as the N—N single bond and chains of nitrogen atoms tend to break up easily forming several N_2 molecules. A molecule with two or more adjacent nitrogen atoms is rarely stable.

Carbon therefore has a fortunate combination of having as many valence electrons as it has valence orbitals, allowing it to bond with itself, forming bonds as strong as a bond with oxygen. Thus carbon is special and the understanding of its chemistry is of utmost importance in our lives.

CHAPTER 2

CRUDE OIL AND ITS PRODUCTS

2.1 Hydrocarbons as Fuels

In general, a fuel is a substance which can be oxidised to produce heat. Hydrocarbons have been found to be excellent fuels. Hydrocarbons can be burned in air or oxygen to release energy. The amount of heat given out by a fuel depends on the number of bonds broken and formed and on the types of bond present. Energy is used to break the bonds and energy is released when bonds are formed. In the case of the combustion of hydrocarbons the bonds broken can be a combination of **C—C, C═C, C≡C, C—H** and the **O═O** double bond, whilst **O—H** and **C═O** are the bonds formed. The bond energies of these bonds are summarised in Table 2.1.

When fuels are burned the energy released is always greater than the energy absorbed and thus combustion reactions are always exothermic. Since it is the addition of oxygen to the fuel that gives out energy, it would be expected that fuels such as methanol, CH_3OH, and ethanol, C_2H_5OH, which already contain oxygen should yield less energy. This is in fact the case. Table 2.2 presents a variety of combustion data for a number of hydrocarbons. It allows comparison of the hydrocarbons in terms of % H, kilogram calorific value, heat generated per litre of hydrocarbon (at s.t.p.) and heat generated per litre of hydrocarbon/oxygen in a stoichiometric mixture.

Bonds broken		Bonds formed	
C—C	348 kJ per mole	C═O	743 kJ per mole
C═C	612 kJ per mole	O—H	463 kJ per mole
C≡C	837 kJ per mole		
C—H	413 kJ per mole		
O═O	496 kJ per mole		

Table 2.1 *Bond energies*

Hydrocarbon	Formula	% H	Heat of combustion (kJ mol^{-1})	Kilogram calorific value (kJ kg^{-1})	kJ per litre gases at s.t.p.	kJ per litre of gas + O_2
Methane	CH_4	25.0	882	55 125	39.4	9.8
Ethane	C_2H_6	20.0	1540	51 330	68.8	11.5
Propane	C_3H_8	18.2	2200	50 000	98.2	12.3
Butane	C_4H_{10}	17.2	2860	49 310	127.7	12.8
Pentane	C_5H_{12}	16.7	3487	48 430	–	–
Hexane	C_6H_{14}	16.3	4140	48 140	–	–
Heptane	C_7H_{16}	16.0	4811	48 110	–	–
Octane	C_8H_{18}	15.8	5450	47 805	–	–
Ethene	C_2H_4	14.3	1387	49 535	61.9	12.4
Ethyne	C_2H_2	7.7	1305	50 190	58.3	14.6
Cyclohexane	C_6H_{12}	14.3	3925	46 725	–	–
Benzene	C_6H_6	7.7	3273	41 960	–	–

Table 2.2 *Combustion data for selected hydrocarbons*

A number of interesting points about fuels can be deduced from the data.

(a) The heats of combustion increase with increased molecular masses.

(b) The kilogram calorific values correlate well with decreasing hydrogen content.

(c) It is more practical to talk about kJ per litre when dealing with liquid or gaseous fuels. The more dense the fuel the more energy is released per litre.

(d) Where the gaseous fuel is mixed with oxygen before ignition, the unsaturated hydrocarbons ethene and ethyne yield higher energy values per litre of the fuel-oxygen mixture than ethane. There are two reasons for this fact. Firstly, ethyne and ethene require less oxygen for complete combustion than ethane.

$$C_2H_2 + 2^1/_2\ O_2 \longrightarrow 2\ CO_2 + H_2O$$

$$C_2H_4 + 3\ O_2 \longrightarrow 2\ CO_2 + 2\ H_2O$$

$$C_2H_6 + 3^1/_2\ O_2 \longrightarrow 2\ CO_2 + 3\ H_2O$$

A direct consequence of this is that a litre of the optimum fuel-oxygen mixture contains more fuel in the case of ethyne and ethene than in the case of ethane. Secondly, water has a very high specific heat capacity and absorbs heat very well. Therefore the less water formed the more heat that is made available.

Subsequent sections deal with the origins of hydrocarbons and how their efficiency as fuels is improved.

2.2 Origins of Hydrocarbons

Hydrocarbons are organic compounds containing only the elements hydrogen and carbon in various ratios. The main source of hydrocarbons is ‘crude oil’. Crude oil is a complex mixture of hydrocarbon molecules of widely varying molecular masses. In an oil refinery these molecules are separated into different fractions. Each fraction contains a variety of molecules all of which boil within a fixed boiling range. The lighter molecules are gases, the heavier molecules are liquids and the heaviest ones are waxy solids.

How Are These Hydrocarbons Formed?

Scientists have put forward the theory that crude oil was formed over millions of years and that this process is in fact continuing today. The theory proposed by **Engler** is that coal, crude oil, and natural gas all had their origins in the vast oceans that covered most of the earth in prehistoric times. Tiny plants and animals living close to the shore died and, over a period of time, their remains sank to the bottom of the ocean where they were covered by layers of mud and silt. Over thousands of years these layers were converted into sedimentary rock. As a result of the action of bacteria, heat and great pressure on the organic material, it was gradually changed into fossil fuels. Over time, with the disappearance of the oceans and due to massive land upheavals the oil deposits came to lie below exposed land masses. The oil and gases percolated where possible through the layers of porous rock above them. Eventually they found their way blocked by solid impervious rock. Here they collected and formed natural underground reservoirs enclosed above by a hard rock called ‘caprock’. It is precisely these non-porous rocks that geologists seek when searching for oil and gas. It is with great difficulty that this rock is drilled to reach the oil below. The history of the search for oil is long and varied.

The Chinese are believed to have found natural gas while drilling for salt and were using it as a fuel as long ago as 1000 BC. Indeed oil has a long association with salt as many oil deposits were accidentally found while drilling for salt. In North America in 1750 saltmakers were finding this oil very much a nuisance. Not all oil had to be drilled. Some deposits were located where oil had seeped under pressure through faults in the rock to form pools of black oil. These were called ‘seepages’. The American Indians used oil found in this way for medicinal purposes.

The first successful commercial oil well was drilled in 1859 by **Edwin I Drake** near Titusville in Pennsylvania. Drake himself was a retired train conductor who, to increase his credibility, adopted the title of colonel. His crew consisted of a blacksmith called **William A Smith** and his two sons. He struck oil on 27 August 1859 at a depth of 21.2 m. Drake used an iron pipe 9.75 m long driven into the ground to protect his well from water and cave-ins. The oil, once located, barely rose to the surface and had to be pumped out. The well produced between 10 and 35 barrels per day. (A barrel is equivalent to 159 litres or 42 US gallons or 35 imperial gallons.) In the beginning the oil was worth $20 dollars a barrel but within three years, when more successful wells had been drilled using Drake's methods, this had fallen to just 10 cents a barrel. Around this time also, Rumania was producing nearly 2000 barrels of oil yearly. This was being brought to the surface by hand in buckets from hand-dug wells.

In 1852 a Canadian, **Abraham Gesner,** discovered kerosine (also called coal oil) which came to be used for street lighting throughout the world. It was produced commercially by the destructive distillation of coal. In 1857 a Canadian, **James Miller Williams,** built the first oil refinery which produced kerosine for lamps. Gasoline (petrol) was also produced as a by-product but was found to explode when ignited in the lamps. Since no other use could be made of this fraction it was dumped in large amounts into rivers and streams. However, by 1900 gas and electric lighting became the norm and this put an end to kerosine production. As the need for kerosine fell, the need for gasoline (petrol) grew. The age of the automobile had begun and the need grew for more and more efficient fuels, a need which has dictated the work of oil refineries to the present day.

In 1900 a barrel of crude oil could yield only 11% petrol. By 1918 this had risen to 25% and by the middle of the 1970s it had reached 46%. Today a full-scale oil refinery can convert the entire barrel of crude oil into useful products – gases, petrols, light oils, heavy oils, tar or bitumen. Hydrocarbons are now produced on a large scale in oil refineries, first by distillation and then by two further processes called 'cracking' and 'reforming'.

Experiment 2.1
Production of Coal Gas and Coal Tar from Coal

Coal may be destructively distilled to produce quantities of coal gas and coal tar which can be examined. Small pieces of coal are placed in a test-tube and heat applied. The assembly of apparatus is arranged to allow the collection of the coal gas over water, Fig. 2.1. An arrangement of apparatus suitable for the collection of the coal tar is illustrated in Fig. 2.2. The tar is condensed by passing it through water. Alternatively, a combined apparatus may be used to collect both the coal gas and the coal tar in a 'one-pot' procedure, Fig. 2.3. It is worth examining the residue in the distillation vessel at the end. This is called coke. Coke is simply a form of carbon made from the destructive distillation of coal. When the gas is being collected some light colourless/pale yellow oil will be observed on the surface of the water. The coal gas can be combusted and the flame and gas produced tested with limewater.

In each case the apparatus needs to be heated quite strongly. Safety glasses should be worn and the delivery tubing should be withdrawn from the water when heating is suspended to prevent a 'suck-back'.

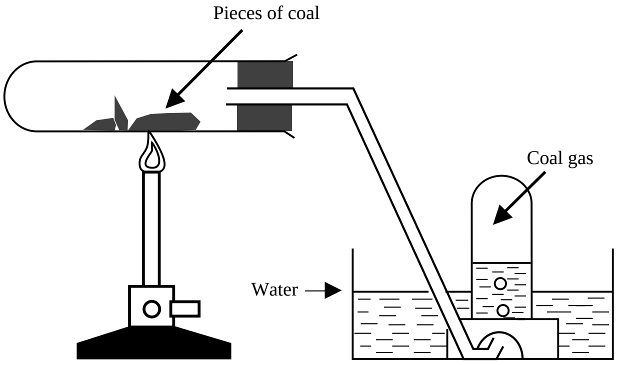


Fig. 2.1 *Collection of coal gas*

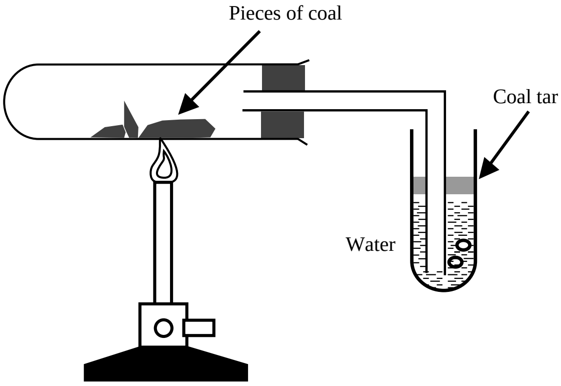


Fig. 2.2 *Collection of coal tar*

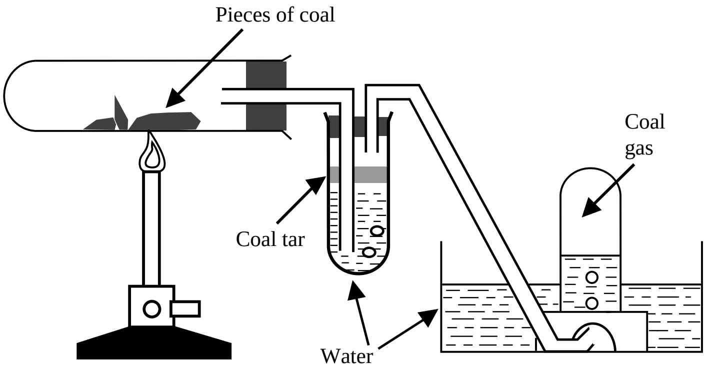


Fig. 2.3 *Collection of coal tar and coal gas*

2.3 Oil Refining

Natural gas is composed of hydrocarbons of low boiling point. The main gases present are methane, ethane, propane and butane. Kinsale gas is almost 99% methane and has no sulphur impurities. Very little must be done to natural gas to make it suitable as a domestic fuel. Crude oil on the other hand is of little or no value in its natural state. The purpose of the refinery is to separate out the various fractions and to modify some of these to improve their ‘octane rating’ (section 2.4).

The crude oil is delivered to the refinery by tanker from the various oil deposits throughout the world. The content of the crude varies from source to source, Fig. 2.4.

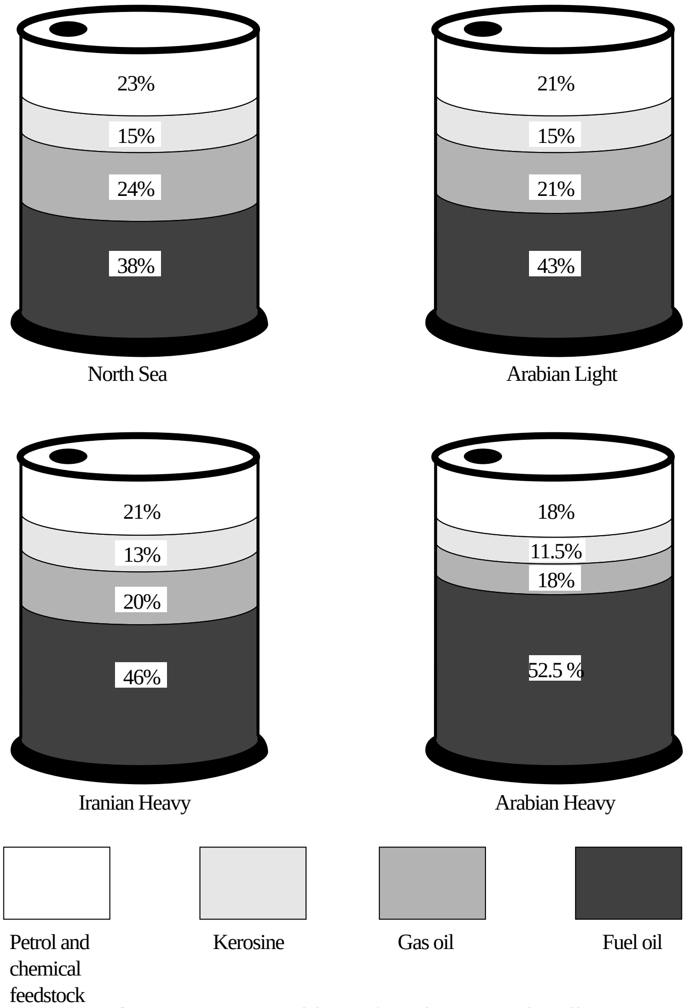


Fig. 2.4 *Composition of various crude oils*

The crude oil is pumped continuously in pipes throughout the refinery so that refinery workers seldom see or handle it. Their work is to keep a constant check on the dials and monitors controlling pressures and temperatures in the control centre. Chemists are also involved in the process in that samples are taken at various points in the plant on a regular basis and these are checked for quality.

The different hydrocarbons are separated out of the crude oil by distillation. This occurs in tall fractionating towers which can reach as high as 65 metres, Figs. 2.5(a) and 2.5(b).

As shown in Figs. 2.5(a) and 2.5(b), the heated crude oil enters the bottom of the tower and rises up through trays. Only a few are illustrated even though a fractionating tower would contain hundreds of trays. These trays may be (i) perforated with tiny holes [sieve trays, Fig. 2.5(a)] or (ii) contain bubble caps, Fig. 2.5(b), or (iii) contain movable valves, all of which allow the hot gases to percolate through and condense on them. The movement of hot vapour up through condensed liquid combined with the down flow of condensed material in the ‘downcomers’ enhances the fractionation occurring in the tower. For economic reasons, sieve trays are more widely used in fractionating towers. From the tower the fractions are drawn off at different levels which correspond to different temperatures. The lightest gases are drawn off the top and are mostly methane, ethane, propane and butane. About 10% of this is used by the refinery as a source of fuel, some is used to blend with petrols and the remainder is stored and bottled as domestic gas. For safety reasons this gas has sulphur compounds called mercaptans or thiols (e.g. ethyl mercaptan or ethanethiol, C_2H_5SH) added to give it a characteristic strong smell. Any gas leaks may be easily detected as a result of the odour of these compounds.

The ‘straight run’ gasoline fraction (i.e. straight from the tower) cannot be used as petrol as it has a very low octane number (i.e. it has poor burning characteristics in a combustion engine, section 2.4). To improve this the gasoline and light

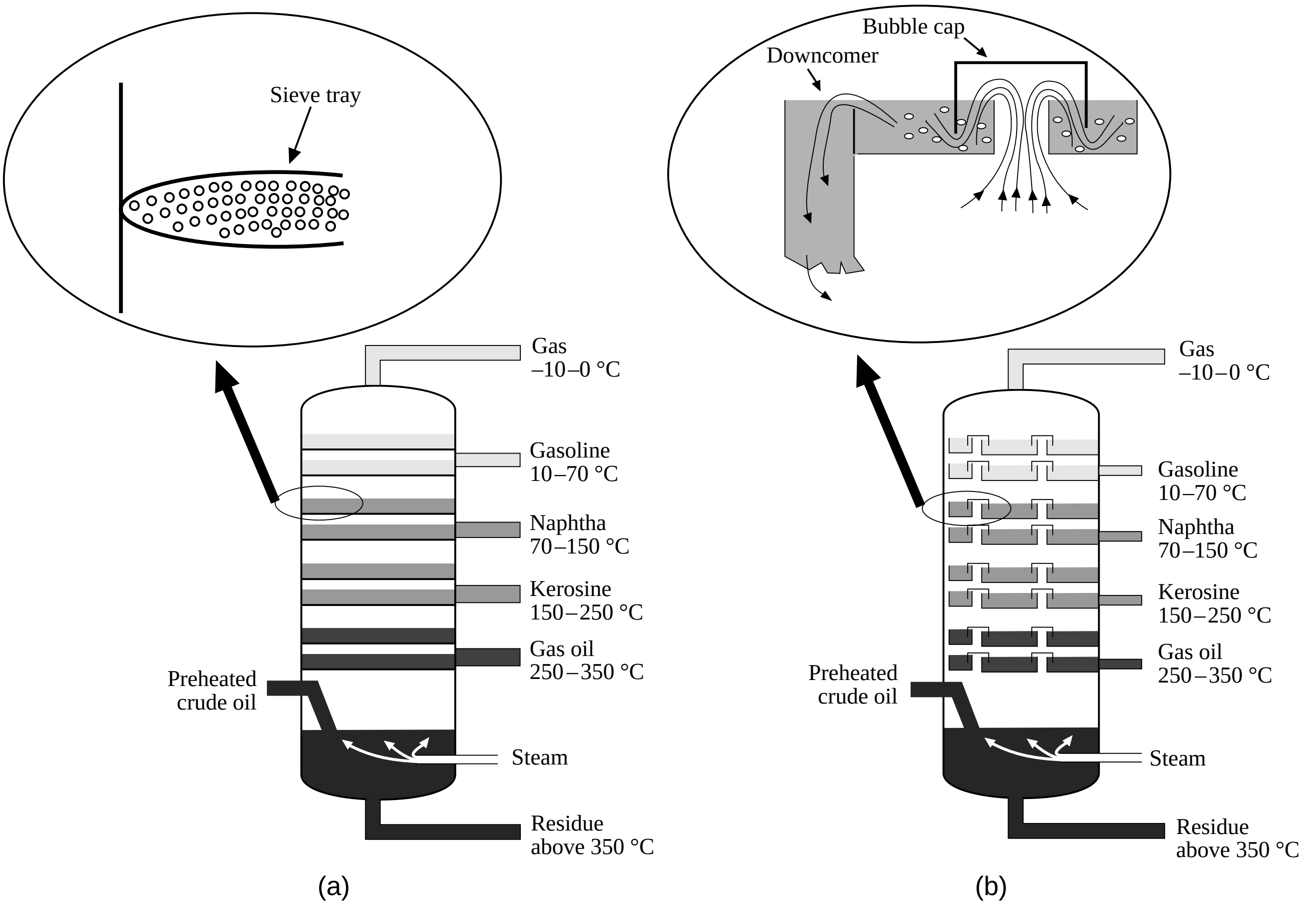


Fig. 2.5 *Fractionating towers*

naphtha fractions are ‘reformed’. Reforming is carried out by passing the hot gases through reactors containing a highly-selective platinum catalyst supported on alumina. Reforming is a process in which the number of carbon atoms remains the same but the molecules have their structure altered. Reforming had its beginnings in the oil business during World War II in order to make toluene needed for the manufacture of TNT and to develop a more efficient petrol. The process of reforming is also referred to as ‘platforming’ or ‘powerforming’. The main processes carried out in an oil refinery can be classed as distillation, reforming and/or cracking as well as desulphurisation.

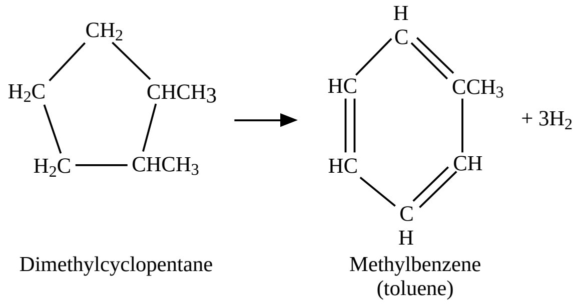
Reforming

Typically, reforming involves the following reactions:

1. dehydrogenation;
2. isomerisation;
3. dehydrocyclisation.

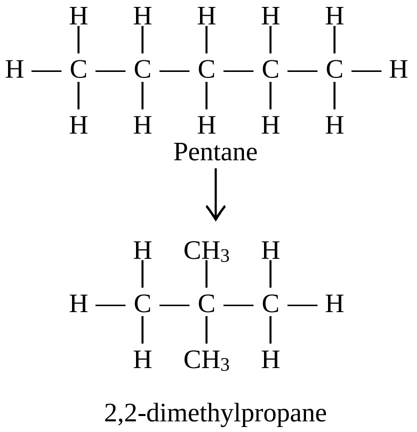
These reactions greatly increase the octane number of the fuel. However, the reactions are endothermic so the gases have to be heated and reheated constantly. The reactors are arranged in a line with the emerging gases from one reactor entering a furnace to be reheated before entering the next reactor. In Whitegate Oil Refinery there is one spare reactor present so that at any time one reactor may be taken off line for routine regeneration of the catalyst without having to shut down the operation. Regeneration of the platinum catalyst is necessary since this catalyst is readily poisoned by sulphur. A **hydrodesulphurisation process** is carried out upstream from the catalytic reforming process. Typical reactions which occur in each step are the following.

1. Dehydrogenation. This involves the removal of hydrogen from C_5 and C_6 cycloalkanes and converting them to aromatics. The formation of aromatic compounds is desirable as aromatic compounds have a high octane rating (section 2.4). An example of a typical dehydrogenation reaction is given in Equation 2.1.



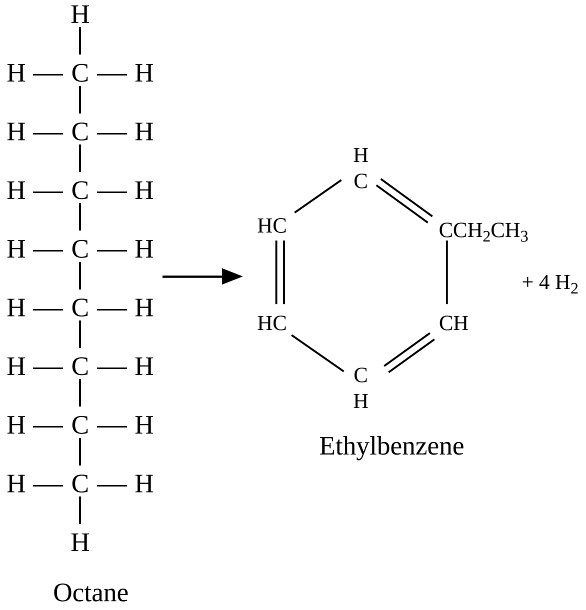
***Equation 2.1** Dehydrogenation*

2. Isomerisation. This is the rearrangement of straight-chained alkanes into branched alkanes. An example is given in Equation 2.2.



***Equation 2.2** Isomerisation*

3. Dehydrocyclisation. This causes the straight-chained alkanes to form aromatic rings with a loss of hydrogens. An example is given in Equation 2.3.



***Equation 2.3** Dehydrocyclisation*

Cracking

Refineries may also have a cracking operation which can convert the heavy gas oil (HGO) and fuel oils into more useful products which are lighter and usually unsaturated. Another name for cracking is 'pyrolysis'. This term means 'splitting using heat'. Very large alkane molecules are heated strongly, causing them to break into smaller molecules. The cracking of these large molecules, for which there is only a small demand, provides a very good source of fuels with a high octane rating, since the chains produced are highly branched. Another side product of cracking is small alkene molecules. These are used as raw materials for the synthesis of many important organic compounds. Whitegate Oil Refinery does not have a 'cat cracker'. Fractionation of crude oil, catalytic reforming of naphtha and desulphurisation of gas oil are carried out there. The chief refining processes employed are Crude Distillation and Catalytic Reforming. Such a refinery is classified as a 'Hydroskimmer'. The heavier residue is 'sold on' to other refineries. Many of the large UK and European refineries have sophisticated 'cat crackers' and can convert virtually all of a barrel of crude oil into valuable 'light' products.

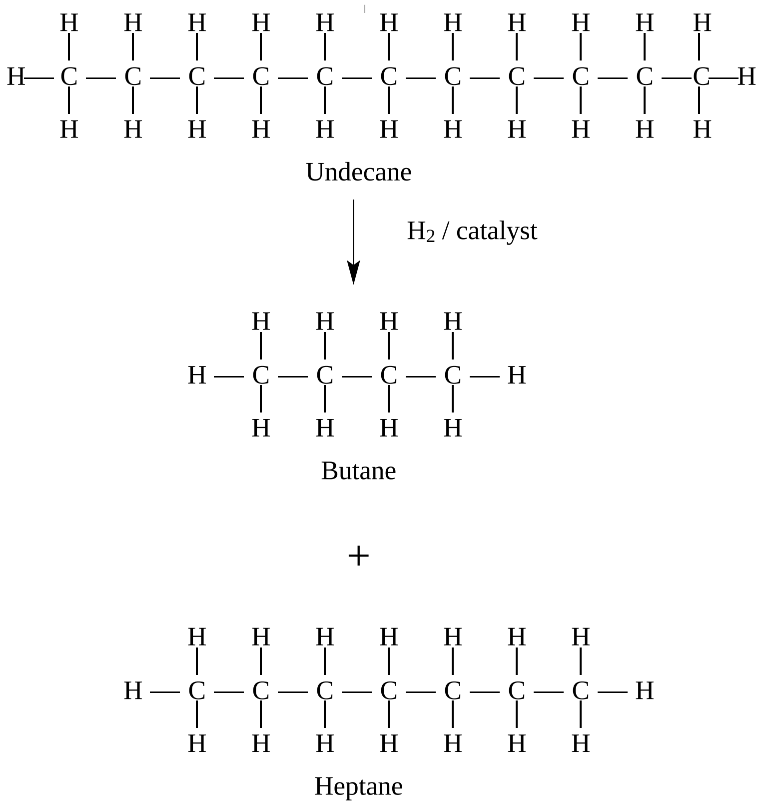
The following are the four types of cracking.

Thermal Cracking. This occurs at temperatures of 800–850 °C. The first thermal cracking method was called the Burton process after its inventor William M. Burton. It was first used in 1913. The chief product is ethene.

Steam Cracking. This is carried out using temperatures of 700–900°C for a fraction of a second and then rapid cooling. The steam reduces radical collisions. The chief products are ethene, propene, butadiene, isoprene and cyclopentadiene.

Hydro Cracking. THis is carried out using hydrogen and high pressures and temperatures of 250–450 °C. This process is found to occur during reforming due to the high temperatures and the presence of hydrogen in the reactors. It cracks long-chained alkanes into more valuable and more useful short-chained ones. An example of this type of reaction is given in Equation 2.4.

Catalytic Cracking. First used in 1936, this process uses a silica/alumina catalyst and temperatures of 450–550 °C. A variation of this is



Equation 2.4 *Hydro cracking*

‘fluid cat cracking’ where a powdered catalyst flows through the petroleum like a fluid. Used first in 1942, chief products are alkenes and alkanes with a highly-branched structure for use in petrol.

Thus the main purpose of cracking is to make use of the heavier fractions produced in the distillation of crude oil. The useful products are fuels and valuable alkenes.

The dehydrogenation and the isomerisation reactions are fast and improve the octane rating of the fuel which has undergone reforming (‘the reformate’) from about 44 to 80. Subsequent dehydrocyclisation and hydrocracking reactions are slow but they do have the desired effect of increasing the octane number to about 98.

Desulphurisation

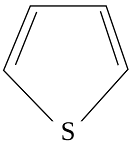
This is the name given to the process of removing/reducing the sulphur content of an oil fraction. As mentioned above there is a need to reduce the sulphur content of naphtha prior to catalytic reforming. This is due to the fact that sulphur acts as a catalyst poison. A process called **‘hydrodesulphurisation’** is employed to reduce the sulphur content of the naphtha prior to catalytic reforming. This involves passing the hydrogen-rich treatment gas (the naphtha plus hydrogen) over a cobalt-molybdate catalyst under conditions of high temperature and pressure. Upon cooling the product gases the sulphur is separated as H_2S vapour which is mixed with mains gas and burned. Reactions which typify the removal of sulphur by hydrodesulphurisation are summarised in Equations 2.5(a), 2.5(b) and 2.5(c).

$$\underset{\text{Butanethiol}}{C_4H_9SH} + H_2 \longrightarrow \underset{\text{Butane}}{C_4H_{10}} + H_2S$$

Equation 2.5(a)

$$\underset{\text{Diethyl sulphide}}{C_2H_5SC_2H_5} + 2H_2 \longrightarrow \underset{\text{Ethane}}{2C_2H_6} + H_2S$$

Equation 2.5(b)



$$+ 4H_2 \longrightarrow \underset{\text{Butane}}{C_4H_{10}} + H_2S$$

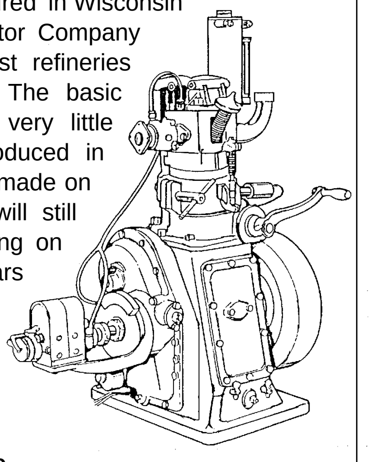
Thiophene

Equation 2.5(c)

Since the crude oil used at Whitegate is ‘Sweet North Sea Crude’ the overall sulphur content of the crude oil is low and consequently the sulphur content of the gas oil (heating and diesel) produced at Whitegate fell well within the legislative demands of the EU up to 1996. However, a further lowering of permitted sulphur limits came into operation in 1996 and to meet this the gas oil now has to undergo a hydrodesulphurisation process. A sulphur recovery process is also now in place where the H_2S produced is oxidised to elemental sulphur and the solid sulphur recovered.

Irish Refining plc, Whitegate, Co. Cork

In Ireland refining is carried on in Whitegate. The company was first set up in 1959 by the major oil companies of the day, i.e. Esso, Shell, BP and Texaco. However, as a result of the oil shortage in the early 1980s it faced closure until the Government stepped in and bought the equity from the oil companies. The Irish National Petroleum Corporation was set up in the late 1970s and Irish Refining became a subsidiary company in 1982. Whitegate refines North Sea crude which is described as a ‘sweet crude’. It contains a high percentage of light fractions and little or no sulphur. The refinery is a ‘hydroskimming’ refinery and basically carries out the primary distillation followed by the reforming (‘powerforming’) of the gasoline and light naphtha fractions. 50 000 barrels of crude oil are distilled per day and up to 9000 barrels of the fractions are reformed. The refinery gases (propane and butane) are stored until bottling, while the heavy oils and residue (about 40%) are immediately exported to larger refineries for cracking. Whitegate also blends the petrols and the different grades are tested under laboratory conditions to ascertain their octane number. The standard test machine is the knock test engine manufactured in Wisconsin by the Waukesha Motor Company and is in use in most refineries throughout the world. The basic design has changed very little since it was first produced in 1930, so that a rating made on the earliest engines will still match the octane rating on today’s engine 60 years later. The unit cost of these engines is of the order of $100 000.



The Waukesha CRF Fuel Research Engine

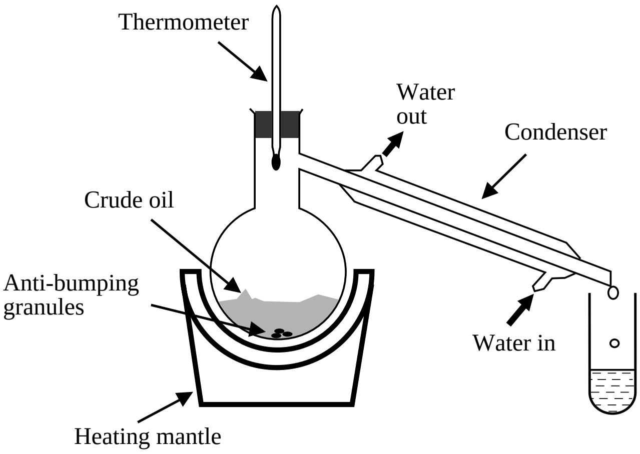


Fig. 2.6

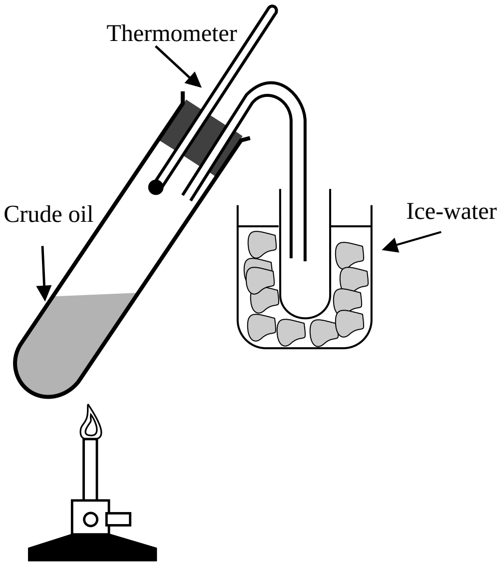


Fig. 2.7

Experiment 2.2
Distillation of Crude Oil

Crude oil is a complex mixture of hydrocarbons varying from gases to bitumen. The first stage in oil refining is to distil the mixture to isolate hydrocarbons of similar boiling points. In industry, large fractional distillations are carried out. In this experiment a simple distillation, Fig. 2.6, is used to separate crude oil into a number of fractions. The appearance of each fraction is noted, then they are burned and the ease with which they burn is observed. A typical set of fractions collected in this type of experiment would be 20–80 °C, 80–120 °C, 120–180 °C and 180–220 °C. A smaller-scale apparatus is shown in Fig. 2.7.

Notes on Procedure

1. The function of the anti-bumping granules is to prevent ‘bumping’, i.e. the sudden violent boiling-over of the reaction mixture into the collection vessel. Anti-bumping granules can be replaced by any of the following which serve the same purpose (prevention of bumping): pumice stones, pieces of porcelain, pieces of glass or, indeed, a magnetic stirring bar if heating is being provided by a hot plate with a built-in magnetic stirrer.
2. Care must always be taken when heating any flammable mixture using a Bunsen burner. A heating mantle is preferable, particularly if a larger-scale preparation is used. Joints in the apparatus must be sealed/connected properly and the apparatus must be clamped safely.
3. When the temperature of the vapour reaches 100 °C it is advisable to turn off the water supply to the Liebig condenser. This avoids the possibility of the condenser cracking as very hot vapour meets a cold condenser.
4. If the crude oil available in your school chemical stores is not yielding adequate quantities of the fractions normally desired, add a **little** 60–80°C-type petrol, available from laboratory suppliers, and diesel from your garage and this (higher quality crude oil!) will give better classroom results. Use of petrol from a garage is not advised as it contains low-boiling components (e.g. butane) that are difficult to trap in simple laboratory distillation. The possibility of flammable gases escaping in a location where there may be ignition sources must be avoided.
5. It will be noted that the lower-boiling fractions continue to burn when ignited. In order to ignite one of these fractions it is necessary to

Property	20–80 °C	80–120 °C	120–180 °C	180–220 °C
Colour	pale yellow	yellow	dark yellow	yellow-brown
Viscosity	runny	fairly runny	fairly viscous	viscous
Behaviour when ignited	burns readily; clear yellow flame	easy to ignite; yellow flame; some smoke	harder to ignite; quite smoky flame	difficult to ignite; flashes; smoky flame

Table 2.3

reach a certain temperature called the 'ignition temperature'. The ignition temperature is the minimum temperature at which there is sufficent vapour above the liquid to sustain combustion when a fuel is exposed to an ignition source, e.g. a spark or flame.

Higher-boiling fractions only 'flash' when ignited (they ignite and quench again, not sustaining combustion). At room temperature there is enough flammable vapour above the liquid to allow a 'flash' but there is insufficient vapour to allow sustained combustion. The 'flash point' is the minimum temperature at which there is enough vapour above a liquid to cause a 'flash' when an ignition source is applied.

The higher ignition temperature of diesel results in the need for a heater in diesel engines. At higher temperatures the 'auto-ignition temperature' can be reached. At this temperature a fuel will spontaneously ignite and continue to burn when in contact with air. Therefore no spark-plugs are required in a diesel engine. The burning characteristics of the fractions are summarised in Table 2.3.

Experiment 2.3
Cracking a Hydrocarbon

Long-chain hydrocarbons are produced in larger quantities than are required and are converted to shorter-chain, more useful and valuable compounds by a process called **cracking.** The products of these reactions are a variety of short-chain alkanes and alkenes.

In this experiment liquid paraffin is cracked using hot porcelain as the catalyst, Fig. 2.8. The gaseous products are collected over water and tested using the standard tests for alkenes (decolourisation of bromine water and of acidified potassium manganate(VII) (potassium permanganate)). The tests give positive results indicating that the products are unsaturated.

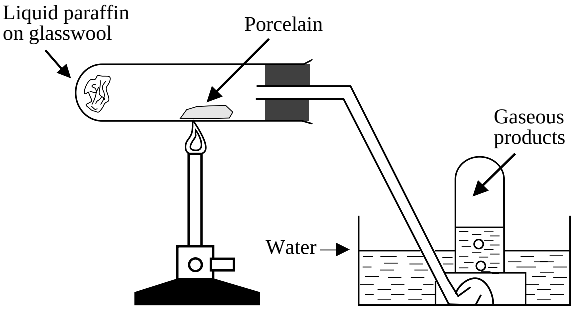


Fig. 2.8

Notes on Procedure

1. When the liquid paraffin is placed in the test-tube a dropper is used and the glass wool is inserted after the liquid paraffin. This avoids a situation arising where the walls of the test-tube become coated with the liquid paraffin. The function of the glass wool is purely to keep the liquid paraffin at the end of the test-tube. Care should be taken when using glass wool as the fibres are dangerous and represent a health hazard.
2. The catalyst is heated until it is red hot and the liquid paraffin may need an occasional slight heating also to keep the reaction proceeding at a reasonable rate.
3. Once the required amount of gas is collected the delivery tube must be removed from the trough before heating is suspended so as to avoid a 'suck-back' into the test-tube.
4. Discard the first few tubes of gas collected. It is mostly displaced air from the system.
5. Steel wool ('wire wool' sold as an abrasive) which is readily available will act as a catalyst in place of porcelain and may prove more convenient.

2.4 Petrol

Petrol is a blend of hundreds of chemical compounds most of which are hydrocarbons. The chief source of these hydrocarbons is the raw gasoline fraction obtained from the distillation of crude oil. The raw gasoline is subsequently reformed in a catalytic reformer to produce high-octane gasoline blend-stock. This contains mostly alkanes which have between 5 and 10 carbon atoms in their make-up and whose boiling points are between 20 °C and 180 °C. Although a barrel of crude oil contains 15–30% gasoline, modern refining methods enable us to increase this yield to 45%. In a refinery it is possible to alter or reform the structure of the hydrocarbons; the long-chained hydrocarbons may be cracked and the tarry residue may be redistilled using high pressures and low temperatures. These processes increase the petrol yield and introduce alkenes and aromatic hydrocarbons into the mixture.

Is All Petrol the Same?

No, it is not. Though we use the same garage and fill our cars from the same pump all year round we are not getting the same petrol blend. Petrol companies change their blends twice in the year, on 1 May and 1 September. The reason for this is the behaviour of liquids in different temperature conditions. During the winter months, when engines are cold, we expect the engine of our car to fire first time when starting. What makes this possible is that winter blends of petrol contain a higher proportion of volatile hydrocarbons which vaporise easily and ignite readily. These blends usually contain butane which is a gas at ambient conditions and readily dissolves in the petrol. Summer blends, however, cannot afford such volatile components in high concentrations. As a result of the heat, the petrol may evaporate in the tank which could be costly or bubbles of gas in the fuel lines could lead to the engine becoming vapour-locked. Summer blends therefore contain hydrocarbons with medium to high volatility.

Other substances found in petrol include the following.

Antioxidants – these prevent the petrol from becoming gummy.

Anti-icers – these prevent ice forming in the fuel lines in winter (very important in aviation fuel).

Anti-rust agents – to prevent tanks and fuel lines from rusting.

Detergents and deposit modifiers – to clean off, or prevent, deposits forming in the engine.

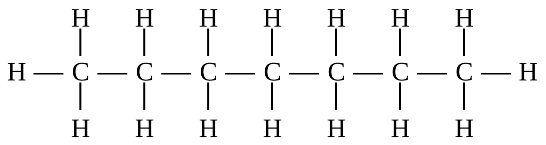
Metal deactivators – to prevent metal impurities interfering with the petrol.

Antiknocking agents – these are used to make the petrol burn more smoothly.

What is 'knocking'?

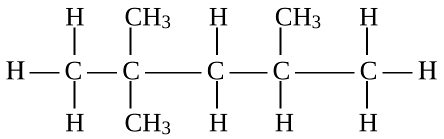
In a car engine the petrol and air mixture becomes compressed in the chamber. This compression can reduce the volume by a factor of 10 (petrol engines) or a factor of 15–20 (diesel engines). As the volume decreases the temperature increases and this can cause the mixture to combust spontaneously before the piston is in position to receive the power from the explosion. (See note below on how a petrol engine works.) The mixture ignites again when the spark is fired. This double ignition causes a 'knocking' or 'pinking' in the engine. It results in poorer performance of the engine and in time can lead to wear and tear of the cylinder.

Petrol contains additives or high percentages of antiknocking hydrocarbons to reduce this unwanted occurrence. An indication of the ability of a petrol sample to perform this function is its 'octane number'. This number is based on a fuel which is a mixture of heptane and a highly-branched isomer of octane, 2,2,4-trimethylpentane, Fig. 2.9. The straight-chain hydrocarbon heptane on its own is assigned an octane number of zero while 2,2,4-trimethylpentane on its own is



$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$

Heptane



$(CH_3)_3C\text{—}CH_2\text{—}CH(CH_3)\text{—}CH_3$

2,2,4-trimethylpentane

Fig. 2.9

assigned an octane number of 100. Thus a fuel with an octane number of 80 burns with the same smoothness as a mixture of 80% 2,2,4-trimethylpentane and 20% heptane.

A table of octane ratings of various petrol components is given in Table 2.4 at the end of this chapter.

How Does a Four-Stroke Petrol Engine Work?

The cycle begins with the **intake stroke**. As the piston moves down it draws in the fuel-air mixture through the intake valve on the left, Fig. 2.10. Next comes the **compression stroke** where the piston moves up, compressing the mixture. At the top of the stroke the spark ignites the mixture. The burning gases force the piston downwards in the **power stroke**. Finally the exhaust valve opens on the right and the piston rises, driving the exhaust gases out of the chamber. This is the **exhaust stroke**. The cycle then repeats itself.

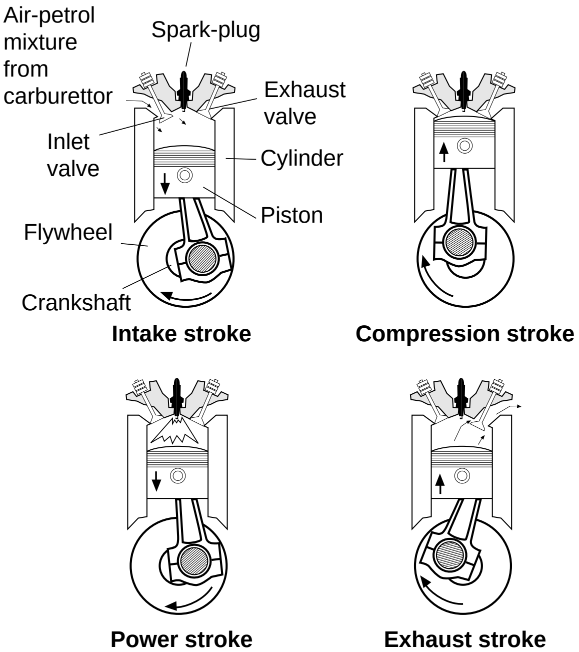


Fig. 2.10 *Combustion cycle in a four-stroke petrol engine*

How Does a Diesel Engine Work?

The cycle begins with the **intake stroke** when the piston moves down and draws air into the cylinder, Fig. 2.11. During the **compression stroke** the temperature rises to about 480 °C. When diesel oil is injected into the cylinder it mixes with the hot air and burns rapidly. There is no spark plug required in the diesel engine as the working temperature is above the autoignition temperature of the fuel. The gases produced by this combustion push the piston down for the **power stroke**. The **exhaust stroke** drives out the waste gases.

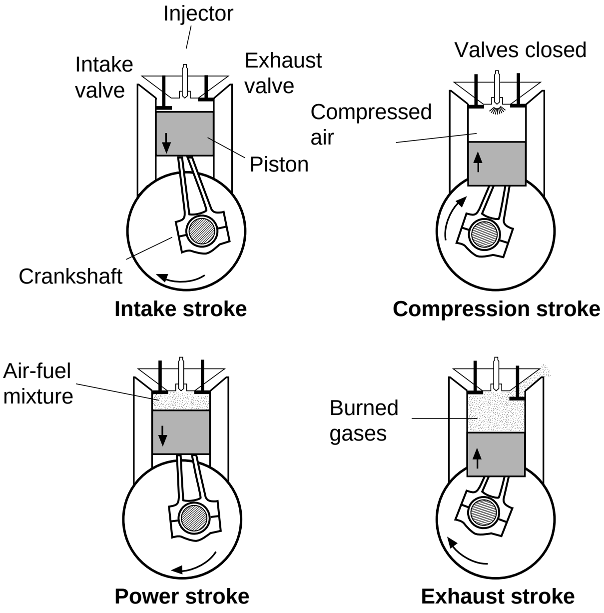
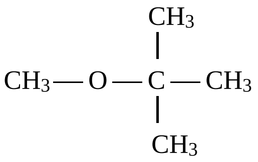


Fig. 2.11 *Combustion cycle in a diesel engine*

Since the early 1920s compounds of lead have been used in petrol to reduce the knocking in engines. One such compound is tetraethyl-lead. It is believed that these antiknocking agents work by forming lead oxide, PbO, a substance which can absorb free radicals. These radicals are formed during the combustion of the fuel and their absorption slows the reaction down giving a smoother burn. Another compound, 1,2-dibromoethane, is used to convert the lead to lead bromide ($PbBr_2$ or $PbBr_4$), which is volatile. This vaporises easily and is swept away in the exhaust gases.

However, lead compounds are poisonous and pollute the atmosphere. In the car they limit the workings of catalytic converters, as lead poisons the catalyst. A catalytic converter fitted to a car minimises gaseous pollutants by oxidising unburned hydrocarbons and carbon monoxide to carbon dioxide and water, and breaking down nitrogen oxides into nitrogen gas and oxygen.

The use of lead in petrol is now on the decline and in some countries has been outlawed. Petrol companies must now spend more money on increasing the percentage of antiknocking hydrocarbons in the fuel. Alternatively, the octane number of petrol can be increased by adding oxygen-containing fuels. Chief among these are methanol and methyl *tertiary*-butyl ether, MTBE for short, Fig. 2.12, and aromatics. Some are predicting that compounds like methanol, and some aromatics used in conjunction with certain ethers, may be the solution to the decrease in oil supplies.



$$\mathrm{CH_3-O-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_3}$$

2-methoxy-2-methylpropane

(Methyl *tertiary*-butyl ether)
Octane number = 118

Fig. 2.12

Methanol

This has been used in racing cars for many years. It has many advantages, including

(a) the amount of carbon monoxide emissions is reduced;

(b) the fuel itself has a high octane number of 114;

(c) there is a plentiful supply;

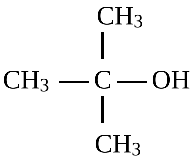
(d) it is cheap;

(e) no aromatic compounds are needed;

(f) it is less likely to explode in accidents.

Unfortunately methanol does have its drawbacks.

(a) Methanol does not mix easily with petrol. However mixing may be achieved if *tertiary*-butyl alcohol, TBA, is added to the petrol.



$$\mathrm{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-OH}$$

2-methylpropan-2-ol

(*tertiary*-butyl alcohol (TBA))

(b) Methanol absorbs moisture from the air and in time a layer of water forms under the fuel in the fuel tank.

(c) Methanol is poisonous and over exposure to its fumes can lead to blindness and brain damage.

(d) As the methanol molecule contains oxygen, methanol does not deliver as much energy per litre.

(e) Methanal, which is carcinogenic, may be produced by the incomplete combustion of methanol.

(f) Methanol is corrosive and attacks the fuel tank and rubber hose lines.

(g) The ability of methanol to absorb water requires that the electrical circuits in the car be well insulated.

Methyl *tertiary*-butyl ether

MTBE is manufactured from methanol and 2-methylpropene. It has a high octane number (118), mixes well with other fuels and is non-corrosive. Petrol may contain up to 15% MTBE. However, if this amount is exceeded the mixture becomes too volatile for use as a fuel. Due to cost of manufacture and availability of supplies, smaller percentages are used. Also, since it contains oxygen, the energy produced per litre is lowered. At present, manufacturers find it more economical to raise the octane number by reforming and cracking, thus limiting the use of MTBE in petrol.

Aromatics

Up to 40% of aromatic compounds may be present in a petrol blend. However, the use of aromatic compounds must be limited as exhaust fumes contain unburned aromatics and high levels of carbon monoxide and nitrogen monoxide. Benzene is particularly dangerous as it is carcinogenic and its use is strictly controlled. Aromatic compounds do, however, greatly increase the octane number, e.g. the octane number for methylbenzene is 120.

Compound	**Octane Number**
Hexane	25
Gasoline fraction of crude oil	70
Methylcyclohexane	70
Cyclohexane	83
2,2,4-trimethylpentane	100
Benzene	100
Methanol	114
Methyl *tertiary*-butyl ether (MTBE)	118
Methylbenzene (toluene)	120

Table 2.4

CHAPTER 3

PHYSICAL PROPERTIES OF THE HYDROCARBONS

3.1 Homologous Series

In order to study the vast and varied number of hydrocarbons it is necessary to classify them into smaller more manageable groups, Fig. 3.1. This division is based on the structure of the molecules. It is convenient and effective to subdivide hydrocarbons into two main classifications and then divide these into further groups. The main classifications are as follows.

(a) **Aliphatic hydrocarbons** which include the alkanes, and the cycloalkanes, the alkenes and the cycloalkenes and finally the alkynes.

(b) **Aromatic hydrocarbons** which include benzene and the arenes, which are benzene rings with aliphatic chains attached. Aromatic compounds also include other compounds that resemble benzene in their chemical behaviour.

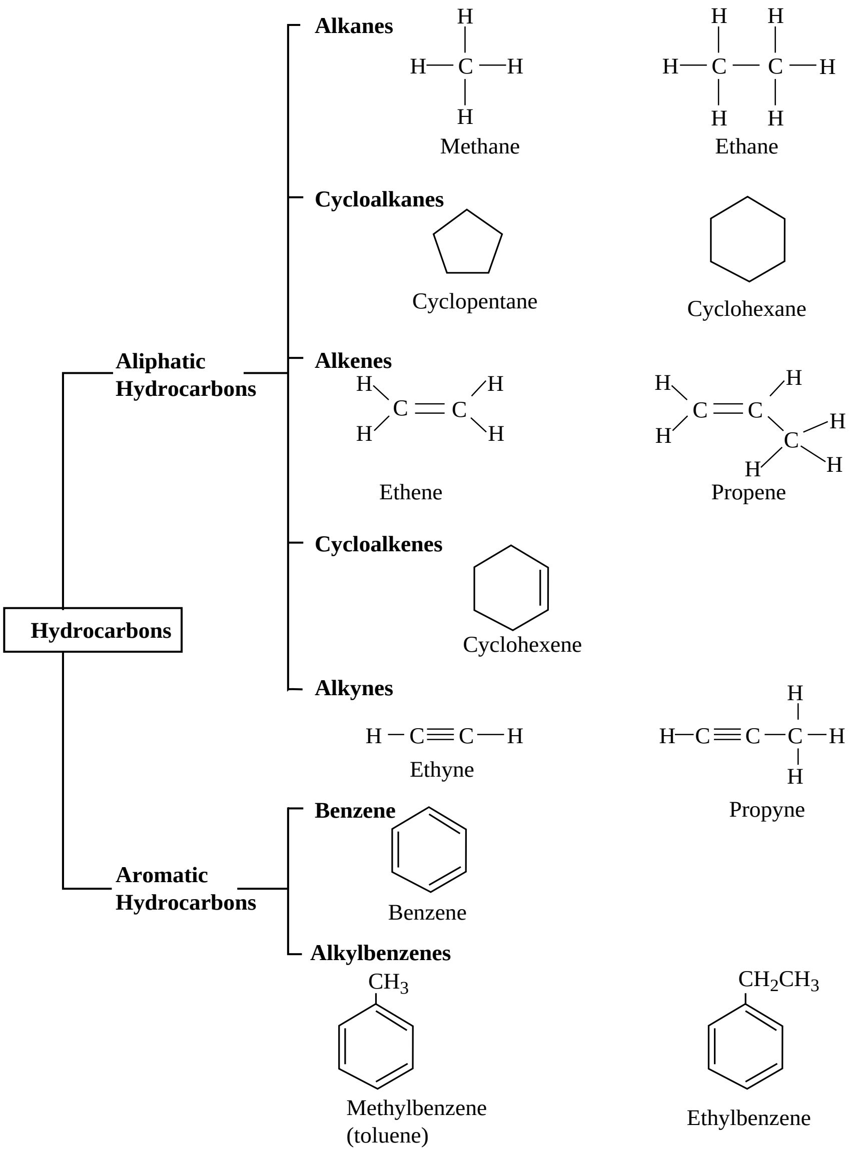


Fig. 3.1

Each group listed above (e.g. alkanes) forms a **homologous series**. All the members of a homologous series have similar chemical properties and their physical properties show a gradual change associated with increasing relative molecular mass. The members also have the same general formula, each member differs from the next by a fixed group of atoms and they all possess the same **functional group**. Functional groups are groups of atoms, or particular bonding arrangements, found in the molecule which dictate the chemical properties of that molecule. The great advantage of grouping compounds into homologous series with characteristic functional groups is that in order to study the series it may only be necessary to study one or more representatives and the properties of the rest can be predicted with a fair degree of accuracy.

3.2 The Alkanes

Formerly known as the 'paraffins' (from the Latin meaning 'lacking affinity') the alkanes are a group of hydrocarbons which conform to the general formula C_nH_{2n+2}, where n is greater than or equal to 1. They are saturated compounds. They consist of carbon atoms joined by four single covalent bonds to either hydrogen or other carbon atoms. The first member of the group is methane (CH_4), the second is ethane (C_2H_6), and the third is propane (C_3H_8), as illustrated in Fig. 3.2. By drawing their structural formulae we can see that each differs from the next by replacing a hydrogen with a CH_3 group, i.e. an extra CH_2 is inserted in the chain.

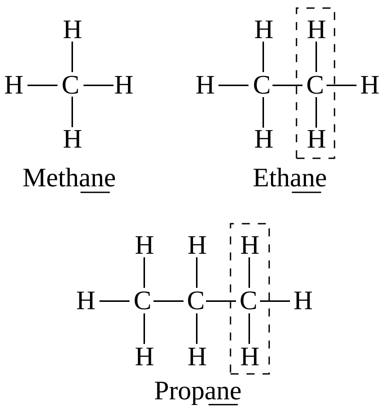


Fig. 3.2

The simplest alkane to study is methane, CH_4. Its sources are the following.

(a) **Natural Gas**. Methane is the largest constituent of natural gas.

(b) **Coal Mines**. Here it is known as 'fire damp' and in the right proportions with air can form an explosive mixture. Indeed accidents were quite common until Davy invented his famous safety lamp.

(c) **Marsh Gas**. It is a product of the decomposition of vegetable matter by bacteria in the absence of air. This, together with phosphine, rises to the surface of stagnant ponds and is spontaneously combusted giving rise to 'Will o' the Wisp'.

(d) **Coal Gas**. When coal or wood is heated in the absence of air, 'coal gas', which contains large amounts of methane, is formed.

A safety lamp, Fig 3.3, used to detect 'fire damp' (methane) was invented by Sir Humphrey Davy in 1815. It was used to provide a safe form of lighting underground. It had two wire gauzes surrounding the flame. A liquid fuel was kept in the bottom of the lamp. The gauzes dissipated the heat of the flame and so any methane outside the gauzes was kept below its ignition temperature. Any gas which diffused inward burned, giving the 'normal' flame a distinctive 'cap'. The appearance of this 'cap' could be used to estimate the concentration of methane in the atmosphere.

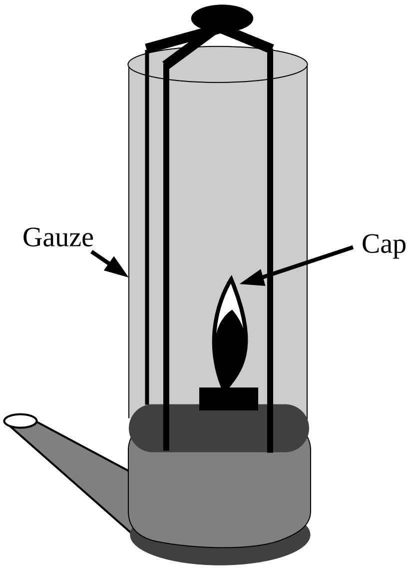


Fig. 3.3 *Davy lamp*

Experiment 3.1
Demonstration of the Principle of the Davy Lamp

Hold a wire gauze above a Bunsen burner. Turn on the gas. Ignite the gas over the gauze. The flame does not 'back light' below the gauze, Fig. 3.4(a). Slide the gauze to the side. Note that the gas coming from the top of the chimney now ignites, Fig. 3.4(b). Now place the gauze over the flame as shown in Fig. 3.4(c). Note that the flame does not spread above the gauze.

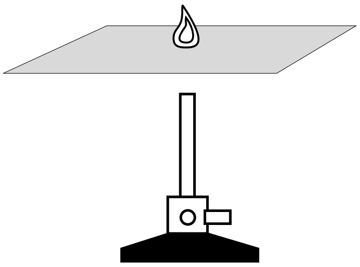


Fig. 3.4(a)

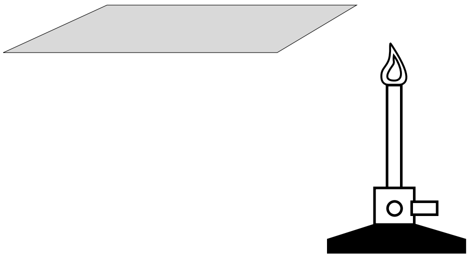


Fig. 3.4(b)

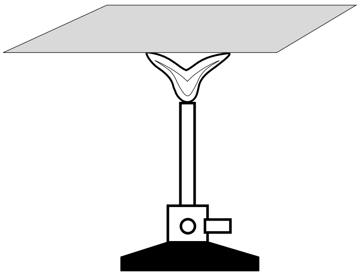


Fig. 3.4(c)

Other Sources of Methane Gas

Methane can be manufactured from organic waste or biomass (pig slurry has proved excellent). This conversion is achieved by micro-organisms which anaerobically break down the organic matter. This type of process is becoming more popular and commercially viable.

The uncontrolled occurrence of this type of process in landfill sites (dumps) is hazardous. The flammable 'biogas' is often piped off and burned as a 'flare'. Land reclaimed from landfill sites cannot be used for building for many years after the closing of the dump because of the hazards associated with gas seepage and build-up. Composting of organic waste rather than dumping to landfill sites would substantially reduce emissions of methane from such sites.

Methane gas is a very effective contributor to the greenhouse effect. Gram for gram it is 21 times more effective in this respect than carbon dioxide. Landfill sites, rice paddies, livestock, termites, burning cereal stubble and straw, as well as gas escaping from coal mines and gas mains, are the principal contributors to this gas in the atmosphere.

Physical Properties of Alkanes

Methane and the other alkanes contain only carbon-carbon and carbon-hydrogen σ-bonds. Since the electronegativities of carbon (2.5) and hydrogen (2.1) are fairly similar the alkanes are non-polar. The alkanes are all insoluble in water, but will dissolve in organic solvents such as 1,1,1-trichloroethane and benzene. They are tasteless, odourless and colourless when pure. Their densities are all less than that of water and so the higher alkanes which are liquids and solids will float on water.

The binding forces between the molecules (intermolecular forces) are weak van der Waals forces. Therefore, we find that the smaller alkanes (C_1–C_4) are gases, the next twelve (C_5–C_{16}) are liquids and the remaining higher alkanes are solids at room temperature. Boiling and melting involve the overcoming of intermolecular forces. Therefore as the molecule gets longer these forces increase and the boiling and melting points must increase accordingly. If the chains are branched then the molecules are not as tightly packed and the intermolecular forces are lessened. This makes the branched molecules more volatile. Branched hydrocarbons are used extensively as petrol ingredients to increase the octane rating.

The melting and boiling points of the first ten straight-chain hydrocarbons as well as their densities are summarised in Table 3.1; the boiling points are illustrated in Fig. 3.5.

It should be noted, however, that branched alkanes do not show this regularity in physical properties as the branching makes the compounds more volatile and also reduces their densities.

Alkane	Formula	b.p./°C	m.p./°C	Density/ g cm^{-3}
Methane	CH_4	–162	–183	0.424
Ethane	C_2H_6	–89	–183	0.546
Propane	C_3H_8	–42	–188	0.501
Butane	C_4H_{10}	–1	–138	0.579
Pentane	C_5H_{12}	36	–130	0.626
Hexane	C_6H_{14}	69	–95	0.657
Heptane	C_7H_{16}	98	–91	0.684
Octane	C_8H_{18}	126	–57	0.703
Nonane	C_9H_{20}	151	–54	0.718
Decane	$C_{10}H_{22}$	174	–30	0.730

Table 3.1

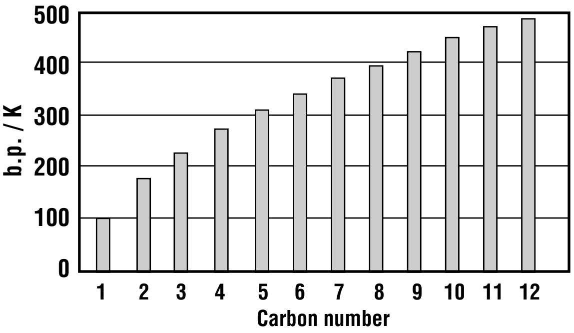


Fig. 3.5 *Boiling points of the alkanes (straight-chained only)*

Experiment 3.2
Preparation of Methane

Methane is conveniently prepared by the reaction of sodium ethanoate and soda lime.

$$CH_3COONa + NaOH \longrightarrow CH_4 + Na_2CO_3$$

Approximately equal quantities of anhydrous sodium ethanoate crystals and soda lime are mixed and heated as shown in Fig. 3.6.

The standard tests on alkanes can then be carried out on test-tubes of the collected gas.

These include the following.

1. Methane is a colourless gas which is essentially odourless.

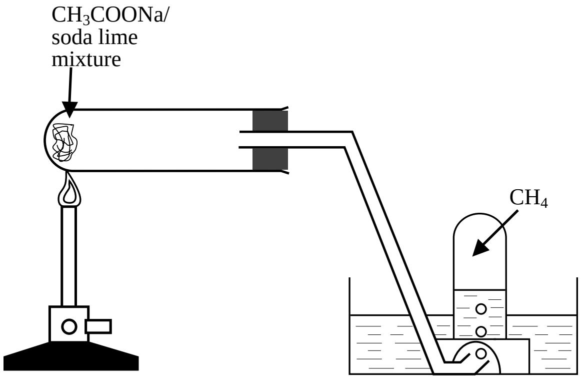


Fig. 3.6

2. Combustion: methane burns with a clean flame. Then test for CO_2 with limewater.

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

3. Bromination: under normal conditions methane does not decolourise a solution of bromine water. However, if bromine water is added to a sample of methane which is then exposed to ultraviolet radiation, the bromine water is slowly decolourised. The reason for this is that a substitution reaction is taking place.

$$CH_4 + Br_2 \xrightarrow{hf} \underset{\text{Bromomethane}}{CH_3Br} + HBr$$

Notes on Procedure

1. The reaction is carried out at an elevated temperature and consequently the delivery tube must be removed from the trough before the apparatus is allowed to cool, otherwise a suck-back of cold water will occur and the test-tube will break.
2. Discard the first few tubes of gas collected. It is mostly displaced air from the system.
3. The test with bromine water is best carried out using gloves. It is more convenient and safer to use a liquid alkane such as cyclohexane instead of methane.
4. A mixture containing about 2 grams each of sodium ethanoate and soda lime is sufficient for this preparation.

Sources of Alkanes – Miscellaneous Tips

It is fortunate that many laboratory gas supplies are natural gas (mostly methane). Simply running a delivery tube to a bee-hive shelf will serve as a quick way of collecting gas jars or test-tubes of methane, Fig. 3.7.

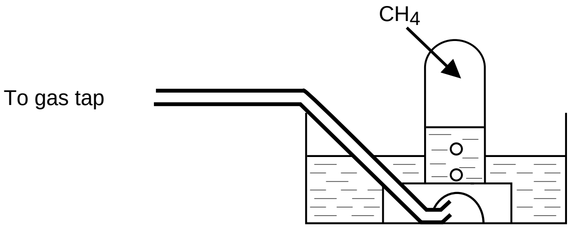


Fig. 3.7

For those who do not have a natural gas supply, the simple preparation of methane given above works well. As a rough guide, the preparation yields about 250 cm^3 of methane per gram of sodium ethanoate used.

If the laboratory is not connected to a natural gas supply, then a butane/propane mixture is available from commercial suppliers of bottled gas.

This mixture though more dense than air (remember methane is less dense than air) can be used to fill gas jars or test-tubes as described above. The butane/propane mixture can be used to illustrate the chemical properties of gaseous alkanes.

Other simple sources of butane/propane are camping gas canisters and cigarette lighters. In both cases it is possible to fill test-tubes by collecting the gas over water.

Cyclohexane and cyclohexene are suitable liquids for use in demonstrating the properties of alkanes and alkenes, respectively.

Bubbling gases through a soap solution can illustrate the densities of the gases. The bubbles when dislodged may be ignited (with care) at a safe distance from the delivery tube. The appearance of the flames can be noted. A thistle funnel fitted to the delivery tube can be dipped in a soap solution (addition of a little glycerol to a soap solution improves the performance of the soap solution) and the bubbles gently dislodged, Fig. 3.8.

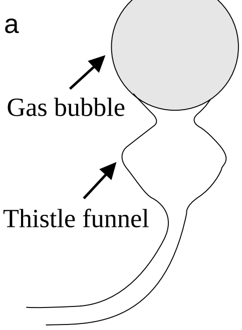


Fig. 3.8

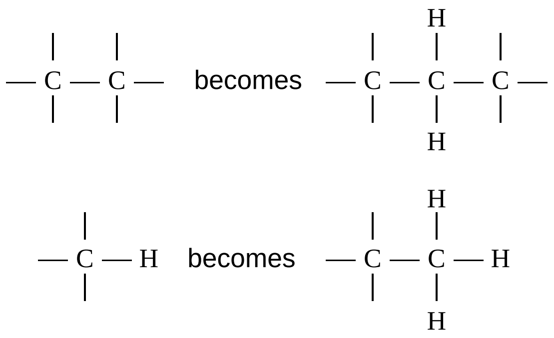
Nomenclature and Isomerism in the Alkanes – Building Up the Alkanes (C_1 to C_5)

As stated above the alkanes form a homologous series of the general formula C_nH_{2n+2}. Each member of the series contains only carbon-carbon single bonds and carbon-hydrogen bonds.

Since the orbitals combining to form a carbon-carbon σ-bond overlap 'end-on' there is free rotation about these bonds.

The geometry about each carbon is tetrahedral (as each carbon has four bonding pairs of electrons).

The members of the homologous series can be built up from the preceeding member by systematically inserting a $—CH_2—$ into one of the carbon-carbon or one of the carbon-hydrogen bonds of the previous member. Thus



$$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}- \quad \text{becomes} \quad -\overset{|}{\underset{|}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{|}{\underset{|}{C}}-$$

$$\text{and} \quad -\overset{|}{\underset{|}{C}}-H \quad \text{becomes} \quad -\overset{|}{\underset{|}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-H$$

An alternative way to build up members of an aliphatic homologous series from the preceding member is by systematically replacing hydrogen in the previous member by a CH_3-group. It is this method which will be employed here. As with any method of building up a homologous series of hydrocarbons a set of molecular models is essential to see the three-dimensional nature of these compounds.

The first member of the series is **methane**, CH_4. Fig. 3.9.

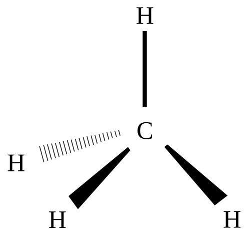


Fig. 3.9 *Methane, CH_4*

The next member of the series is got simply by replacing an H in CH_4 by a CH_3 group. The resulting compound is called **ethane** and has a formula C_2H_6, Fig. 3.10.

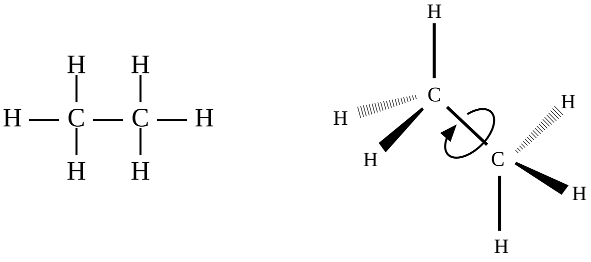


***Fig. 3.10** Ethane, C_2H_6*

All six of the hydrogen atoms in ethane are identical as there is free rotation about the C—C bond. The third member is got by replacing one of these hydrogens by a CH_3 group. The formula for **propane** is C_3H_8, Fig. 3.11.

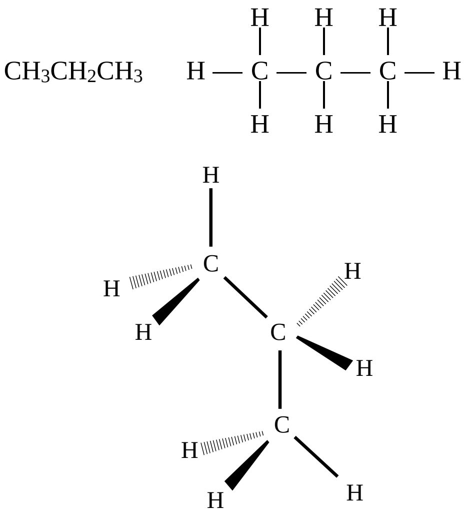


***Fig. 3.11** Propane, C_3H_8*

Examining the propane molecule we note that **six** of the hydrogen atoms in propane have an identical environment and **two** are in a different environment. Fig. 3.12.

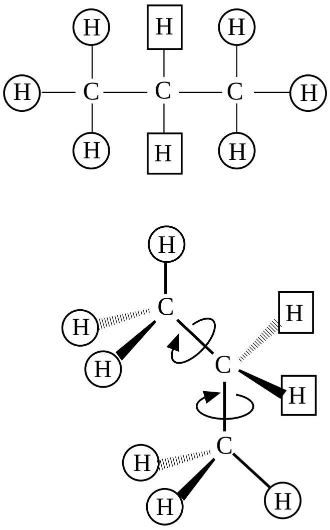


Fig. 3.12

Two possible structures for compounds of the formula C_4H_{10} are generated when a hydrogen atom of each type is replaced by a CH_3 group, Fig. 3.13.

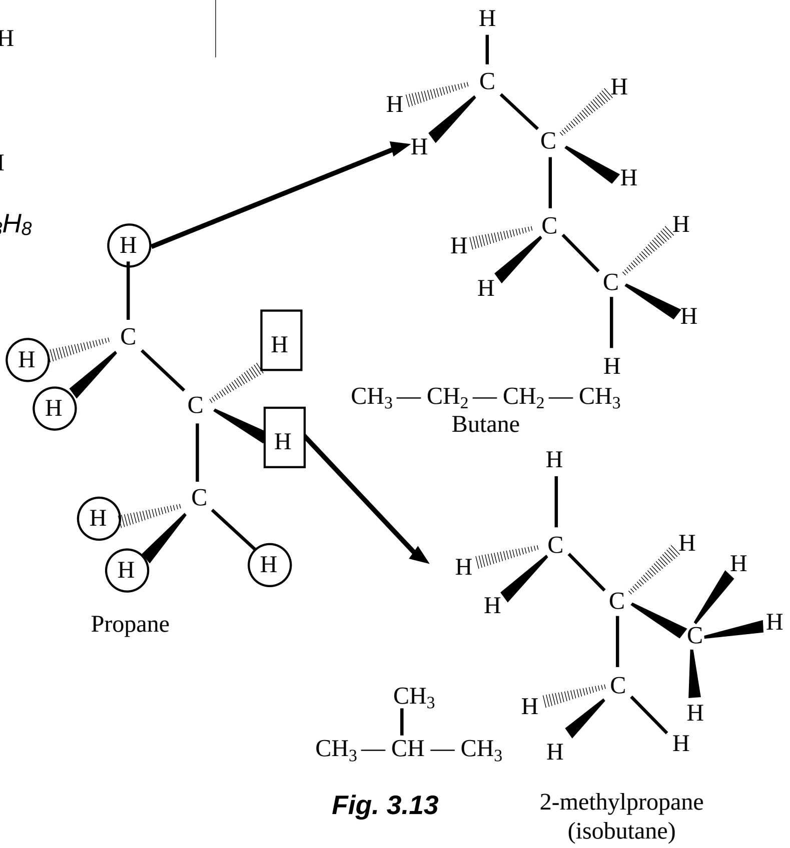
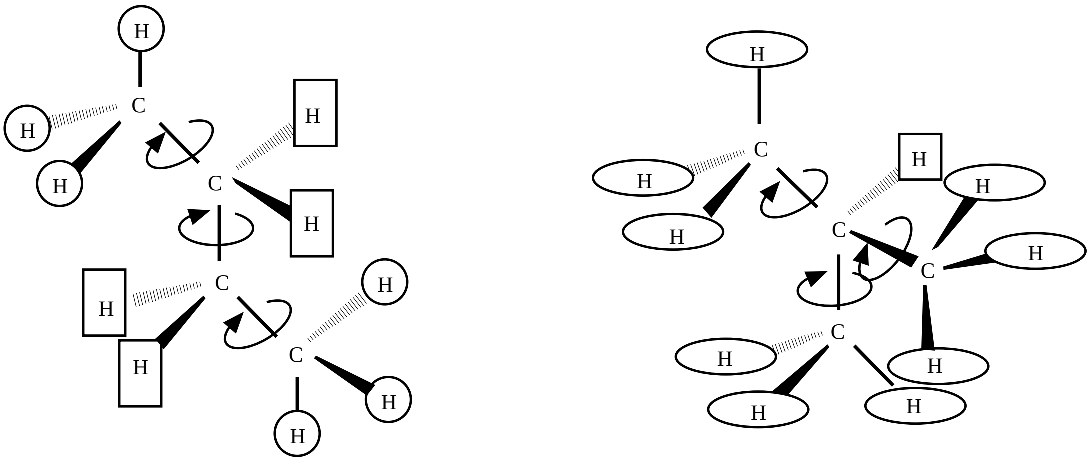


Fig. 3.13

These compounds are said to be **structural isomers.**

Structural isomers are compounds of the same molecular formula but with different structural formulae.

To build up the possible structures for the next (C_5) member of the series we must examine each of the two structural isomers of C_4H_{10} (butane and 2-methylpropane), bearing in mind the 'free-rotation' about the C—C bonds. We note that there are **two** 'different' hydrogen atoms in butane (the three hydrogens on each of the terminal carbons are in one environment and the two hydrogens on each of the two internal carbons are in a separate distinct environment). There are also hydrogens in **two** different environments in 2-methylpropane (nine hydrogens – three on each of the three terminal carbons share a similar environment whilst one hydrogen on the internal carbon is in a unique environment). These are illustrated in Fig. 3.14 below.



Butane

Butane has hydrogens in two distinct environments

2-methylpropane (isobutane)

2-methylpropane also has hydrogens in two distinct environments

Fig. 3.14

Systematically replacing a hydrogen from one of the three different environments in the isomers of butane by a CH_3 group generates three isomeric members corresponding to the formula C_5H_{12}, Fig. 3.15.

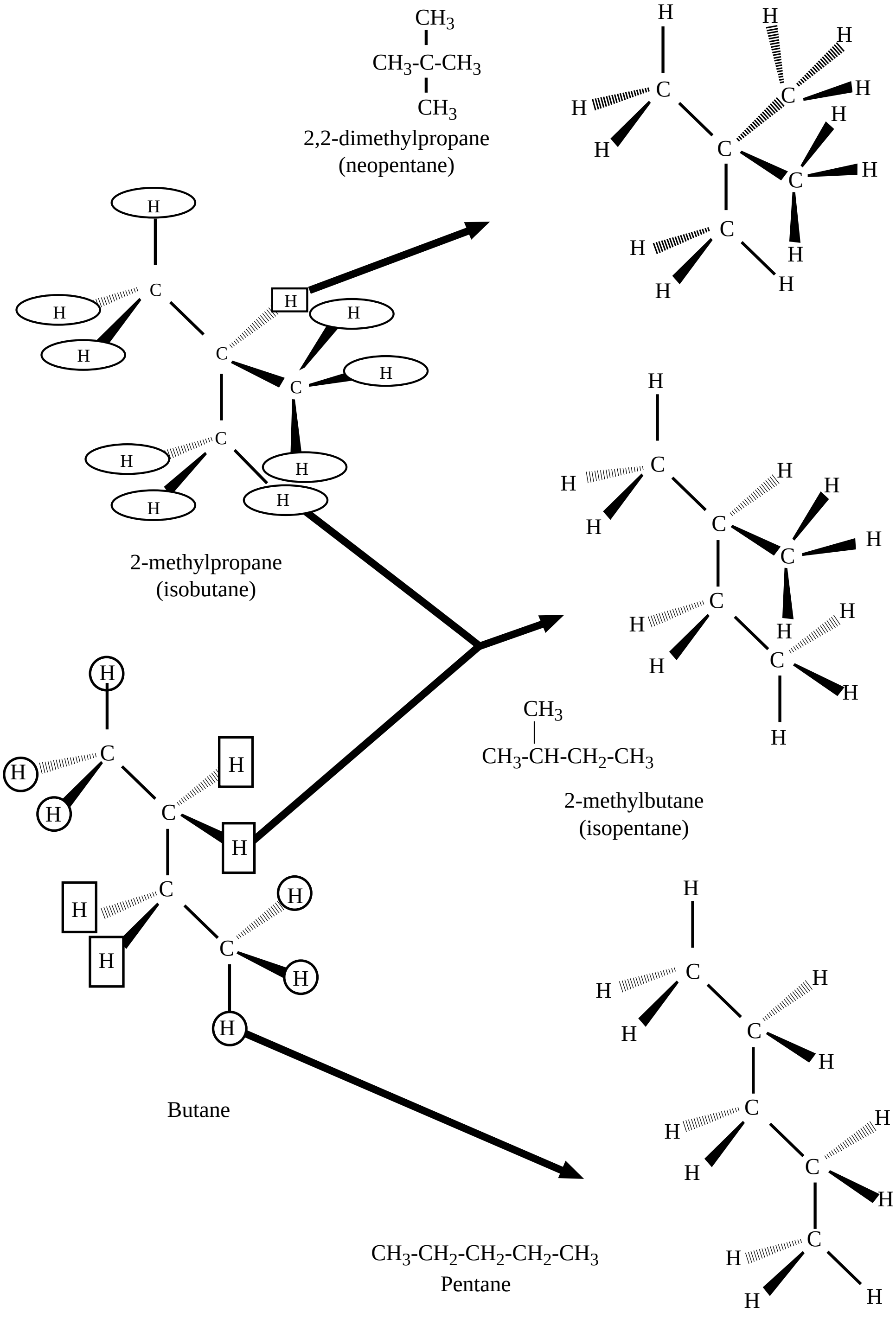


Fig. 3.15

A shortened version of these diagrams is presented in Fig. 3.16 below.

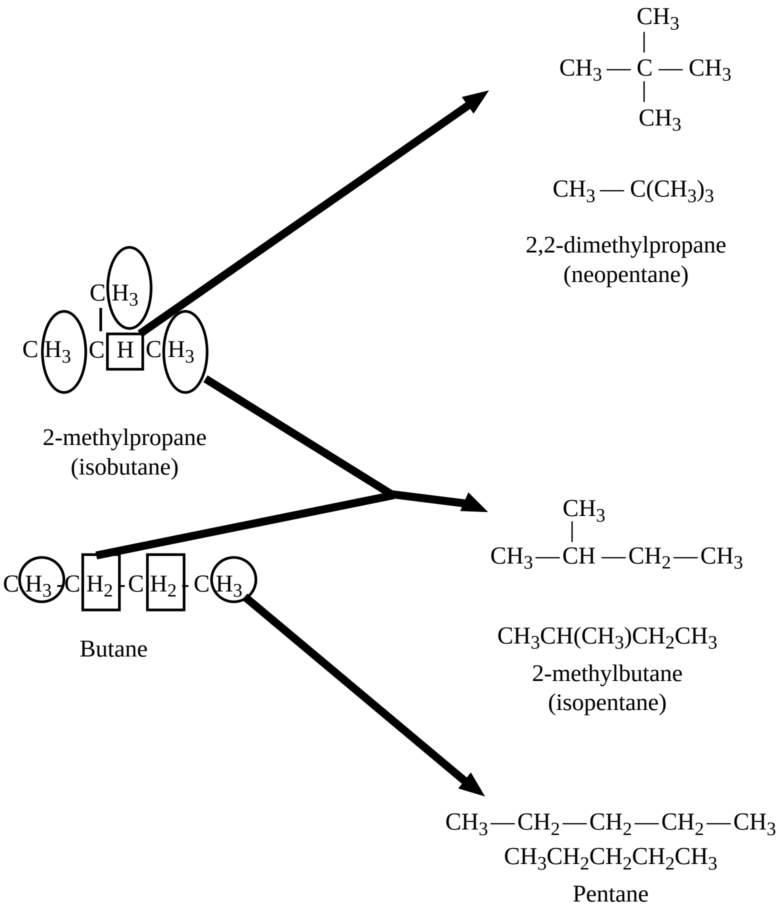


Fig. 3.16

3.3 The Alkenes

These organic compounds contain a carbon-carbon double bond. They form a homologous series of formula C_nH_{2n}, $n \geq 2$. The alkenes are unsaturated and are much more reactive than the alkanes. The old name for the alkenes was the ‘olefins’, which means ‘oil formers’, because the lower members yielded oily products when added to chlorine and bromine. The first of the alkenes is called ethene, C_2H_4; the second is propene, C_3H_6; the third is butene, C_4H_8; etc. It can be seen from the names that the first part of the name gives the number of carbon atoms in the main chain and the last part of the name gives the homologous series, i.e. pentene starts with *pent-* indicating a five carbon chain and ends with *-ene* indicating that it is an alkene – it has a double bond within the chain. Numbers are used to indicate the position of the double bond. Hence, pent-2-ene (2-pentene) has the double bond between carbon number two and carbon number three of its five-carbon chain.

Physical Properties of the Alkenes

The presence of the double bond creates a region of high electron density in the molecules. This can make some of the unsymmetrical isomers more polar than the alkanes but this is not sufficient to make them soluble in water. They are soluble in 1,1,1-trichloroethane or benzene. Their melting and boiling points show the gradual increase common to all homologous series. They have densities less than that of water. The first three members are gases at room temperature, C_5—C_{18} are liquids and the rest are solids. Some data on simple terminal alkenes (i.e. alkenes where the double bond is located at carbon number one of the carbon chain) is presented in Table 3.2 and Fig. 3.17.

Alkene	Formula	b.p./°C	m.p./°C	Density/ g cm^{-3}
Ethene	C_2H_4	–105	–169	0.566
Propene	C_3H_6	–48	–185	0.514
But-1-ene	C_4H_8	–6	–185	0.595
Pent-1-ene	C_5H_{10}	30	–165	0.641
Hex-1-ene	C_6H_{12}	63	–140	0.674
Hept-1-ene	C_7H_{14}	93	–119	0.689
Oct-1-ene	C_8H_{16}	123	–104	0.716
Non-1-ene	C_9H_{18}	146	–81	0.731
Dec-1-ene	$C_{10}H_{20}$	171	–87	0.743

Table 3.2 *Alkenes*

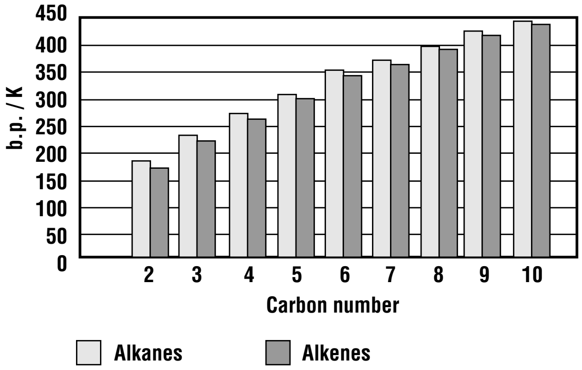


Fig. 3.17 *Alkanes vs alkenes – boiling points*

Nomenclature and Isomerism in the Alkenes – Building Up the Alkenes (C_2–C_4)

As stated earlier hydrocarbons which contain at least one carbon-carbon double bond as well as carbon-hydrogen bonds are called alkenes. Like the alkanes, the alkenes also form a homologous series. Alkenes have the general formula C_nH_{2n} (for $n \geq 2$).

The geometry about each alkene carbon is trigonal planar with the doubly-bonded carbons forming one σ- and one π-bond to each other and each of these carbons also forming two σ-bonds to hydrogen atoms or other carbon atoms.

The first member of the series is **ethene**, C_2H_4, Fig. 3.18.

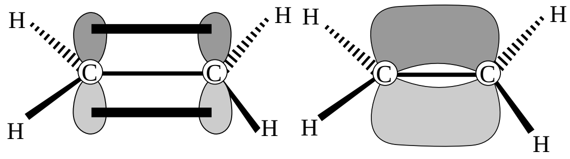
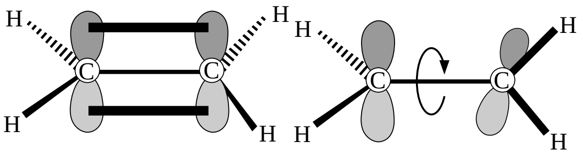


Fig. 3.18 *Ethene, C_2H_4*

There is **no free rotation** about the C═C double bond, as the π-bond involves 'side-on' overlap of p orbitals. Rotation is achieved only by breaking the π-bond, Fig. 3.19.



Here the p orbitals are parallel and they overlap.

On rotation the orbitals are at right angles and no overlap is possible.

Fig. 3.19

The next member of the series is got simply by replacing an H in C_2H_4 by a CH_3 group. Since all four hydrogen atoms in ethene occupy identical environments only one possible structure for the next member exists. It is called **propene** and has a formula C_3H_6, Fig. 3.20.

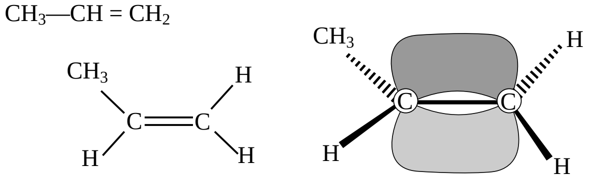


Fig. 3.20 *Propene, C_3H_6*

To get the possible structures for butene, C_4H_8, we first examine the hydrogen atoms in propene in detail, Fig. 3.21. We note that there is **no free rotation** about the C═C double bond, but there is free rotation about the C—C single bond. There are in fact **four** 'different hydrogen environments' in propene. All three hydrogen atoms on the methyl group, CH_3, are identical as they can interchange position by rotation of the C—C single bond. The hydrogen atom on carbon number two also has a unique environment. The remaining two hydrogens on carbon number one actually occupy differing environments from each other as one of them is *trans* (opposite) the CH_3 group and the second is *cis* (on same side of the double bond).

The next member of the series is got simply by replacing one of the H atoms in C_3H_6 by a CH_3 group.

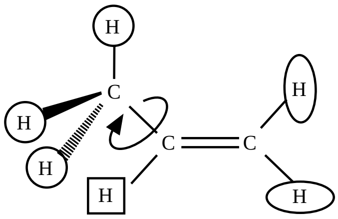


Fig. 3.21

This generates four possible isomeric structures of **butene,** C_4H_8, Fig. 3.22.

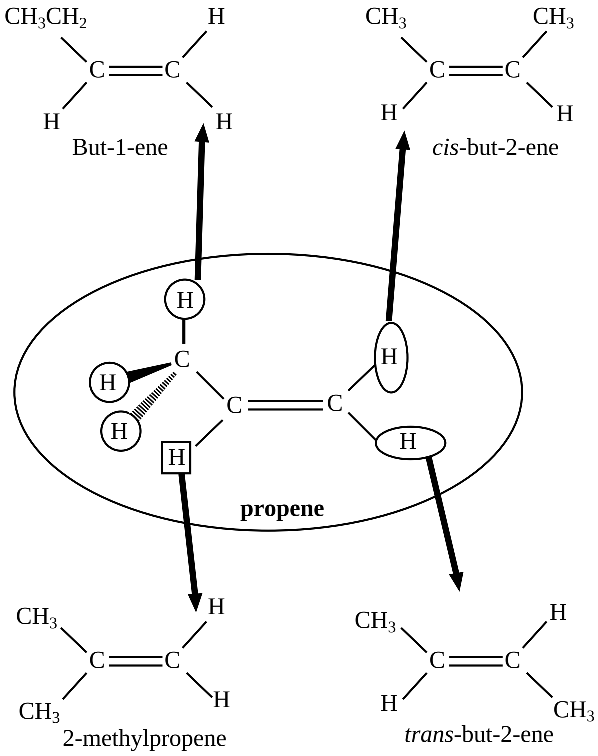


Fig. 3.22

It should be noted that two of the four structures possible for butene have the double bond located between the second and third carbons of the four-long carbon chain (i.e. C_2 and C_3) and are named but-2-ene. However, because of the lack of free rotation about the carbon-carbon double bond the CH_3 groups can reside opposite each other, *trans*, or on the same side of the double bond, *cis*, as shown in Fig. 3.23. This phenomenon is often referred to as ***cis*** and ***trans*** **isomerism**.

The *trans*-but-2-ene isomer is found to be more stable than *cis*-but-2-ene. This is due to the fact that bulky methyl groups are further apart and the molecule has a higher degree of symmetry. This is demonstrated by the heats of hydrogenation of the two isomers of but-2-ene as the *trans* isomer yields 4 kJ mol^{-1} less energy than the *cis* isomer. In both cases the same product, butane, is formed, Fig. 3.24.

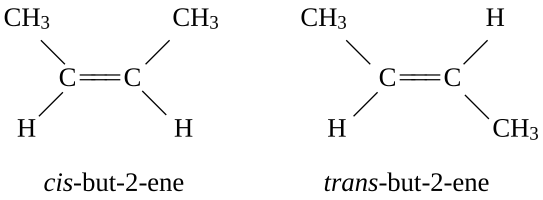


Fig. 3.23

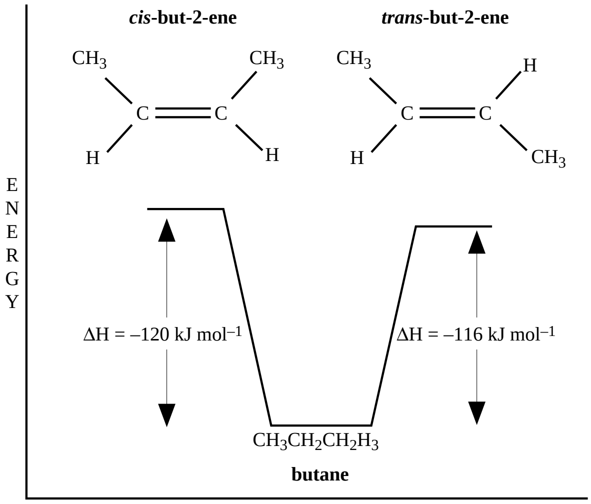


Fig. 3.24

Even though the energy difference between the two isomers is small (4 kJ mol^{-1}) the rate of conversion of one isomer to the other is extremely low at room temperature. At first glance, this may seem odd when one bears in mind that molecules of a gas have average kinetic energy of about 20 kJ mol^{-1} at room temperature. However, the conversion involves breaking and remaking the π-bond between the two central carbons and the breaking of the C—C π-bond requires about 300 kJ mol^{-1} and only a very small number of collisions of this energy take place.

cis and *trans* Isomerism in More Complex Alkenes

The *cis* and *trans* terminology works well for simple di- and tri-substituted derivatives of ethene but within more complex alkene molecules and their derivatives it is necessary to use a more sophisticated method of labelling the arrangement of different substituents about the double bond.

The four substituents attached to the carbons of the double bond are first prioritised according to the Cahn-Ingold-Prelog sequence. This is a method of labelling the substituents a, b, c and d giving priority in the first instance based on the atomic number of the attached atom. (This process is repeated out along the chain if initial application of the rule is not conclusive. This procedure, and the use of a further rule, are too detailed for discussion here.) The isomers can then be labelled ***Z-*** to mean on the same side like the simple *cis* and ***E-*** to mean on the opposite side like the simple *trans* (these labels are derived from the German: *zusammen,* together and *entgegen,* opposite).

The simple example below, Fig. 3.25, helps illustrate the use of the system. Bromine being the element of highest atomic number attached to the alkene carbons is labelled ‘a’, chlorine is next getting ‘b’. We note that when the bromine (the highest priority element on one end of the double bond is *cis* to the highest priority element on the other end of the double bond (the carbon of the methyl group) the isomer is designated as *Z*- and when the higher priority elements are *trans* to each other the *E*- designation applies.

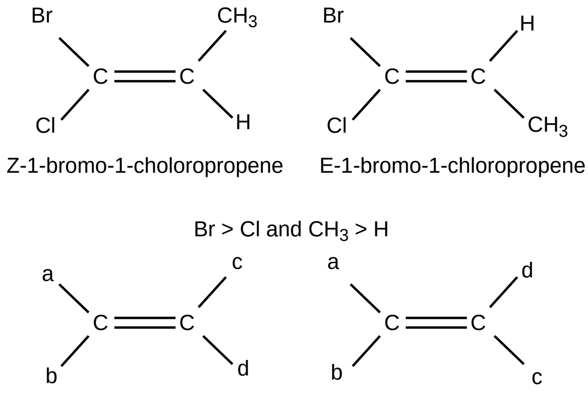


Fig. 3.25

Experiment 3.3
Preparation of Ethene

Ethene is conveniently prepared by the dehydration of ethanol using hot aluminium oxide, Fig 3.26.

$$C_2H_5OH \xrightarrow[\text{Heat}]{Al_2O_3} C_2H_4 + H_2O$$

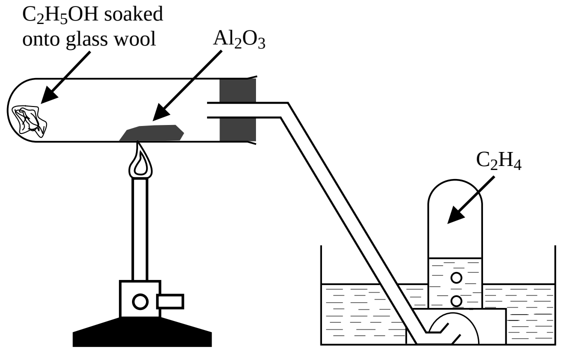


Fig. 3.26

The standard tests on alkenes can then be carried out on test-tubes of the collected gas.

These include the following.

1. Ethene is a colourless gas with a sweetish odour.
2. Combustion: ethene burns with a slightly luminous flame. Then test for CO_2 with limewater.

$$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$$

3. Bromination: ethene decolourises a solution of bromine water.

$$C_2H_4 \xrightarrow{Br_2/H_2O} CH_2OHCH_2Br$$

2-bromoethanol

4. Reaction with acidified potassium manganate(VII) (potassium permanganate): the purple solution is decolourised.

$$C_2H_4 \xrightarrow[H_2SO_4]{KMnO_4} CH_2OHCH_2OH$$

ethane-1,2-diol

Notes on Procedure

1. The reaction is carried out at around 200 °C and consequently the delivery tube must be removed from the trough before the apparatus is allowed to cool, otherwise a ‘suck-back’ of cold water will occur and the the test-tube will break.
2. Discard the first few tubes of gas collected. It is mostly displaced air from the system.
3. The purpose of the glass wool is merely to keep the ethanol at the end of the test-tube. It should be noted that there are health risks associated with the use of glass wool so care must be taken.

3.4 The Aromatic Hydrocarbons

These compounds are hydrocarbons which contain a benzene ring in their molecules or that have similar properties to benzene. They were called ‘aromatic’ because the few compounds known in the early days had pleasant smells. However, the scope of aromatic compounds has greatly increased and many of these have very unpleasant smells. In general their vapours tend to be toxic and to classify them as aromatic by smell alone would be unwise.

Benzene was first isolated from whale oil by Michael Faraday in 1825. Benzene derivatives have also been isolated from the naturally-occurring ‘gum benzoin’. Hence the name ‘benzene’. The group derived from benzene, C_6H_5, is called ‘phenyl’ from the Greek ‘pheno’ meaning ‘I bear light’, a reference to Faraday’s experiments on illuminating gas. The molecular formula for benzene, C_6H_6, has been known since 1834, and this combination of atoms could only suggest a highly unsaturated arrangement. Yet in chemical reactions the compound behaved as a saturated compound, undergoing substitution reactions instead of addition reactions. Its structural formula was not unravelled until 1865 by Kekulé who proposed a six-membered carbon ring containing alternating single and double bonds between the carbons, Figure 3.27.

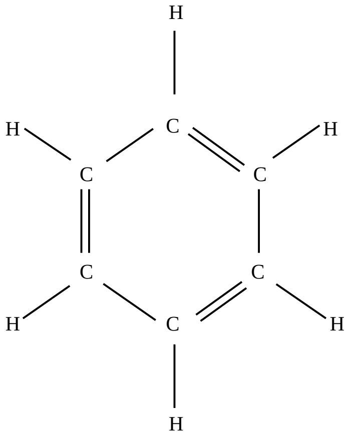


Fig. 3.27 *Benzene, C_6H_6*

Later, the detail of the structure proposed by Kekulé was to conflict with bond length measurements. The average bond length for a C—C single bond is 0.154 nm and for a C═C double bond is 0.134 nm. The structure proposed by Kekulé, with alternate single and double bonds, should give rise to alternate short and long carbon-carbon distances within the benzene molecule. Crystallographic data show that all six carbon-carbon distances in benzene are equal (that all the carbon-carbon bonds are identical) and are of the order of 0.139 nm, an intermediate figure between that of carbon-carbon single and double bonds. This suggests that the double bond could move, giving an average bond order of 1.5 between carbons. As a result the diagram for benzene is modified to show a ring inside the hexagon indicating the intermediate nature of all the bonds, Figure 3.28.

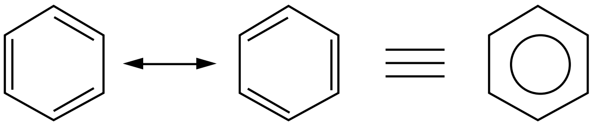


Fig. 3.28

More detailed examination of the bonding in the planar benzene indicates that it contains six carbon-carbon σ-bonds and each carbon has another σ-bond with hydrogen. This gives each carbon a trigonal planar arrangement of bonded pairs which fits nicely with the hexagon structure. The ring is flat, which places the singly-filled p orbital on each carbon at right angles to the plane of the ring. These p orbitals overlap and form a delocalised cloud of electrons above and below the ring. Six electrons are present in the delocalised π-cloud in benzene. There is great stability associated with this delocalisation of electrons or resonance, Fig. 3.29.

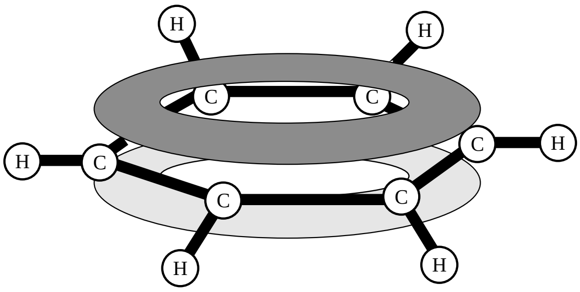
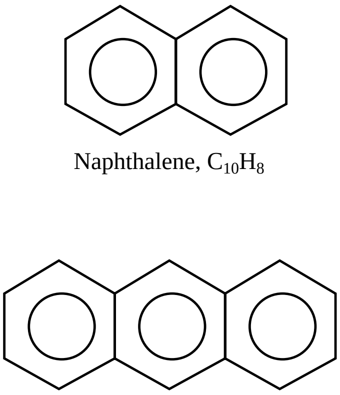


Fig. 3.29

Benzene is about 150 kJ mol^{-1} (which corresponds to 50 kJ mol^{-1} per double bond) more stable than one might anticipate by viewing the molecule in the Kekulé structure of isolated single and double bonds (this deduction can be made from analysis of bond energy and combustion data). Other systems containing (4n + 2) delocalised π-electrons, where n = number of rings, are also aromatic and enjoy similar stability. Naphthalene, $C_{10}H_8$, and anthracene, $C_{14}H_{10}$, are two such compounds, Figure 3.30.


Naphthalene, $C_{10}H_8$

Anthracene, $C_{14}H_{10}$

Fig. 3.30

A consequence of this stability is a marked reluctance of aromatic compounds to undergo addition reactions. The reason for this is that addition reactions would eliminate this delocalisation. Benzene undergoes substitution reactions of the hydrogens and keeps its stable structure. This reactivity contrasts strongly with the strong tendency of alkenes to undergo addition reactions.

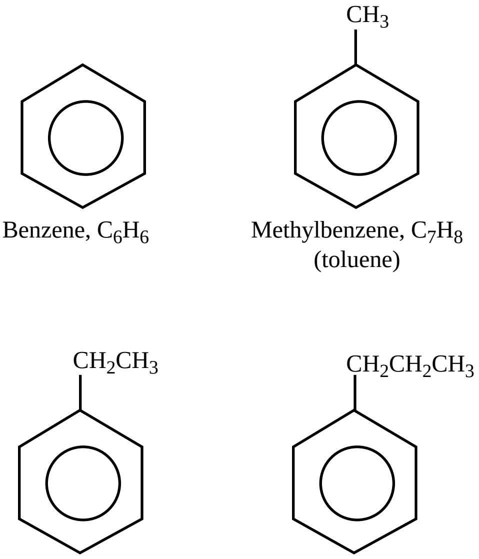
In many ways, the physical properties of the aromatics are similar to those of the aliphatic hydrocarbons. They are non-polar, they will not dissolve in water but are soluble in organic solvents. Benzene itself is a good solvent, but because of its carcinogenic properties it is safer to use the less harmful methylbenzene. Some physical data on the lower alkylbenzenes is summarised in Table 3.3. As is evident from the data the lower members are liquids at room temperature and the insertion of CH_2 to the side chain serves to add about 30 °C to their boiling points.

Name	Formula	b.p. / °C	m.p. / °C
Benzene	C_6H_6	80.1	5.5
Methylbenzene	$CH_3–C_6H_5$	110.6	–95
Ethylbenzene	$C_2H_5–C_6H_5$	136.2	–95
Propylbenzene	$C_3H_7–C_6H_5$	159.4	–99.5

Table 3.3 *Benzene compounds*

Nomenclature and Isomerism of the Aromatic Hydrocarbons (C_6—C_8)

When there is only one group attached to the benzene ring, then the name is often got by simply naming the substituent and this becomes the prefix and benzene becomes the suffix, Fig. 3.31.



Benzene, C_6H_6

Methylbenzene, C_7H_8 (toluene)

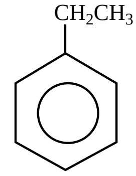
Ethylbenzene, C_8H_{10}

Propylbenzene, C_9H_{12}

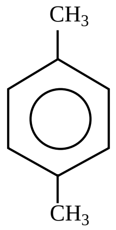
Fig. 3.31

Unfortunately for those not well-aquainted with aromatic compounds, non-systematic names are very commonly used, e.g. toluene above.

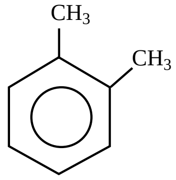
Because all the carbon bonds in benzene are identical there is only one isomeric structure of the formula C_7H_8, methylbenzene (toluene). The structure is illustrated in Fig. 3.31 above. Where there are two substituents present on the benzene ring, three isomeric compounds are possible. The numbers 1 to 6 may be used to indicate the position on the ring of the substituents. Alternatively, the prefixes ***ortho-*** (position 2), ***meta-*** (position 3) and ***para-*** (position 4) can be used. Note positions 5 and 6 are positions 2 and 3 from behind. This is conveniently illustrated when one considers the structural isomers of C_8H_{10}. Apart from ethylbenzene there are three isomers of dimethylbenzene which also fit this formula, Fig. 3.32.



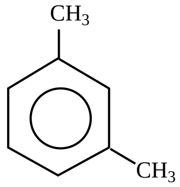
Ethylbenzene



1,4-dimethylbenzene
(*p*-xylene)



1,2-dimethylbenzene
(*o*-xylene)



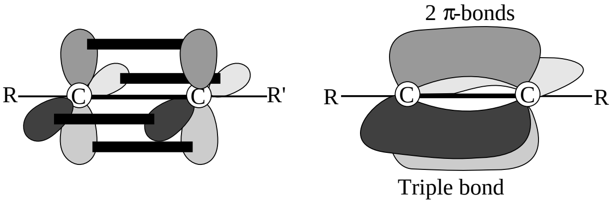
1,3-dimethylbenzene
(*m*-xylene)

***Fig. 3.32** Structural isomers of C_8H_{10}*

3.5 The Alkynes

Alkynes are the next homologous series of hydrocarbons. The general formula for the series is C_nH_{2n-2} (for $n \geq 2$). These compounds all have a carbon–carbon triple bond. The triple bond consists of a σ-bond (end-on overlap of orbitals) and two π-bonds (side-on overlap of p orbitals), Fig. 3.33. The geometry about the two triple-bonded carbons is linear.

$$R{-}C{\equiv}C{-}R'$$



R, R' = hydrogen, alkyl or aryl
(the general formula C_nH_{2n-2} ($n \geq 2$) refers to hydrogen or alkyl substituted alkynes)

Fig. 3.33

Physical Properties of Alkynes

The melting points and boiling points and densities of the alkynes are in general higher than the corresponding alkenes and alkanes. $C_{18}H_{34}$ is the first member to exist as a solid. The alkynes are only slightly polar and do not dissolve in water but will dissolve in organic solvents. It might be expected that alkynes should have lower boiling points than the corresponding alkanes or alkenes due to their smaller relative molecular masses. However, the slight increase in polarity due to the triple bond serves to increase the m.p. and b.p. values, Table 3.4.

Alkyne	**Formula**	**b.p./°C**	**m.p./°C**	**Density/ g cm^{-3}**
Ethyne	C_2H_2	–84	–81	0.613
Propyne	C_3H_4	–23	–103	0.691
But-1-yne	C_4H_6	8	–126	0.65
Pen-1-yne	C_5H_8	40	–106	0.69
Hex-1-yne	C_6H_{10}	72	–132	0.716
Hept-1-yne	C_7H_{12}	100	–81	0.733
Oct-1-yne	C_8H_{14}	126	–79	0.746
Non-1-yne	C_9H_{16}	151	–50	0.757
Dec-1-yne	$C_{10}H_{18}$	174	11	0.766

***Table 3.4** Alkynes*

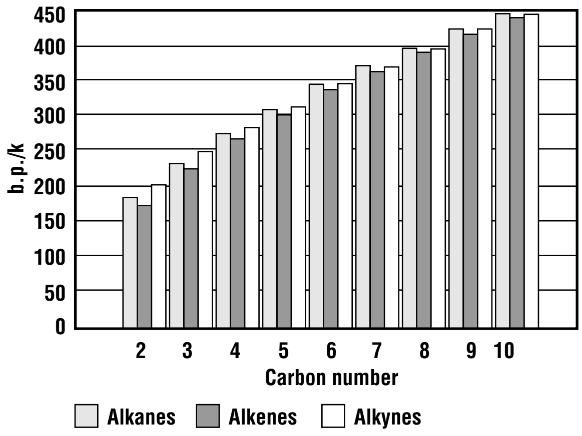


Fig. 3.34 *Boiling points alkanes vs alkenes vs alkynes*

Nomenclature and Isomerism in the Alkynes (C_2–C_4)

As indicated above the alkynes are the next homologous series of hydrocarbons. The general formula for the series is C_nH_{2n-2} (for $n \geq 2$). These compounds all have a carbon–carbon triple bond The geometry about the two triple-bonded carbons is linear.

The first member of the series is **ethyne** (acetylene), C_2H_2, Fig. 3.35.

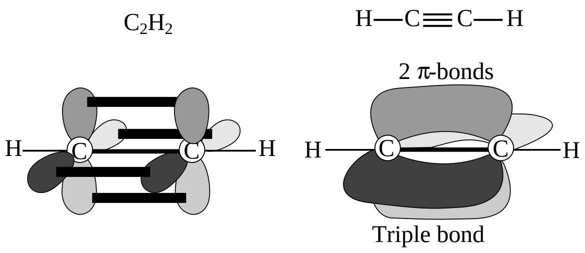


Fig. 3.35

Within the ethyne molecule all four atoms are in a linear arrangement. Because of the symmetry of the molecule both hydrogen atoms in ethyne occupy identical environments. The second member of the alkynes is got by replacing one of these hydrogens by a CH_3 group. It is called **propyne,** C_3H_4, Fig. 3.36.

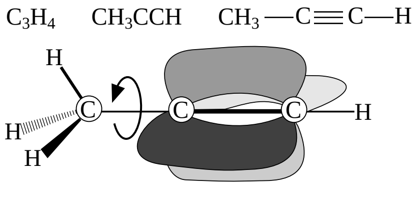


Fig. 3.36 *Propyne, C_3H_4*

There are **two** 'different types' of hydrogen environment in propyne. The three hydrogens of the CH_3 group share one environment and the single hydrogen on the alkyne carbon has a different environment. Two possible isomers of **butyne**, C_4H_6, are produced when these two hydrogens are systematically replaced by CH_3 groups, Fig 3.37.

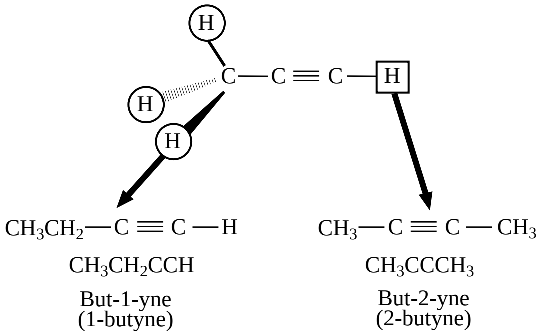


Fig. 3.37

Experiment 3.4
Preparation of Ethyne

Ethyne can be prepared by the reaction of water with calcium dicarbide. Calcium dicarbide is not available in a pure state and so the gas is purified by passing it through an acidified solution of copper sulphate before it is collected over water.

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

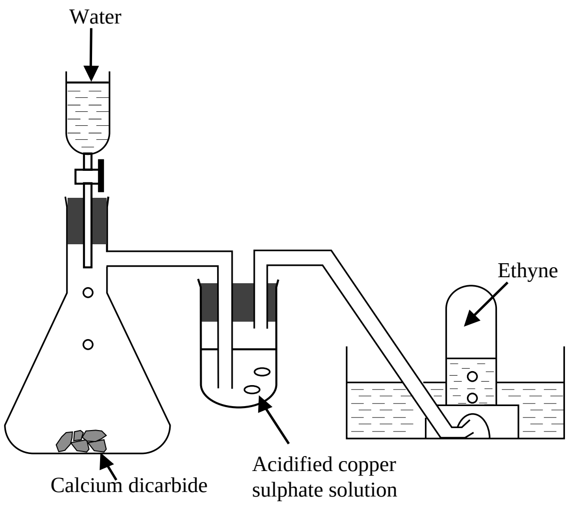


Fig. 3.38

The tests carried out on ethyne include the following.

1. Ethyne is a colourless gas with an unpleasant odour.

2. Combustion: ethyne burns with a smoky luminous flame, generating a lot of soot.

$$2C_2H_2 + 5O_2 \longrightarrow 4CO_2 + 2H_2O$$

3. Bromination: ethyne decolourises a solution of bromine water. The reaction is complicated and a number of products, including α-brominated ethanals, are possible.

4. Reaction with acidified potassium manganate (VII) (potassium permanganate): the pink solution is decolourised. The products of this reaction depend on the concentration of the potassium manganate(VII) solution.

5. Tests for terminal alkynes (i.e. alkynes with an H on one of the triple-bonded carbons).

   (a) Test with ammoniacal silver nitrate: a pale precipitate results. This solid is explosive when dry.

$$C_2H_2 + 2Ag^+ \longrightarrow \underset{\text{Silver dicarbide}}{Ag_2C_2} + 2H^+$$

   (b) Test with ammoniacal copper(I) chloride: a pale precipitate results. This solid is also explosive when dry.

$$C_2H_2 + 2Cu^+ \longrightarrow \underset{\text{Copper(I) dicarbide}}{Cu_2C_2} + 2H^+$$

Notes on Procedure

1. Calcium dicarbide is a brown or grey solid which contains impurities such as calcium sulphide, CaS, calcium nitride, Ca_3N_2, and perhaps calcium phosphide, Ca_3P_2. These impurities give rise to hydrogen sulphide, H_2S, ammonia, NH_3, and phosphine, PH_3.

2. When the water is added an immediate reaction takes place and a 'smoky' evolution of gas occurs. The gas 'clears' as it passes through the copper sulphate solution. The impurities in the gas are trapped by the copper ions in the copper sulphate solution.

3. If the gas produced is passed through a warm solution of mercury(II) sulphate (mercuric sulphate) in dilute sulphuric acid, ethanal is produced, Fig. 3.39. This can be tested using any of the diagnostic tests for aldehydes. The reaction adds H_2O across one of the π-bonds forming an enol which tautomerises to ethanal.

$$C_2H_2 \xrightarrow[60\ °C]{H_2SO_4\ /\ HgSO_4} CH_3CHO$$

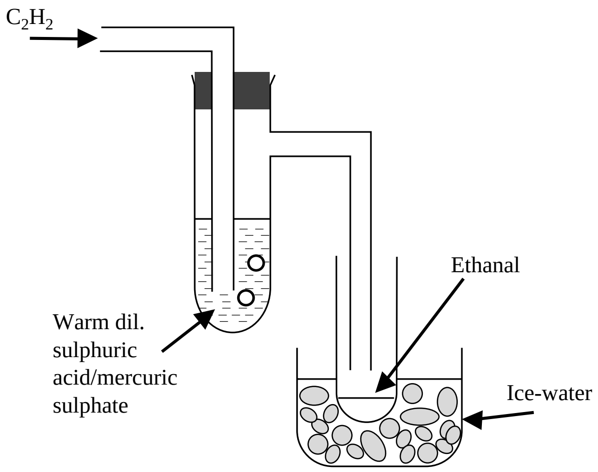


Fig. 3.39

CHAPTER 4

CHEMICAL REACTIONS OF THE HYDROCARBONS

4.1 Introduction

The reactions of a hydrocarbon vary according to the homologous series to which it belongs. All of them, however, burn in oxygen to give carbon dioxide and water. The saturated compounds (the alkanes and cycloalkanes) undergo substitution reactions as each carbon atom has all of its outer electrons already involved in σ-bonding with hydrogen or other carbon atoms. Most of the unsaturated compounds will undergo addition reactions involving the breaking of one or more π-bonds, thus freeing the carbons to bond with other reacting species. Aromatic compounds [those with (4n + 2) delocalised π-electrons] as stated already tend to undergo substitution rather than addition reactions, thus enabling them to retain the stability associated with the aromatic system.

4.2 Reactions of the Alkanes

Since the alkanes are saturated (contain only single bonds) either a carbon-carbon or a carbon-hydrogen bond has to be broken in order to allow the formation of a bond to a new species. However, as the alkanes are rather inert, they do not undergo a wide variety of reactions. This is due to the strength of the carbon-carbon and carbon-hydrogen bonds [C—C (348 kJ mol^{-1}) and C—H (412 kJ mol^{-1})] coupled with the fact that these bonds are essentially non-polar. Alkanes are unaffected by acids, alkalis, or aqueous oxidising agents. They do, however, undergo the following reactions.

(a) Combustion

Alkanes can be burned in excess oxygen to produce carbon dioxide and water, Equations 4.1 and 4.2.

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

Equation 4.1

$$C_4H_{10} + 6^1/_2\ O_2 \longrightarrow 4CO_2 + 5H_2O$$

Equation 4.2

(b) Pyrolysis (cracking)

Larger alkanes undergo thermal destruction to produce smaller molecules. This has been dealt with in some detail in Chapter 2. One interesting example not mentioned in Chapter 2 is the production of ethanoic acid (acetic acid) from butane using heat and cobalt(II) ethanoate as catalyst, Equation 4.3.

$$2C_4H_{10} + 5O_2 \xrightarrow{Co(CH_3COO)_2} 4CH_3COOH + 2H_2O$$

Equation 4.3

(c) Halogenation

Since the alkanes are saturated, halogenation must involve replacement of one or all of the hydrogens in an alkane by halogen atoms. This is called a **substitution** reaction. The reactions with chlorine and bromine typify this substitution and the mechanism is commonly referred to as **free radical substitution**. These reactions may produce many products due to the high reactivity of free radical species. As in the case of the combustion reactions, the substitution reaction needs energy to be supplied before the reaction can proceed. This energy may be supplied by heating or by shining ultraviolet radiation on the reaction mixture. The reaction will proceed in diffuse sunlight (ordinary daylight, which contains ultraviolet radiation). It may be explosive in direct sunlight which contains too much ultraviolet radiation. The reaction of chlorine with methane is summarised in Fig. 4.1.

$CH_4 + Cl_2 \longrightarrow HCl + CH_3Cl$
Chloromethane

$CH_4 + 2Cl_2 \longrightarrow 2HCl + CH_2Cl_2$
Dichloromethane

$CH_4 + 3Cl_2 \longrightarrow 3HCl + CHCl_3$
Trichloromethane

$CH_4 + 4Cl_2 \longrightarrow 4HCl + CCl_4$
Tetrachloromethane

Fig. 4.1

4.3 Proposing a Mechanism for Free Radical Substitution

The reaction between alkanes and halogens is not as straightforward as it may seem. However, by studying the reactions we can put forward a mechanism which leads to the observed products and is consistent with the experimental facts. The proposed mechanism is presented as if one were examining the experimental observations and trying to elicit from these observations the reaction mechanism.

Facts

* *The reaction will not occur in the dark at room temperature*.

* *The reaction will occur in the dark at 300 °C*.

For a reaction to occur between the methane and the chlorine the reacting particles must collide. The collisions between methane and chlorine molecules must provide enough energy to cause bonds to break. Since the reaction will not occur in the dark at room temperature, the normal collisions alone will not supply enough energy for the reaction to proceed. The reaction requires large amounts of energy to get the chlorine molecule close enough to the carbon in methane for a reaction to take place. This is due to electron repulsion, Fig. 4.2. Another more plausible pathway must be suggested.

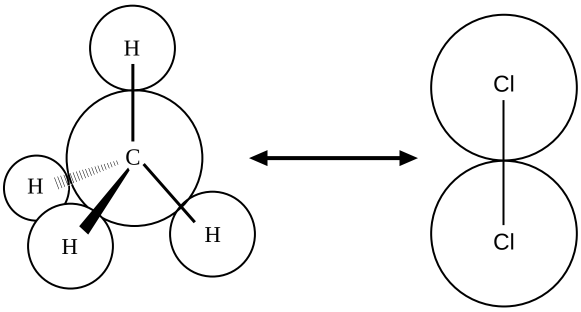


Fig. 4.2

Facts

* *The reaction will occur at room temperature if strong violet light or ultraviolet radiation is shone on the reactants.*

* *No molecular hydrogen (H_2) is formed.*

This raises the question as to what reactions can occur using the energy supplied by ultraviolet radiation?

The reactions in Fig. 4.3 are possible.

A $CH_4 \xrightarrow{hf} CH_3^{\cdot} + H^{\cdot}$

B $Cl_2 \xrightarrow{hf} 2\,Cl^{\cdot}$

Fig. 4.3

Reaction **A,** Fig. 4.3, involves homolytic fission (homolysis) of a C—H bond forming a methyl free radical and a hydrogen free radical, whilst Reaction **B,** Fig. 4.3, involves homolytic fission of a chlorine molecule giving two free chlorine atoms (chlorine free radicals).

Photons of violet light can supply up to about 300 kJ mol^{-1}. This is also the energy produced by a temperature of 300 °C in the dark. Reaction **A**, Fig. 4.3, requires 435 kJ mol^{-1} so this pathway is ruled out. In any case this reaction yields hydrogen atoms ($H^{\cdot}$) as one of the products, thus presenting the possibility that at some future stage two of these free atoms would combine to form H_2. No molecular hydrogen is produced in the reaction.

The splitting of chlorine (Reaction **B**, Fig. 4.3 above), however, requires only 242 kJ mol^{-1}. We can deduce that the reaction mechanism must therefore begin with the homolytic fission of the chlorine molecule. Two atoms of chlorine with unpaired electrons are formed. These are very reactive and, as stated above, are called **free radicals**.

What happens next?

Facts

- * *No molecular hydrogen (H_2) is formed.*
- * *Hydrogen chloride is a major product.*
- * *Many 1000s of molecules of chloromethane are produced for every one photon of light used.*

Concentration of the reactants will play a large part in what species is now attacked by these free radicals. The possibilities are presented in Fig. 4.4.

A $Cl^{\bullet} + Cl_2 \longrightarrow Cl_2 + Cl^{\bullet}$ (no change)

B $Cl^{\bullet} + CH_4 \longrightarrow HCl + CH_3^{\bullet}$

C $Cl^{\bullet} + CH_4 \longrightarrow CH_3Cl + H^{\bullet}$

Fig. 4.4

Reaction **A**, Fig. 4.4, does not lead to further reaction and reaction **C**, since it generates hydrogen free radicals, gives the possibility of producing molecular hydrogen. Reaction **B**, Fig. 4.4, needs 435 kJ mol^{-1} to break the C—H bond but 431 kJ mol^{-1} is obtained from the formation of the H—Cl bond. Since this is endothermic by only 4 kJ mol^{-1} it will readily occur.

However, if we accept Reaction **B,** Fig. 4.4, as occurring we must ask what now happens to the $CH_3^{\bullet}$?

Once again there are three possibilities, Fig. 4.5.

A $CH_4 + CH_3^{\bullet} \longrightarrow CH_3^{\bullet} + CH_4$

B $CH_3^{\bullet} + Cl^{\bullet} \longrightarrow CH_3Cl$

C $CH_3^{\bullet} + Cl_2 \longrightarrow CH_3Cl + Cl^{\bullet}$

Fig. 4.5

Again here Reaction **A**, Fig. 4.5, does not lead to further reaction.

Reaction **B**, Fig. 4.5, is possible but, as the concentrations of both species are very low, a collision between them is highly unlikely.

Reaction **C**, Fig. 4.5, gives us one of the desired products, CH_3Cl. In so doing it yields another chlorine free radical. If this follows the same pathway it will yield more products and more free radicals. We now have a ***chain reaction*** initiated by chlorine radicals and ending with new chlorine radicals. This also explains why a large number of chloromethane molecules are produced for every photon absorbed.

Fact

* *Ethane is produced in small amounts.*

Will reaction **C** go on forever?

No. Two reasons for this are that the number of free radicals is increasing and the concentrations of methane and chlorine are falling. A single free radical has caused many thousands of methane and chlorine molecules to be broken down.

Eventually, the probability of one of the reactions in Fig. 4.6 occurring increases.

A $2Cl^{\bullet} \longrightarrow Cl_2$

B $CH_3^{\bullet} + Cl^{\bullet} \longrightarrow CH_3Cl$

C $CH_3^{\bullet} + CH_3^{\bullet} \longrightarrow CH_3CH_3$

Fig. 4.6

In each of these reactions two free radicals combine, giving a stable covalent molecule. Thus even though a single photon can give rise to the generation of very many molecules of chloromethane the reaction gradually slows down and stops. The reactions in Fig. 4.6 are all referred to as **termination steps**. In general a reaction such as the chlorination of methane is irradiated continuously to avoid the slowing down and stopping of the reaction. Reaction **C** in Fig. 4.6 above accounts for the presence of ethane in small amounts in the products.

Facts

* *Tetramethyl-lead greatly speeds up the reaction*.

* *Molecular oxygen slows down the reaction*.

What about these other facts?

Studies have shown that tetramethyl-lead, $Pb(CH_3)_4$, decomposes to give lead, Pb, and four $CH_3^{\bullet}$ radicals. This would greatly increase the concentration of methyl radicals, thus increasing the reaction rate, i.e it serves as an **accelerator**.

On the other hand oxygen, O_2, combines with methyl radicals, $CH_3^{\bullet}$, to form the less reactive peroxymethyl radical, $CH_3OO^{\bullet}$. This slows down the reaction as a single oxygen molecule prevents thousands of CH_3Cl molecules being formed. Oxygen is an **inhibitor** and the slowing down of a reaction by small amounts of a substance is a sure indication that a chain reaction is involved.

Facts

* *Di-, tri- and tetra- chloromethane are also produced in the reaction*.

As the concentration of chloromethane increases, chlorine radicals will begin to attack the monochloromethane. This will also instigate a chain reaction, the result of which will be dichloromethane, Fig. 4.7(a). In order to reduce the occurrence of this and further substitutions [by attack of chlorine radicals on dichloromethane and trichloromethane, Fig. 4.7(b)] the concentration of chlorine must be limited.

$$Cl^{\bullet} + CH_3Cl \longrightarrow HCl + CH_2Cl^{\bullet}$$

$$CH_2Cl^{\bullet} + Cl_2 \longrightarrow Cl^{\bullet} + CH_2Cl_2$$

Fig. 4.7(a)

$$Cl^{\bullet} + CH_2Cl_2 \longrightarrow HCl + CHCl_2^{\bullet}$$

$$CHCl_2^{\bullet} + Cl_2 \longrightarrow Cl^{\bullet} + CHCl_3$$

$$Cl^{\bullet} + CHCl_3 \longrightarrow HCl + CCl_3^{\bullet}$$

$$CCl_3^{\bullet} + Cl_2 \longrightarrow Cl^{\bullet} + CCl_4$$

Fig. 4.7(b)

We can now propose a mechanism for the chlorination of methane which may be broken down into three stages: an **initiation** stage where chlorine free radicals are generated by homolytic fission of chlorine molecules by ultraviolet radiation followed by a **propagation** stage which consists of a self-sustaining chain reaction and finally a **termination** stage where free radicals combine, thus slowing and eventually stopping the reaction. This is summarised in Figure 4.8.

Initiation

$$Cl_2 \xrightarrow{hf} 2Cl^{\bullet}$$

Propagation

$$CH_4 + Cl^{\bullet} \longrightarrow CH_3^{\bullet} + HCl$$

$$CH_3^{\bullet} + Cl_2 \longrightarrow CH_3Cl + Cl^{\bullet}$$

Termination

$$2Cl^{\bullet} \longrightarrow Cl_2$$

$$CH_3^{\bullet} + Cl^{\bullet} \longrightarrow CH_3Cl$$

$$CH_3^{\bullet} + CH_3^{\bullet} \longrightarrow CH_3CH_3$$

Fig. 4.8

4.4 Reactions of the Alkenes

The bond energy of the C═C bond (612 kJ mol^{-1}) is higher than the bond energy of the C—C bond (348 kJ mol^{-1}). Yet alkenes are much more reactive than alkanes. To understand this we look at the nature of the C═C bond.

There are four electrons shared in the double bond. Two electrons are found in the σ-bond formed by the 'end-on' overlap of two orbitals. The second bond is a π-bond. This π-bond results from the 'side-on' overlap between two parallel p orbitals giving a region of high electron density above and below the σ-bond, Fig. 4.9.

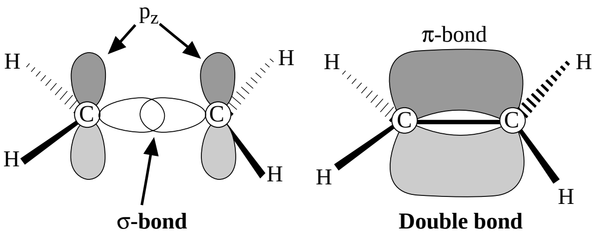


Fig. 4.9

From thermodynamic data we can deduce that the carbon-carbon double bond has an average dissociation energy of 612 kJ mol^{-1} whilst the carbon-carbon single bond has an average dissociation energy of just 348 kJ mol^{-1}. We can safely assume that the difference must be mainly due to the second bond in the double bond. This would imply that the π-bond has an energy of around 264 kJ mol^{-1}.

The double bond with its region of high electron density and moderately weak π-bond is the reactive site on the carbon chain of an alkene molecule. In fact it is reactions of the double bond that dominate the reactions of alkenes as a homologous series. When a group of atoms, or a particular bonding arrangement, dictates the reactions of a family of compounds, that group of atoms becomes known as the **functional group** of the series. The C═C double bond is the functional group of the alkenes.

In particular, **addition reactions** are the reaction type that are characteristic of alkenes. In these reactions two or more molecules combine to form one larger molecule. When an alkene undergoes addition across the double bond, it is this π-bond that is broken, Fig. 4.10. In the process both carbons can now form new bonds, releasing energy.

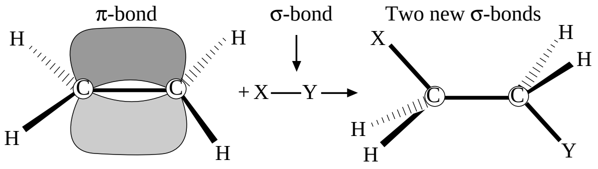
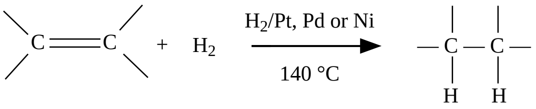


Fig. 4.10

Hydrogenation of alkenes, Equation 4.4, is an exothermic process liberating about 120 kJ mol^{-1} for almost every alkene. The reason for this energy release is that the energy produced from the formation of two C—H σ-bonds is greater than the energy required to break the π-bond of the alkene and the H—H σ-bond of the hydrogen molecule. However, the activation energy for this reaction is very high and the reaction will not proceed at room temperature. The presence of any of the catalysts listed (usually present as a deposit on carbon to increase surface area) allows the reaction to proceed rapidly at room temperature. The reactants are adsorbed onto the catalyst surface in a process which not only catalytically breaks the necessary bonds but also increases the surface concentrations of the reactants over their concentrations in the overlying gas.



Equation 4.4

Hydrogenation of alkenes is a very important reaction in the food industry as it is used to convert polyunsaturated fats (liquids) into saturated fats (solids). It is also possible to carry out the hydrogenation under controlled conditions and thus hydrogenate only some double bonds. Hence, the degree of unsaturation can be selectively reduced. Vegetable oils tend to be unsaturated while animal fats are saturated. Some medical research has suggested that saturated fats lead to heart and circulatory disease and therefore should be avoided.

A number of addition reactions are summarised in Fig. 4.11.

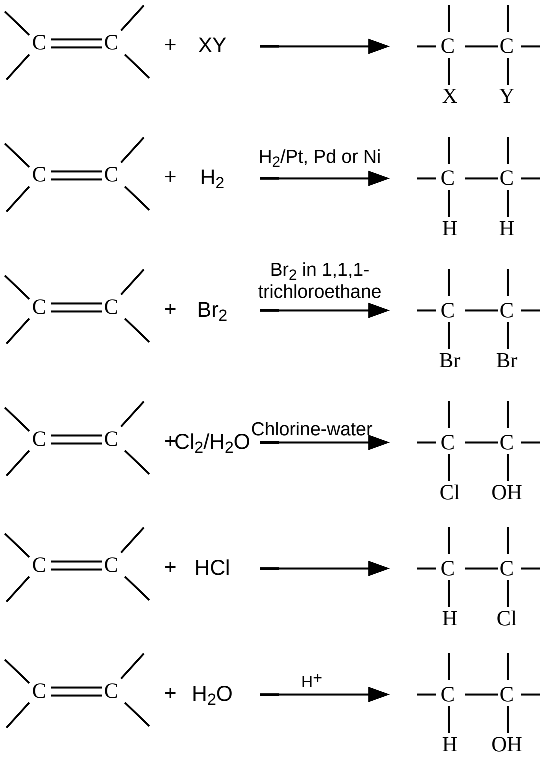


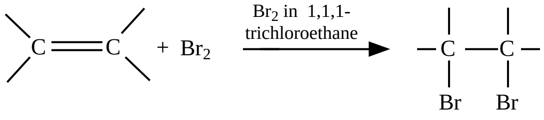
Fig. 4.11 *Addition reactions*

4.5 Ionic Additions to Alkenes

As stated earlier, the double bond of the alkenes is a source of electrons. Electron-seeking species will be attracted to this area of the molecule and hence the reaction is referred to as ‘electrophilic addition’. In fact it is via electrophilic addition that most additions to alkenes occur.

Bromination of Ethene

Bromine as a solution in 1,1,1-trichloroethane adds across the double bond of an alkene, Equation 4.5. In contrast to the halogenation of alkanes the reaction proceeds rapidly and does not require ultraviolet radiation. The rapid decolourisation of a bromine solution by a hydrocarbon is regarded as a good qualitative test for unsaturation.



Equation 4.5

Ionic Mechanism of Bromination of Ethene

The first stage in the mechanism involves a bromine molecule becoming momentarily polarised on approach to the region of high electron density of the double bond. The bromine molecule undergoes heterolytic fission (unequal splitting), forming a bromonium ion (Br^+) and a bromide ion ($Br^–$), Fig. 4.12(a).

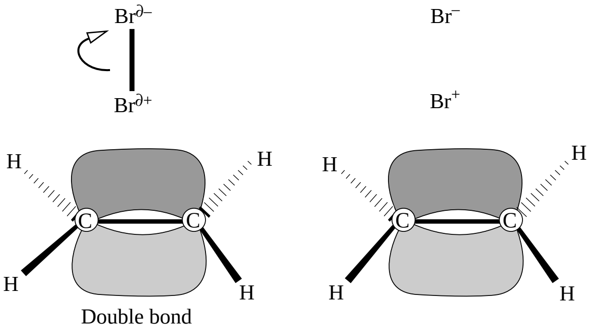


Figure 4.12(a)

The bromonium ion is an electrophile (it is electron deficient) and will seek to attack the electron-rich centre of the double bond. A three-centre, two-electron bond is formed with the positive charge delocalised over the three centres, Figure 4.12(b). The bromine is large enough to bridge the two carbons and no discrete carbonium ion is formed.

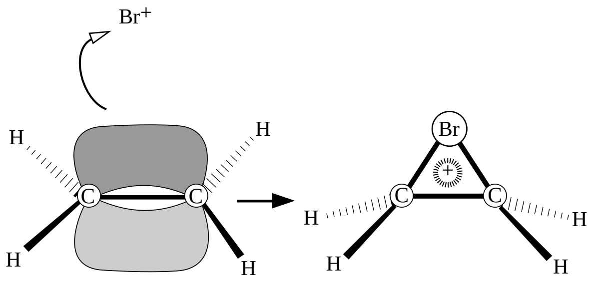


Figure 4.12(b)

A bromide ion, now acting as a nucleophile (‘nucleus seeker’), attacks one of the alkene carbons from below the molecule. A lone pair of electrons from the bromine is used to form a C–Br σ-bond and the two electrons from the three-centre, two-electron bond are used to form a σ-bond between the second carbon and the first bromine, Figure 4.12(c).

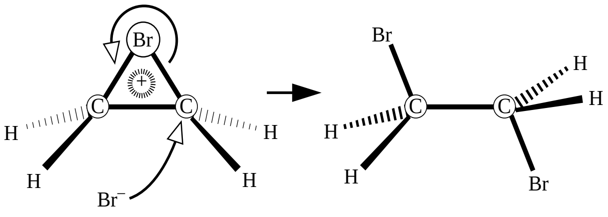


Figure 4.12(c)

There are several pieces of information which lead us to proposing an ionic mechanism with a bridged intermediate.

1 The reaction is more favourable in solvents with high dipole moments. These serve to stabilise ionic intermediates.

2. The presence of nucleophiles other than bromide (e.g. water) gives rise to competing reactions and the products observed include evidence for their intervention in the reaction (i.e. CH_2BrCH_2OH, 2-bromoethanol is produced). This is consistent with the formation of a cationic intermediate, which gives rise to *anti-* addition (i.e. the nucleophile attacks from below).

3. When the addition of bromine to *cis* and *trans*-but-2-ene is studied, vital information regarding the existence of a bridged intermediate emerges. *trans*-but-2-ene gives rise to *meso*-2,3-dibromobutane (see Appendix A) as the sole product, Fig. 4.12(d). On the other hand addition of bromine to *cis*-but-2-ene produces a racemic mixture of 2,3-dibromobutane, Fig. 4.12(e). If a simple localised carbonium ion were formed, both reactions would give rise to the *meso* and a racemic mixture of the optically active enantiomeric R,R- and S,S-2,3-dibromo-butanes (see p. 55).

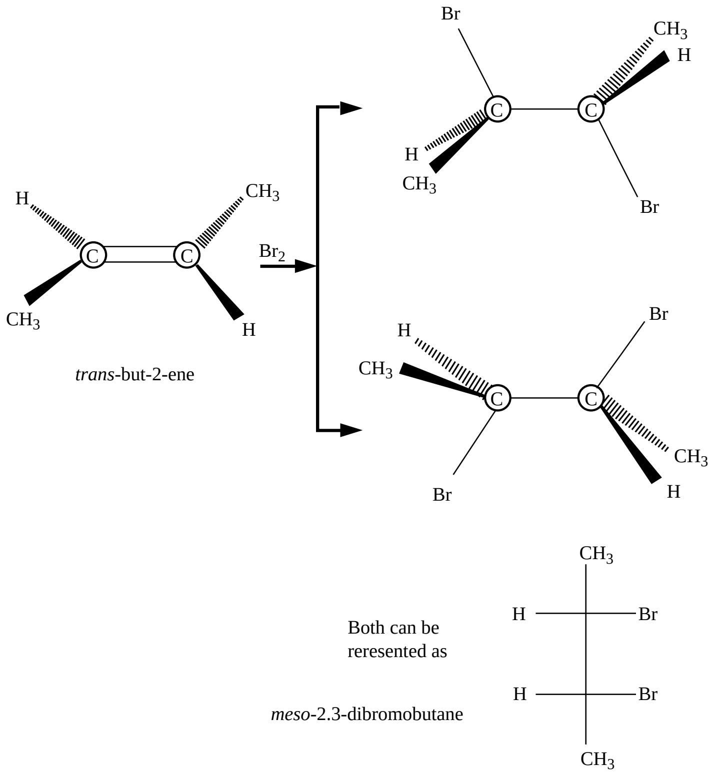
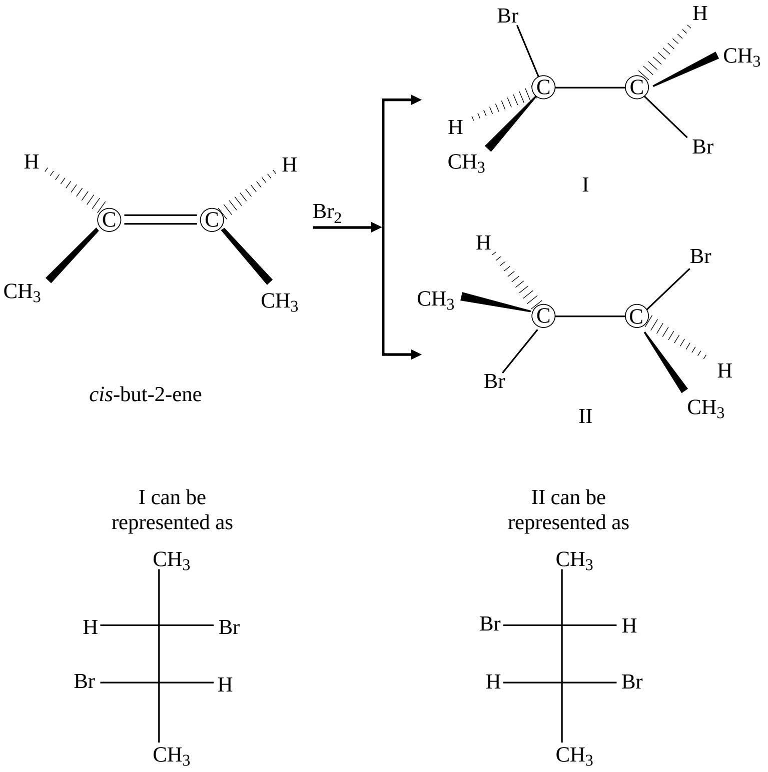


Fig. 4.12(d)



I and II are a racemic mixture of 2,3-dibromobutane

Fig. 4.12(e)

4.6 Other Ionic Additions to Alkenes

It is the large size of the bromine which allows it to form the bridged intermediate in the ionic addition of bromine to ethene. However, with other smaller electrophiles the formation of a bridged intermediate is not possible and a discrete carbonium ion results. This is so in the case of addition of substrates of the form HX (X = Cl, Br, OH, CN, etc.) In all these cases the electrophile is H^+ and it will become attached to one or other of the alkene carbons. Where the alkene is asymmetric, the H^+ will attack and become attached so as to generate the most stable carbonium ion. The stability of carbonium ions decreases as one moves from tertiary to secondary to primary, Fig 4.13. This is due to the positive inductive effect of the carbon-containing groups attached to the carbonium ion.

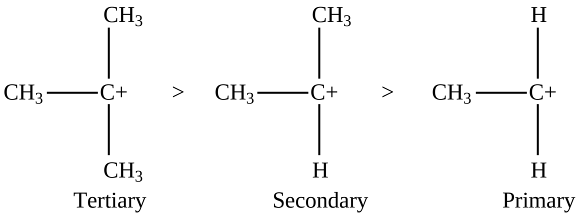


Fig. 4.13

It follows that the incoming electrophile becomes attached to the alkene carbon which initially bears the greater number of hydrogen atoms. This generates the most substituted (and so most stable) carbonium ion. The products of these reactions may be predicted if we know how the reacting molecule will split. This is the essence of a rule put forward by the Russian chemist Markovnikov who studied the outcomes of additions to alkenes. He found that one of the products always predominates. He concluded that *'when a molecule adds to the double bond, the more electropositive atom/group will attach itself to the carbon atom which already has the most hydrogens'*. This is known as Markovnikov's rule.

As an example one can examine the addition of HCl to propene. In this reaction 2-chloropropane is the major product. The initial attack of a hydrogen ion could give rise to a primary or a secondary carbonium ion. The secondary carbonium ion is far more stable than the primary carbonium ion and so it is more likely to be formed, Fig. 4.14, and the product derived from it, 2-chloropropane, is the major product.

We can now look at a summary of some of the other ionic additions to alkenes which follow Markovnikov's rule, Fig. 4.15. As stated above, the addition of bromine can be viewed as that of Br^+/Br^-. The addition of Cl_2/H_2O can be viewed as Cl^+/OH^-, HCl as H^+/Cl^- and H_2O as H^+/OH^-.

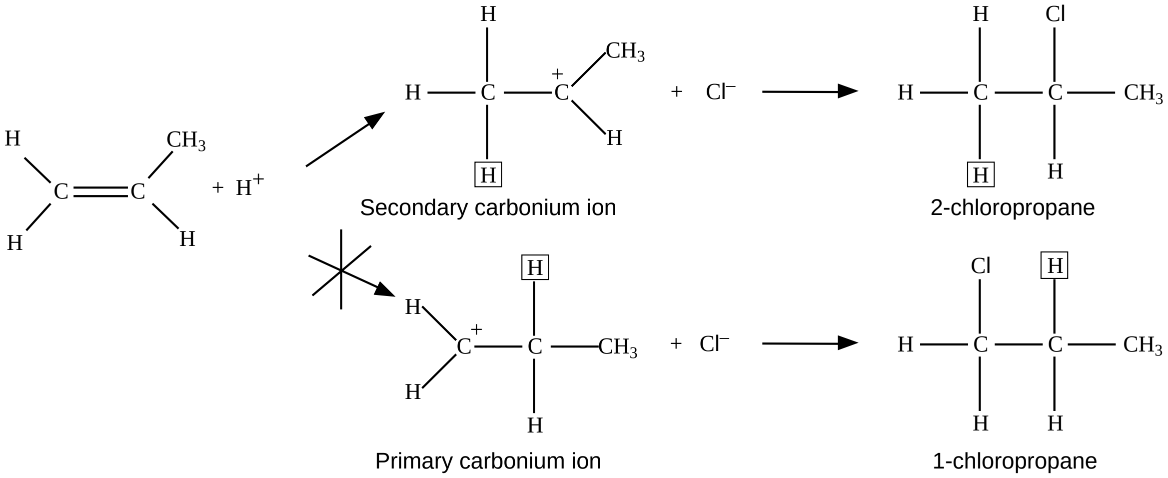


Fig. 4.14

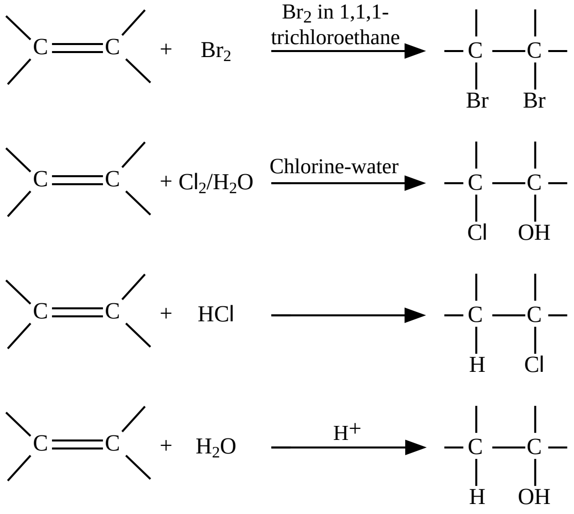
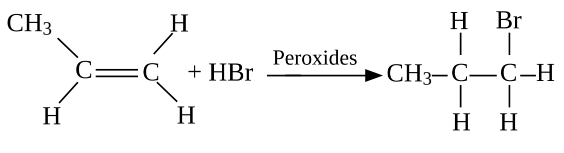


Fig. 4.15

Anti-Markovnikov Additions

Anti-Markovnikov addition is the name given to the addition of a species HX to an alkene where X becomes attached to that carbon of the alkene bearing the most hydrogens, i.e. exactly opposite to the product predicted by Markovnikov's rule.

Hydrogen bromide will add in an anti-Markovnikov fashion in the presence of peroxide, Equation 4.6. This is due to the fact that the ionic mechanism outlined above does not operate. Instead a free-radical mechanism involving generation of a bromine free radical occurs. The bromine free radical attacks the alkene forming a C—Br σ-bond and the most-substituted alkyl free radical is produced and this gives rise to the anti-Markovnikov product.



Equation 4.6

Hydroboration-oxidation reactions also proceed to anti-Markovnikov products, Equation 4.7. This is an important process as it adds H_2O to an alkene in the opposite orientation to the H_2O/H_2SO_4 mentioned earlier.

4.7 Combustion of Alkenes

Alkenes burn in excess oxygen to produce carbon dioxide and water, Equations 4.8 and 4.9.

$$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$$

Equation 4.8

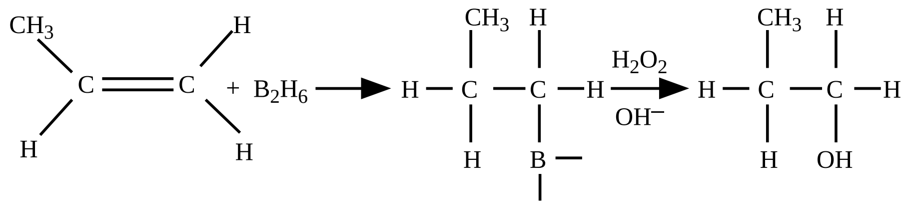
$$C_3H_6 + 4^1/_2\ O_2 \longrightarrow 3CO_2 + 3H_2O$$

Equation 4.9

4.8 Polymerisation of Alkenes

Using high temperatures and pressures and in the presence of a catalyst, alkenes can be made react with each other to form long chains of carbon atoms. These chains are called **polymers**. The mechanism for these addition reactions is similar to the free radical mechanism of the alkanes. The polymer of ethene is polyethene or polythene. Synthetic polymers are cheaper than naturally-occurring polymers and can be designed to fit a required specification. However, as a general rule, bacteria cannot break them down – they are said to be non-biodegradable – and as a result they are amongst the worst forms of litter. In practice they are difficult to recycle (partially due to the difficulty in sorting them). Four factors are thought to influence the properties of polymers.

Chain length. The basic characteristics of polymers, i.e. flexibility and tensile strength, are achieved with chain lengths of 50 or more monomers. Over 500 monomers gives mechanical strength. Also, the longer the chain the higher is the melting point.



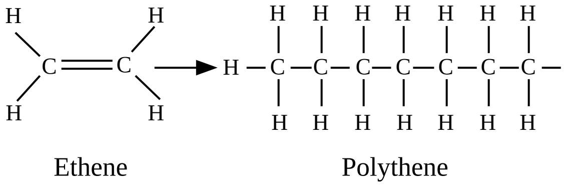
Equation 4.7

Intermolecular forces. The groups present on the side chains greatly influence the intermolecular forces of the polymer, making it stronger and more difficult to melt.

Branching. Highly branched polymer chains are difficult to pack together, making these polymers lighter with low tensile strength and low melting points.

Cross-linking. This makes the polymer rigid, hard and fairly brittle.

Ethene polymerises to yield polythene, Equation 4.10.

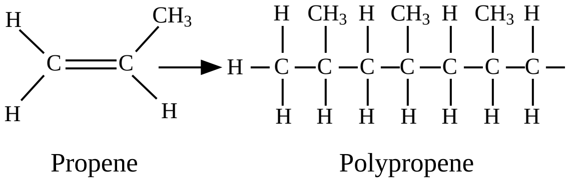


Equation 4.10

Uses

Plastic bags, squeezy bottles, buckets, washing up bowls, 'Tupperware'.

Propene (propylene) polymerises to yield polypropene (polypropylene), Equation 4.11.



Equation 4.11

Uses

Kitchenware, ropes, fibres for carpets, waterproofing sealants.

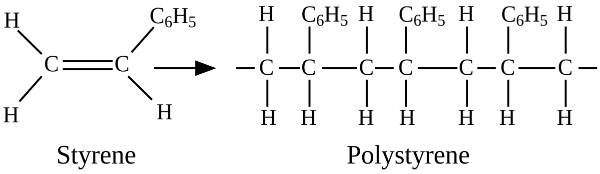
Polythene and Related Polymers

Polythene was discovered in 1933 at ICI by accident by Eric Fawcett and Reginald Gibson in trying to form a ketone from benzaldehyde and ethene. A leak had occurred in the apparatus and a white waxy solid, of empirical formula CH_2, formed. This reaction when repeated proved dangerous and was difficult to control. By 1935, using better equipment, they found that the heat given off could be controlled if the ethene was added cold and at the correct rate. Michael Perrin took charge of the operation in 1935 and it was he who discovered the role of oxygen in the reaction. No reaction took place in the absence of oxygen. It was the accidental leak that had initially allowed the oxygen to be present. He also showed that the benzaldehyde could be removed altogether and the polymer would still form.

The polythene, formed at 200 °C and a pressure of 1200 atm in the presence of traces of oxygen, has a melting point of 105 °C, contains branching, and is called low-density polythene. In the 1950s Karl Ziegler found that organometallic compounds of aluminium had catalytic properties in polymer production. His catalysts became known as Ziegler catalysts and his polythene can be produced at about 60 °C and 1 atm. This has little branching, melts at 135 °C, and is called high-density polythene.

Giulio Natta, an Italian chemist, used Ziegler catalysts to polymerise propene in 1954. Although it has branching, it is regular and the chains can pack tightly together. It can be made into fibres and is used in the manufacture of ropes. The advantage of being non-biodegradable is that it will not rot. It was Natta who developed the catalyst so that chemists can now produce tailor-made polymers with precise properties.

Phenylethene (styrene) polymerises to yield polyphenylethene (polystyrene), Equation 4.12. This polymerisation can be carried out in the presence of a volatile liquid (e.g. pentane) to yield expanded polystyrene which is used as an insulating material (aeroboard). Up to recent times, CFCs were used extensively as the volatile liquid.



Equation 4.12

4.9 Reactions of Aromatic Hydrocarbons

The reactions of aromatic hydrocarbons are not discussed in any detail here. However, it is noted that the reactions of aromatics are dominated by substitution reactions. Addition reactions would destroy their aromatic character and they would lose the stability that goes with it. In general these reactions proceed by an electrophilic aromatic substitution mechanism.

An example is used to illustrate this type of mechanism.

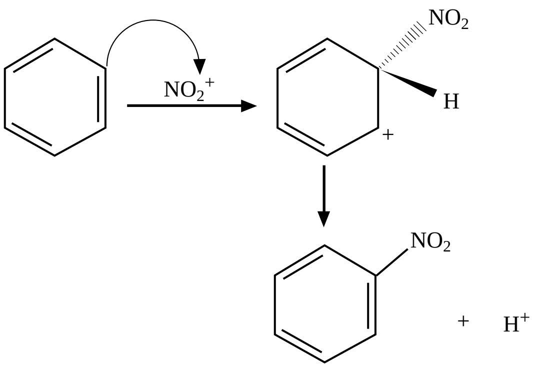


Fig. 4.16

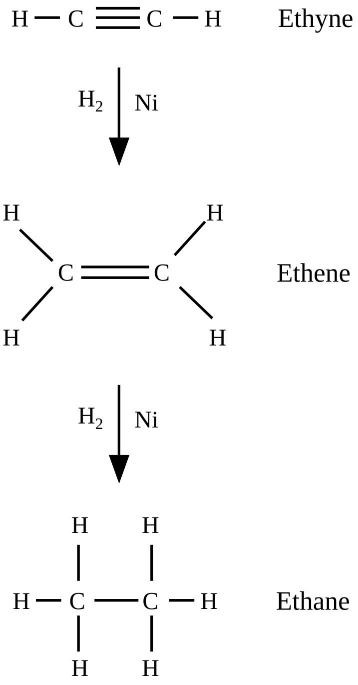
The outline mechanism for the nitration of benzene is shown in Fig. 4.16. The active electrophile is NO_2^+ and it attacks the π-cloud forming a carbonium ion. The aromatic delocalised character of the ring is lost. To restore the aromatic character of the ring a hydrogen ion is lost, reforming the aromatic system. Thus, substitution is achieved rather than addition. Where electrophilic substitutions are carried out on substituted aromatic compounds the substituents already in place dictate the position of further substitution as they influence the stability of the intermediate carbonium ion formed.

4.10 Reactions of Alkynes

We have seen in the case of alkenes that the centre of high electron density associated with the double bond dictates much of their chemistry. The same pattern of chemical behaviour is noticed in the case of alkynes with a strong tendency towards electrophilic addition, again due to the availability of weakly-held π-electrons. The carbon-carbon triple bond is in fact less reactive towards electrophilic reagents than the double bond of alkenes.

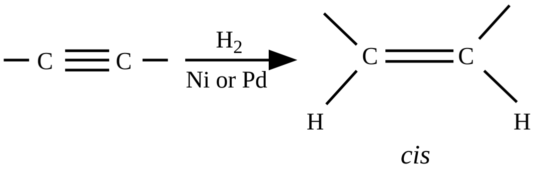
(a) Addition of Hydrogen

Hydrogen can be added to yield alkenes and alkanes, Equation 4.13.

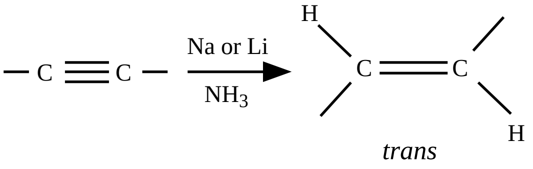


Equation 4.13

The orientation of addition of hydrogen to an alkyne can be regulated by employing different conditions, Equations 4.14 and 4.15.



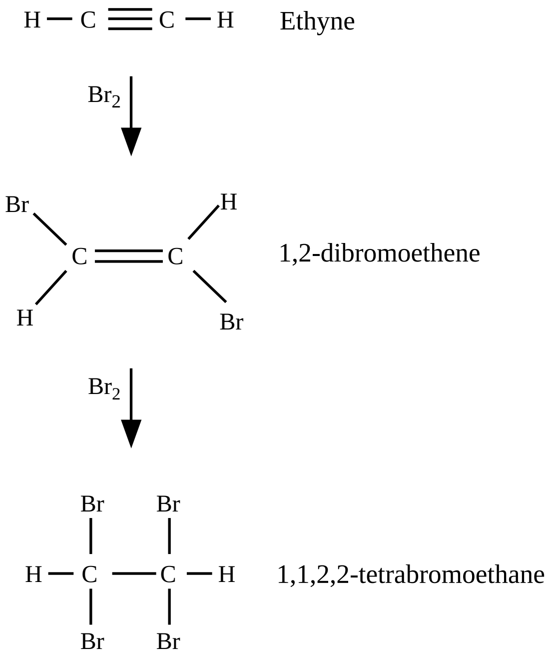
Equation 4.14



Equation 4.15

(b) Addition of Halogens

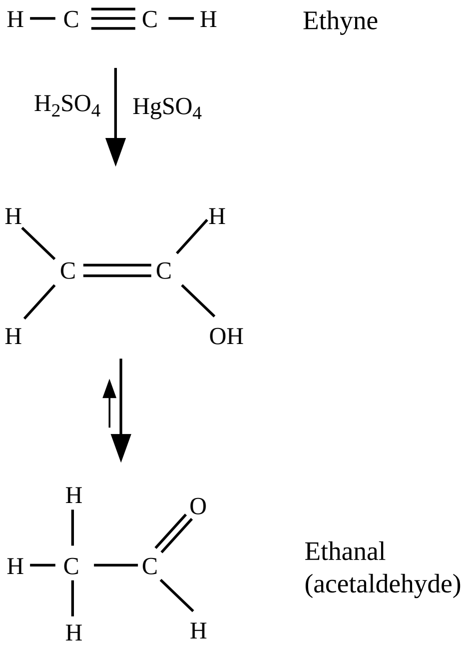
Bromine as a solution in 1,1,1-trichloroethane will add across the multiple bond giving first dibromoalkene and then the saturated tetra-bromoalkane, Equation 4.16.



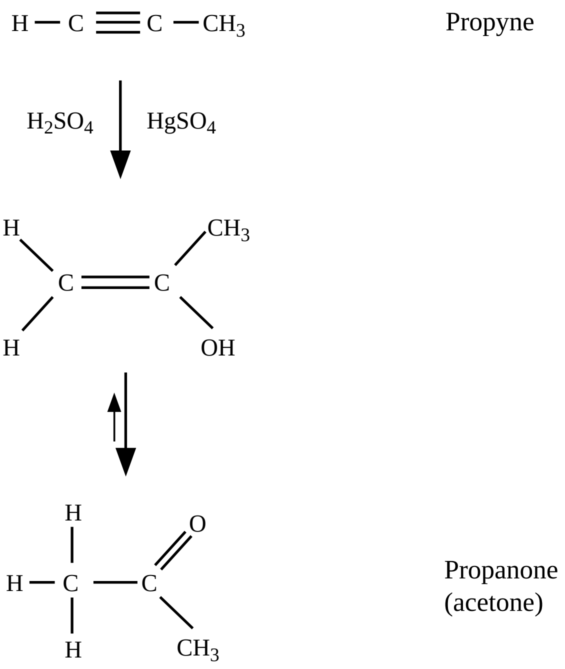
Equation 4.16

(c) Addition of Water

Hydration of alkynes is achieved using warm dilute sulphuric acid and mercury (II) sulphate (mercuric sulphate). One molecule of water is added across the triple bond and an enol is formed. This tautomerises immediately to the aldehyde (if ethyne is the alkyne used) or ketone form (for all other alkynes), Equations 4.17 and 4.18.



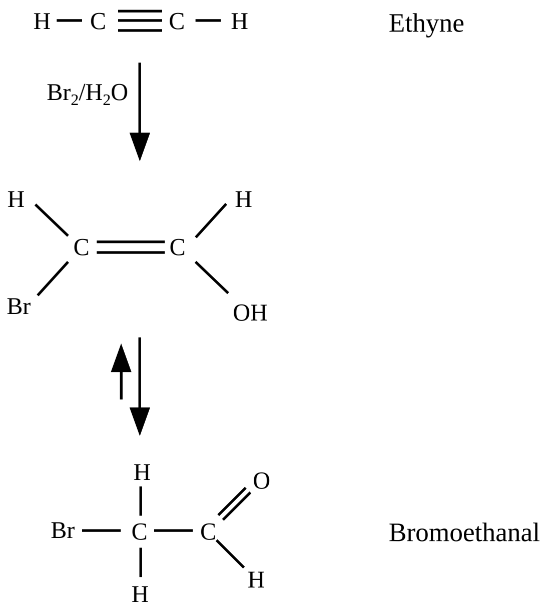
Equation 4.17



Equation 4.18

(d) Reaction with Bromine Water

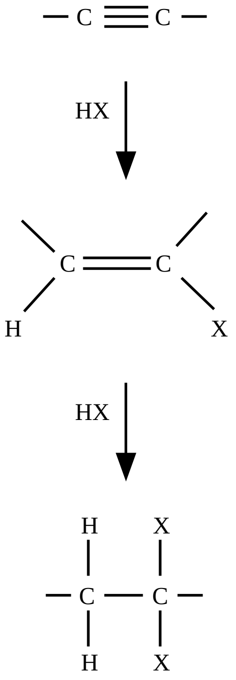
Ethyne will decolourise bromine water. The reaction will initially yield bromoethanal but the remaining hydrogens α- to the carbonyl are very readily substituted by bromine, Equation 4.19.



Equation 4.19

(e) Addition of Hydrogen Halides

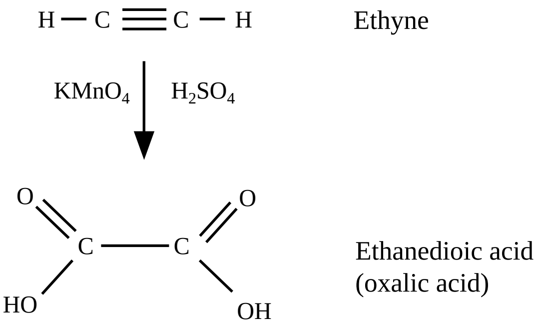
Hydrogen halides (HCl, HBr, HI) add to alkynes much like their addition to alkenes. However, two molecules can be added across the triple bond, Equation 4.20. It is usually possible to limit this addition by careful control of conditions and reagents.



Equation 4.20

(f) Reaction with Acidified Potassium Permanganate

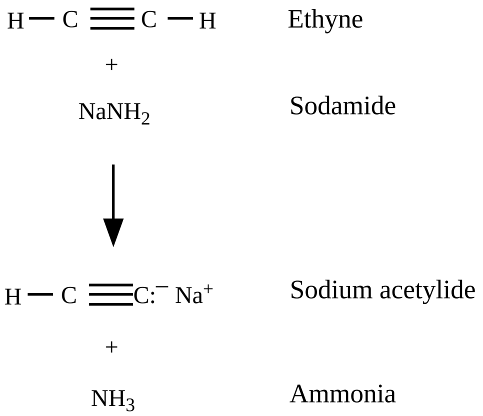
Ethyne will decolourise a solution of acidified potassium manganate(VII) (potassium permanganate). This reaction leads to the formation of ethanedioic acid (oxalic acid), Equation 4.21.



Equation 4.21

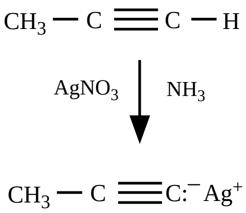
(g) Reactions as Acids

Terminal alkynes (i.e. one of the triple-bonded carbons bears a hydrogen) have a very weakly acidic hydrogen. In general they are weaker acids than water but they are stronger acids than ammonia. Consequently, terminal alkynes react with sodamide, $NaNH_2$, producing the sodium salt of the alkyne, Equation 4.22.



Equation 4.22

Terminal alkynes form insoluble heavy metal salts when reacted with certain heavy metal ions (Ag^+ and Cu^+), Equation 4.23. The insoluble salts formed may explode when dry and should be destroyed while wet by warming with dilute nitric acid. The strong mineral acid regenerates the alkyne. The production of these insoluble metal acetylides is one of the qualitative tests for terminal alkynes.



Equation 4.23

APPENDIX A ISOMERISM

Isomerism is the name given to the existence of compounds of the same molecular formula but different structural formulae due to different arrangements of their atoms within the molecule. This means that two or more compounds have the same numbers of each kind of atom but the atoms are attached to one another in a different manner. This difference in structure can result in isomers belonging to the same family, thereby having somewhat similar chemical properties, but having different melting and boiling points, or they may belong to different chemical families. When the latter occurs the isomers have distinctly different chemical and physical properties. To illustrate this, some of the isomers of molecular formula C_6H_{12} are given in Fig. A.1.

If we compare methylcyclopentane and cylcohexane we find that they have the molecular formula C_6H_{12} and are both cycloalkanes. They are isomers and belong to the same family of compounds.

We also find that the compounds hex-1-ene, hex-2-ene, hex-3-ene, 2-methylpent-1-ene, 3-methylpent-1-ene and 4-methylpent-1-ene all have the molecular formula C_6H_{12} and are alkenes.

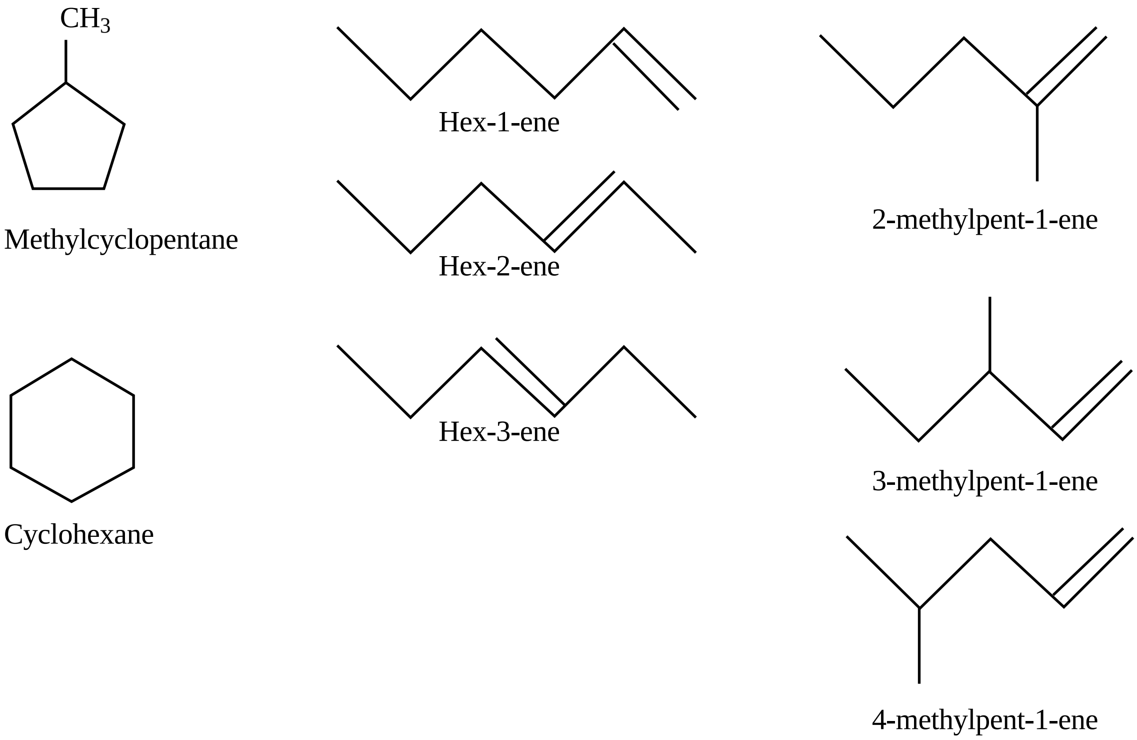
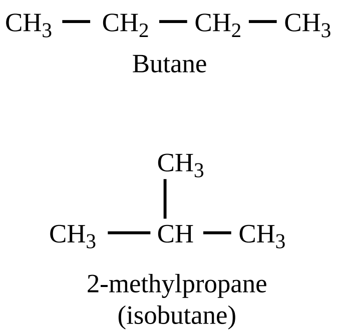


Fig. A.1

In the case of the alkanes the greater the number of carbon atoms present the greater the number of isomers possible. In fact the number of isomers rises rapidly as carbon number increases, e.g. the compound $C_{30}H_{62}$ has 4.11 × 10^9 isomers. The lowest alkane which forms isomers is butane, C_4H_{10}. These are butane and 2-methylpropane (isobutane), Fig. A.2.



$$CH_3 - CH_2 - CH_2 - CH_3$$

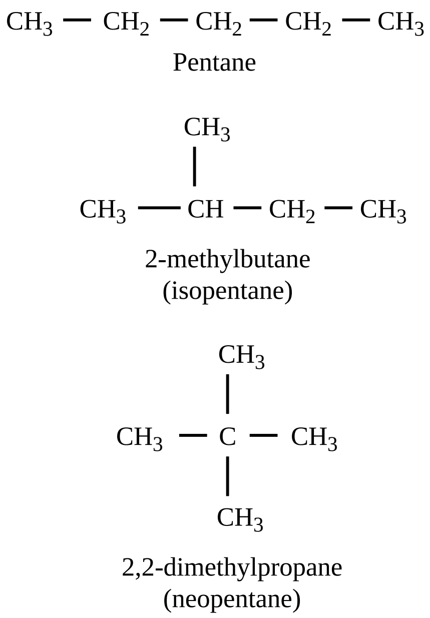
Butane

$$CH_3 - CH(CH_3) - CH_3$$

2-methylpropane
(isobutane)

Fig. A.2 *Isomers of butane*

Pentane, C_5H_{12}, has three isomers, Fig A.3.



$$CH_3 - CH_2 - CH_2 - CH_2 - CH_3$$

Pentane

$$CH_3 - CH(CH_3) - CH_2 - CH_3$$

2-methylbutane
(isopentane)

$$CH_3 - C(CH_3)_2 - CH_3$$

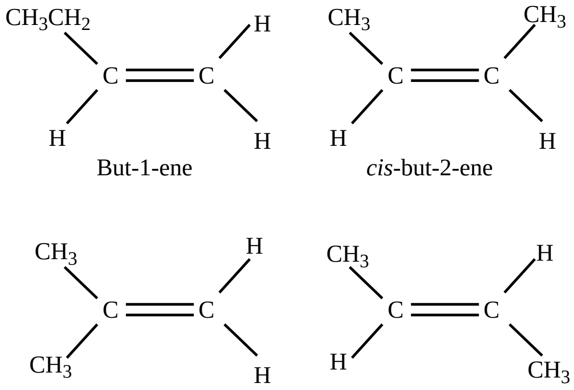
2,2-dimethylpropane
(neopentane)

Fig. A.3 *Isomers of pentane*

There are five isomers of hexane.

In the above examples, as the atoms are simply arranged differently within the molecule, this type of isomerism is called structural isomerism.

Butene is the lowest alkene to exhibit isomerism, Fig. A.4.



But-1-ene

cis-but-2-ene

2-methylpropene

trans-but-2-ene

Fig. A.4 *Isomers of butene*

The lack of free rotation about the double bond in but-2-ene gives rise to *cis-trans* isomerism (formerly called *geometrical isomerism*).

Butyne is the lowest alkyne to exhibit structural isomerism, Fig. A.5.

$$H - C \equiv C - CH_2 - CH_3$$

But-1-yne

$$CH_3 - C \equiv C - CH_3$$

But-2-yne

Fig. A.5 *Isomers of butyne*

Where four different substituents are attached to a single tetrahedral carbon atom two non-superimposable mirror image structures are possible. The two compounds have identical physical and chemical properties except that one rotates the plane of polarised light in a clockwise direction and the other rotates polarised light to an equal extent in an anticlockwise direction. This structural phenomenon is best illustrated using models, Fig. A.6.

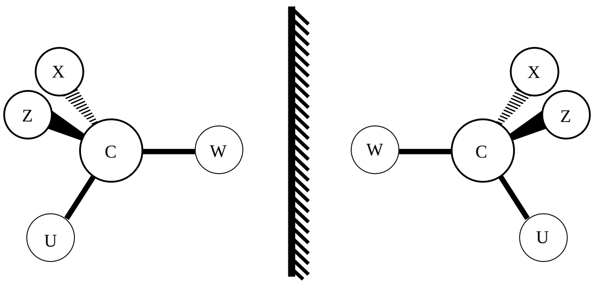
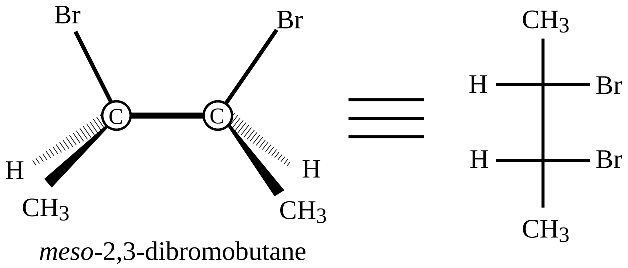


Fig. A.6

The carbon at the centre is said to be asymmetric. The naming of optically active compounds can be done using *d*- and *l*- (for *dextro*- and *laevo*-rotatory) indicating their effect on polarised light or using the **R-** and **S-** notation which uses the Cahn-Ingold-Prelog method of prioritising the groups attached to the asymmetric (chiral) carbon. Details of this method of naming are not presented here. The most commonly used method of denoting *d-/l-* optical compounds is by using the signs (+) and (–), respectively. For example, *d*-lactic acid is usually shown as (+)-lactic acid; *l*-lactic acid is usually shown as (–)-lactic acid; *dl*-lactic acid is usually shown as (±)-lactic acid.

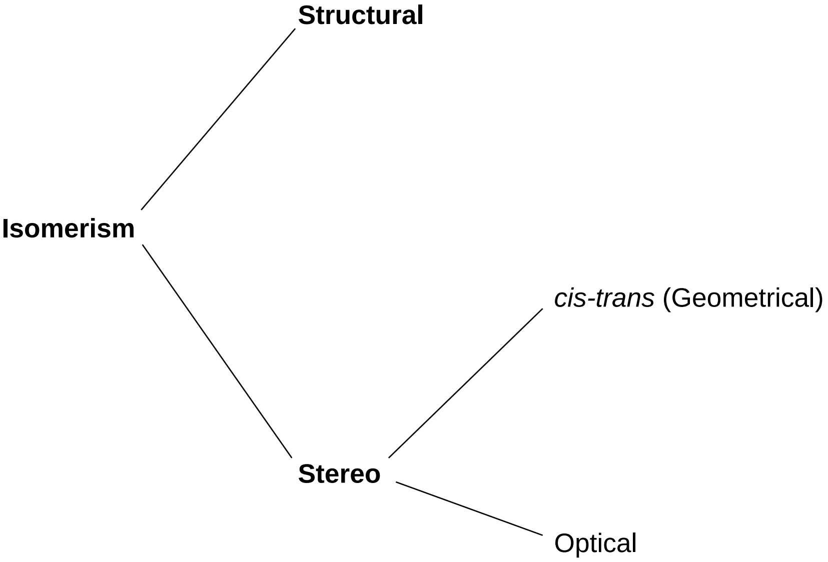
Where a molecule contains an internal plane of symmetry no rotation of the plane of polarised light is observed and the compound is called a *meso*-compound, Fig. A.7.



meso-2,3-dibromobutane

Fig. A.7

The main types of isomerism are:



Different structures arising from different arrangements of atoms within the molecule or different positions of functional groups.

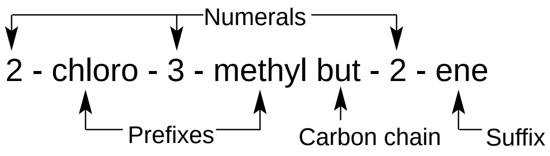
Associated with different arrangement of groups about a double bond and cyclic compounds.

Isomerism giving rise to rotation of the plane of polarised light. It arises in compounds with asymmetric carbons, allenes and biphenyls.

APPENDIX **B**

NOMENCLATURE OF ALKANES, ALKENES AND ALKYNES

The unambiguous naming of chemical compounds is very important. This is particularly true within the published literature where new and often complex compounds need to be readily identified. With the vast number of known compounds a systematic naming system is essential so that the name of any compound conveys a unique structural formula. One of the most satisfactory and widely used naming systems has been devised by the International Union of Pure and Applied Chemistry (IUPAC). However, generic or non-systematic names for compounds are common throughout organic chemistry. This normally occurs where compounds are either very well known or had widespread use before it was deemed necessary to apply a systematic name.



The IUPAC system names all compounds by first identifying and naming the basic carbon skeleton of the molecule. Then, using prefixes, suffixes and numerals, any non-hydrogen atoms or groups which are attached to the skeleton are identified and named.

It is a relatively simple operation for small simple molecules, but it can be complicated and often a tedious operation when the naming of complex molecules with many rings is undertaken. Only a very basic treatment suited for the naming of simple alkanes, alkenes and alkynes is given here.

The following is a summary of the relevant information for the naming of simple hydrocarbons. The examples which follow should elucidate the rules more clearly. Examples will be first taken where the structural formula is given and the name is found by following the set rules. This will be followed by examples where the systematic name is given and the structure drawn using the information provided in the name.

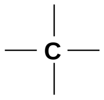
Carbon Chains

C_1 Meth	C_2 Eth	C_3 Prop	C_4 But	C_5 Pent
C_6 Hex	C_7 Hept	C_8 Oct	C_9 Non	C_{10} Dec

Suffixes

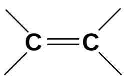
A numeral is written before the suffix (or directly before the name of the skeletal name) to give the position of the **functional group**. This number is found by counting the carbons in the skeleton from the end closest to the functional group.

Alkane



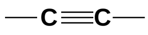
-ane

Alkene



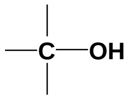
-ene

Alkyne



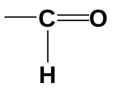
-yne

Alcohol



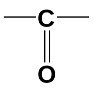
-anol

Aldehyde



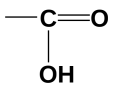
-anal

Ketone



-anone

Acid



-anoic acid

Prefixes

The presence of substituents on the main skeleton such as alkyl groups or others such as halogens are indicated as prefixes with a numeral immediately in front of the prefix indicating the carbon of attachment.

If two of the same group are present then two numerals are used even if they are the same numerals separated by a comma and 'di' is added to the prefix. For three of the same group add

Alkyl groups

—CH_3 Methyl	—C_2H_5 Ethyl	—C_3H_7 Propyl	—C_4H_9 Butyl	—C_5H_{11} Pentyl
—C_6H_{13} Hexyl	—C_7H_{15} Heptyl	—C_8H_{17} Octyl	—C_9H_{19} Nonyl	—$C_{10}H_{21}$ Decyl

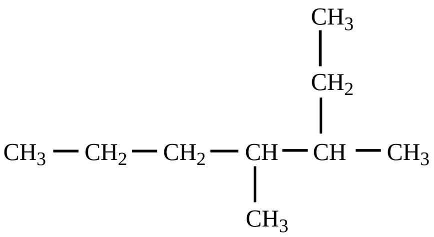
Others

—Cl Chloro	—Br Bromo	—OH Hydroxy	—NO_2 Nitro

‘tri’ and for four add ‘tetra’. If more than one prefix is present they are placed in alphabetical order. Hyphens are used to separate numerals from letters and commas to separate numerals from numerals.

Example 1

Name the compound.



Proceed as follows.

1. It is an alkane (i.e. saturated). Identify the longest chain ⇒ it is heptane.
2. Identify all substituents or branches ⇒ it is dimethylheptane.
3. Identify the location of branches so that the first branch is located as near as possible to one end of the main chain (or skeleton) ⇒ it is 3,4-dimethylheptane, Fig. B.1.

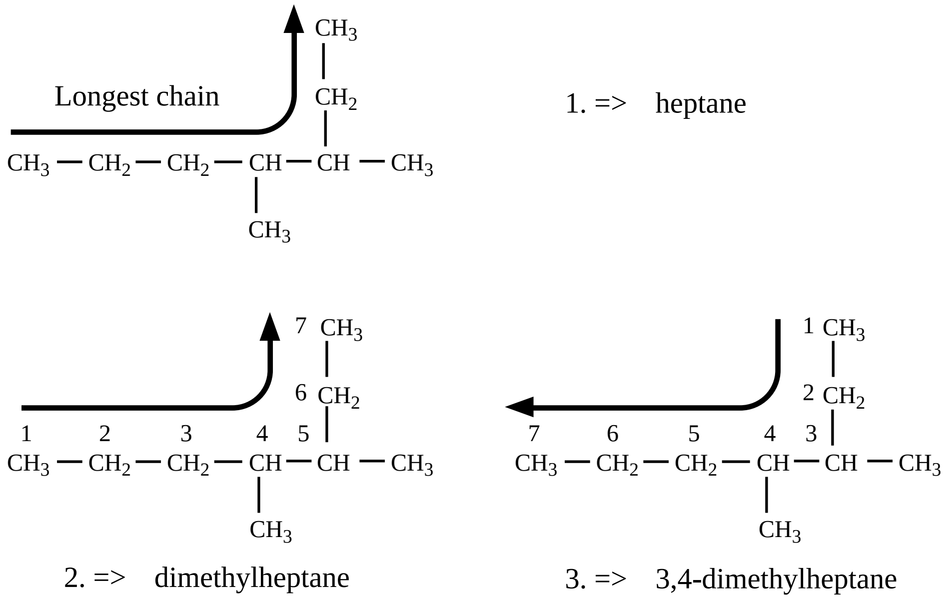
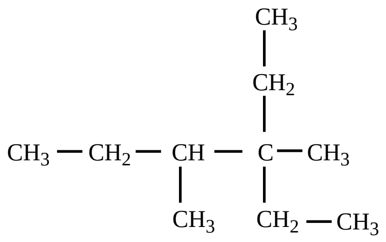


Fig. B.1

Example 2

Name the compound.



1. It is an alkane (i.e. saturated). Identify the longest chain ⇒ it is hexane.
2. Identify all substituents or branches – it has one ethyl and two methyl groups ⇒ it is ethyl-dimethylhexane.
3. Identify the location of branches so that the first branch is located as near as possible to one end of the main chain (or skeleton) ⇒ it is 3-ethyl-3,4-dimethylhexane, Fig. B.2.

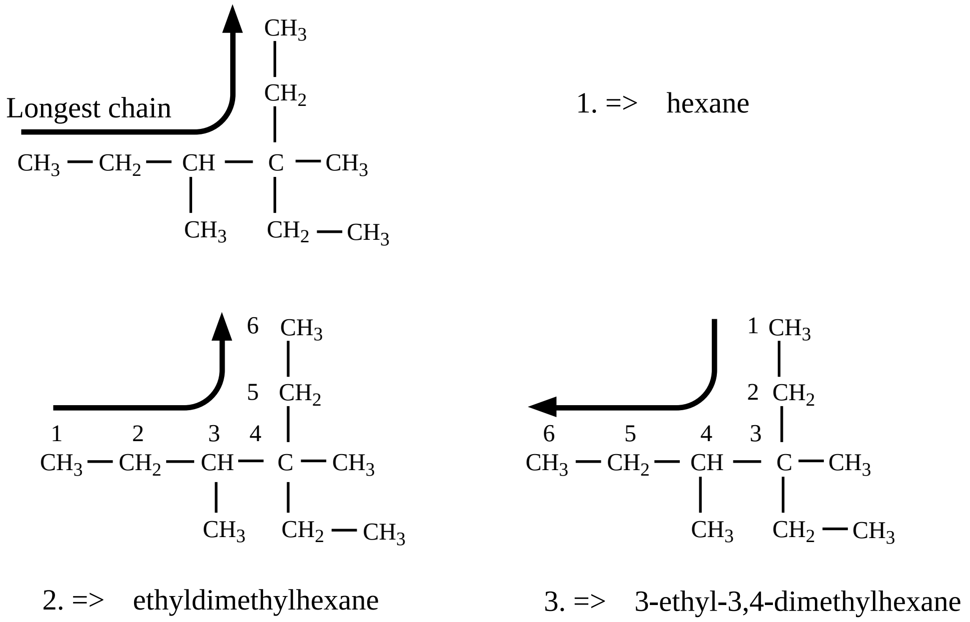


Fig. B.2

Example 3

Draw the structure of 2,2,4-trimethylpentane.

1. Pentane skeleton.
2. Place methyl groups at carbons 2, 2 and 4.
3. Arrive at final structure, Fig. B.3.

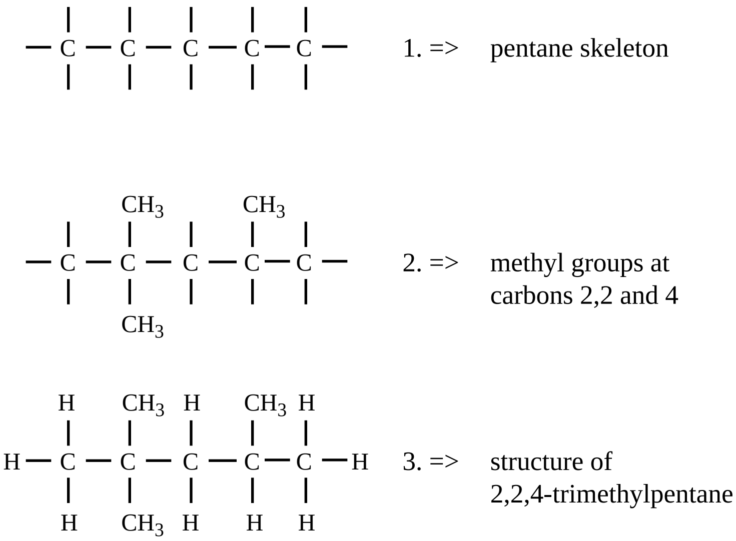


Fig. B.3

Example 4

Draw the structure of 2,4-dimethyl-3-ethylheptane.

1. Heptane skeleton.
2. Place methyl groups at carbons 2 and 4 and an ethyl group at carbon 3.
3. Arrive at final structure Fig. B.4.

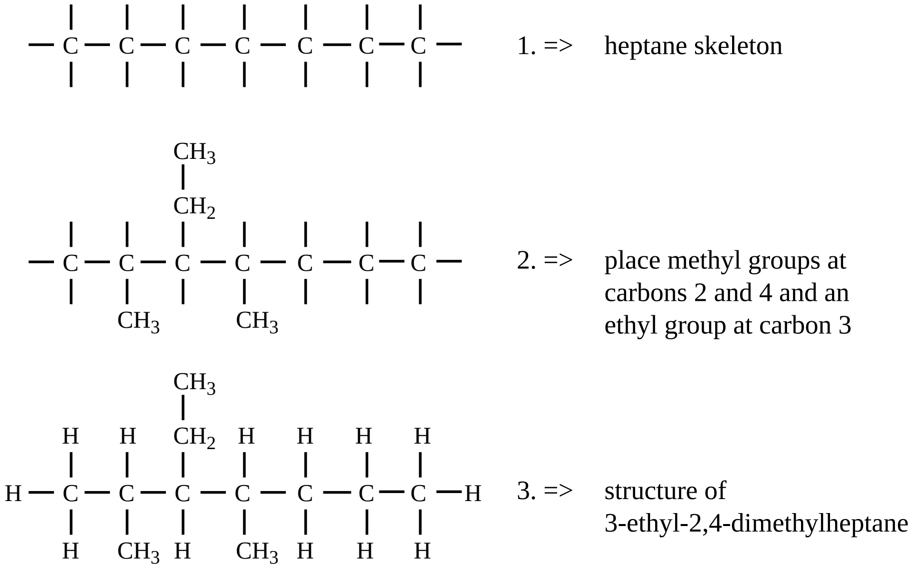
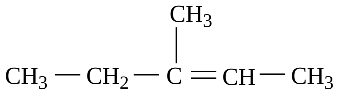


Fig. B.4

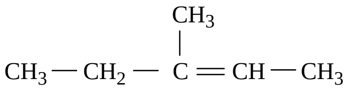
Example 5

Name the compound.



$$\mathrm{CH_3-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_3}$$

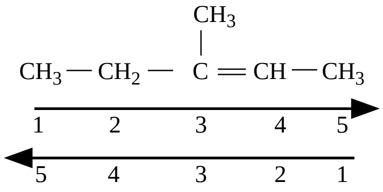
1. It is an alkene. Identify the longest chain containing the double bond ⇒ it is pentene.



$$\mathrm{CH_3-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_3}$$

1. => it is an alkene – longest chain
5 carbons => pentene

2. The double bond is located by numbering the carbon where it starts so that it is as near as possible to one end of the main chain ⇒ it is pent-2-ene.

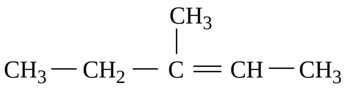


$$\mathrm{CH_3-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_3}$$

2. => it is pent-2-ene

3. Identify all substituents or branches ⇒ it is methylpent-2-ene.

4. Identify the location of branches so that the first branch is located on the main chain (or skeleton) ⇒ it is 3-methylpent-2-ene, Fig. B.5.



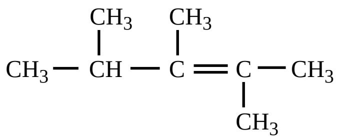
$$\mathrm{CH_3-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_3}$$

4. => it is 3-methylpent-2-ene

Fig. B.5

Example 6

Name the compound.



$CH_3-CH(CH_3)-C(CH_3)=C(CH_3)-CH_3$

1. It is an alkene. Identify the longest chain containing the double bond ⇒ it is pentene.
2. The double bond is located by numbering the carbon where it starts so that it is as near as possible to one end of the main chain ⇒ it is pent-2-ene.
3. Identify all substituents or branches ⇒ it is trimethylpent-2-ene.
4. Identify the location of branches so that the first branch is located on the main chain (or skeleton) ⇒ it is 2,3,4-trimethylpent-2-ene, Fig. B.6.

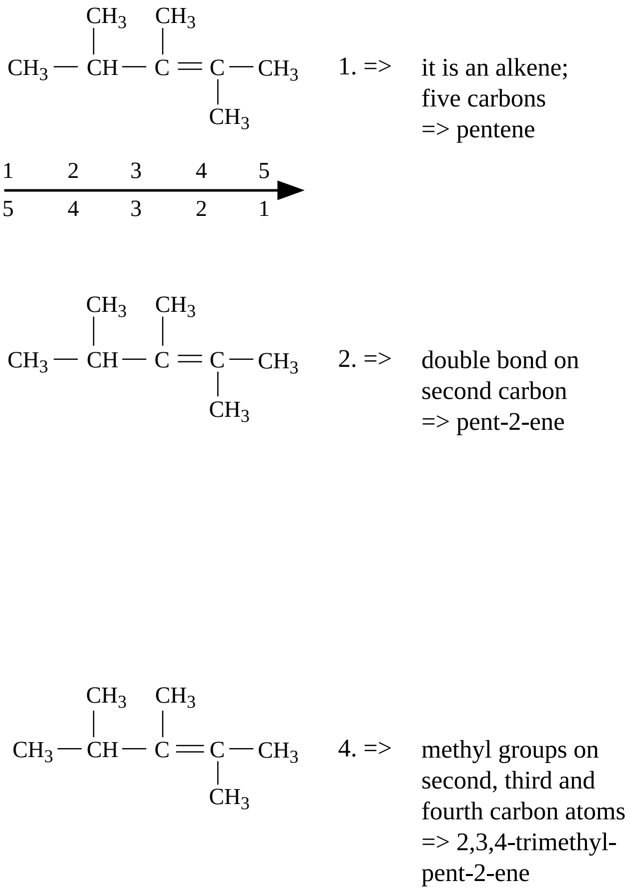
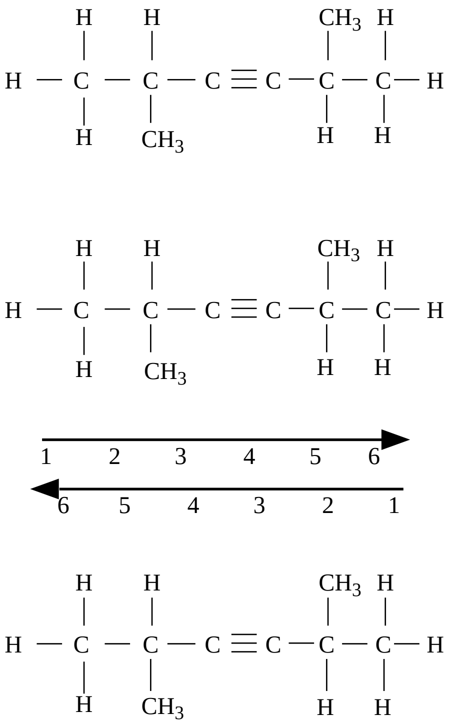


Fig. B.6

Example 7

Name the compound.



1. => identify longest chain – it is hexyne

2. => it is hex-3-yne

3. => it is 2,5-dimethylhex-3-yne

Fig. B.7

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MODULE 3

Industrial Chemistry

CONTENTS

Chapter 1 The General Principles of Industrial Chemistry

Chapter 2 The Manufacture of Ammonia and Urea by IFI at Cobh, Co. Cork

Chapter 3 The Manufacture of Nitric Acid and Calcium Ammonium Nitrate by IFI at Arklow

Chapter 4 Manufacture of Magnesium Oxide by Premier Periclase at Drogheda, Co. Louth

CHAPTER 1

THE GENERAL PRINCIPLES OF INDUSTRIAL CHEMISTRY

1.1 Introduction

The purpose of this booklet is to provide teachers with some useful background and resource material to assist in the teaching of Option 1A, entitled *Additional Industrial Chemistry,* of the Leaving Certificate syllabus.

In this section of the syllabus it is intended that students should learn to appreciate the importance and implications of having a chemical industry in this country. The need for a clear understanding and appreciation of the chemical industry has never been as important as at the present time, bearing in mind the strongly-held views against it from certain quarters, which have tended to gain very ample media coverage.

In addition to covering the characteristics of an effective and successful industrial chemical process, students will be expected to make a case study of one of three named important chemical industries.

The three named case studies specified on the syllabus are:

1. the manufacture of ammonia and urea by IFI, Cobh;
2. the manufacture of nitric acid and fertilisers by IFI, Arklow;
3. the manufacture of magnesium oxide by Premier Periclase, Drogheda.

It should be noted that it is strongly recommended within the syllabus that students should visit a particular local chemical industry. This visit should be a structured one, but does not necessarily have to be one of the above-mentioned industries. It could, for example be to a local water treatment plant.

When undertaking a case study of a particular chemical industry the ten main characteristics as listed in Section 1A.1 of the syllabus should be addressed. These are:

1. FEEDSTOCK (raw materials, preparation);
2. RATE (temperature, pressure variables, catalyst, etc.);
3. PRODUCT YIELD;
4. CO-PRODUCTS (separation of, disposal or sale);
5. WASTE DISPOSAL AND EFFLUENT CONTROL (waste water treatment, emission control);
6. QUALITY CONTROL;
7. SAFETY (monitoring of hazards, safety features, on-site training);
8. COSTS (fixed costs, variable costs, cost reduction by heat exchangers, catalysts, recycling and selling of useful co-products, costs of waste disposal);
9. SITE LOCATION;
10. SUITABLE MATERIALS FOR THE CONSTRUCTION OF CHEMICAL PLANT (unreactive, resistant to corrosion).

However, it should be stressed that not all of these characteristics will require equal and detailed coverage in any one particular case study.

It is suggested that the teaching of this section on Industrial Chemistry should be delayed until the second year of the course. This is because so much important material in this area of study relies on a good sound understanding of many fundamental concepts and principles of chemistry e.g. chemical equilibrium, oxidation-reduction, rates of reaction, catalysis, etc.

1.2 Poor Image of Chemistry and the Chemical Industry

Over the last number of years there has been a realisation that the image of chemistry and the chemical industry is very poor among the general public. Even those who are well disposed towards the chemical industry would agree that the words ‘chemistry’ and ‘chemical industry’ tend to conjure up negative images in the minds of many people.

The first National Chemistry Week in 1988 was set up to counter this poor image and was quite successful at the time. However, since then it is clear that the public, swayed by an often one-sided and negative viewpoint from the media, still views the chemical industry with suspicion and distrust.

This poor perception of chemistry is also reflected in the decline in the numbers of students studying chemistry at Leaving Certificate level in recent years.

Among the reasons for this sad state of affairs was the failure of the chemical industry in Ireland in the past to publicise what it does, the precautions it takes to protect the environment and its importance not only to the Irish economy but in everyday life. In many cases the policy appeared to be that of the adoption of a low profile. This often meant that little was done, instead of getting in first with an active programme of providing full information and opening doors to local groups. Thankfully, things have changed now and many industrial representatives have made very positive efforts to inform and communicate with the public and local groups.

Progress is definitely being made in this regard, but much still remains to be done to educate large sections of the community to a better understanding of the chemical industry.

It should also be recognised that the establishment of the Schools Information Centre on the Irish Chemical Industry (SICICI) in Limerick, by Dr P. E. Childs in 1989 has made a most significant and valuable contribution towards improving relations and contact between schools and industry in this country.

1.3 The History of the Irish Chemical Industry

The history of the Irish chemical industry from its small beginnings back in the 18th century up until today is a story that still needs to be written. At present, it is possible only to outline some of the highlights of this history, and there is much that remains untold and probably unknown. Some key dates are shown in Table 1.

The modern European chemical industry started around two hundred years ago. One of the pioneers of the UK chemical industry was James Muspratt, a Dubliner, who started manufacturing chemicals in Dublin in 1819 but who moved to Liverpool in 1822 where he set up a sodium carbonate works in 1823. He introduced the manufacture of this on a large scale and has often been referred to as the ‘father’ of the modern chemical industry.

In 1808 James Murray, a Belfast physician (who moved to Dublin in 1831) first introduced superphosphate by treating phosphate rock with sulphuric acid and patented the process in 1842. This discovery was first commercially exploited in London in 1843 by J. B. Lawes and marked the start of the synthetic fertiliser industry.

Another industrial pioneer was Josias Gamble, born in Enniskillen in 1776. He was a Presbyterian minister who became interested in chemistry and started making bleach for the linen industry in Co. Monaghan. He moved to Dublin to make chemicals and eventually emigrated to England and settled in St Helen’s to make sulphuric acid and soda. He was another of the founders of the British chemical industry.

The chemical industry grew in Britain around Glasgow, Newcastle-on-Tyne and Liverpool and soon became a large-scale enterprise. In Ireland in the nineteenth century small industries were the norm and large-scale industrialisation never took off except around Belfast. It appears there were small factories around the country making bleach, soap, alkali, fertilisers, etc. In 1898, for example, a report of the alkali inspector indicated no less than 69 factories in Ireland producing chemicals, mostly for making ‘chemical manure’, i.e. synthetic fertilisers. These industries included:

> ‘One alkali manufacture, thirteen sulphuric acid manufactures, sixteen chemical manure manufactures, three nitric acid manufactures, two cement manufactures and eight tar distilling and felt manufactures’ (Shaw, Irish Chemical News, Autumn, 1987).

This list didn’t include brewing and distilling, vinegar production, or soap manufacture. The modern chemical industry in Ireland, dominated by health care, pharmaceuticals and fine chemicals, owes little to this early beginning. It is only companies like Irish Cement and Nítrigin Éireann Teoranta (NET, now Irish Fertiliser Industries, IFI) which can trace their roots back to the early chemical industries.

The modern chemical industry is usually dated from 1969 when the Pfizer Corporation located a plant near Cork to produce citric acid (and later bulk pharmaceuticals).

The 1970s marked the start of a period of expansion in the pharmaceutical and fine chemicals sector which is still continuing. In the early 1970s Pfizer was followed by Smith Kline, Merck Sharp and Dohme, Gaeleo, Syntex, Henkel, FMC, Eli Lilly, Shering Plough, Sandoz, etc. At present twelve of the top fifteen North American pharmaceutical companies have manufacturing plants located in Ireland.

Bulk chemicals (organic and inorganic) are poorly represented in Ireland except for fertiliser manufacture – even sulphuric acid is no longer made in the Republic of Ireland. Nitric acid is made by IFI at Arklow, where NET started making compound fertilisers in 1965. NET also built a modern ammonia synthesis plant at Marino Point. This plant uses natural gas from the Kinsale gas field and started production in 1979 making ammonia, urea and by-product carbon dioxide. The NET plant (now IFI) supplies ammonia to the former Richardsons factory in Belfast. Premier Periclase Limited started extracting magnesia (magnesium oxide) from seawater at Drogheda in 1979, utilising the assets of an obsolete cement plant. Ireland also boasts Europe’s most modern alumina plant, Aughinish Alumina, set up on the west coast in 1983 with a rated capacity of 800 000 tonnes per year and space to double or

Table 1. History of Chemical Industry in Ireland – some important dates

1808	James Murray is first to make superphosphate from phosphate rock using sulphuric acid, patented 1842, exploited in London in 1843 by J. B. Lawes.
1819	James Muspratt makes chemicals in Dublin, moves to Liverpool in 1822 and starts first large-scale le Blanc alkali works in 1823. Considered the ‘father of the alkali industry’ in the UK.
1969	Pfizer Chemical Corporation opens first large-scale fine chemical plant in Ireland at Ringaskiddy, Co. Cork.
1973	Marathon discovers natural gas off Kinsale, brought ashore in 1978.
1974/6	Merck, Sharp and Dohme locates at Ballydine, near Clonmel, Co. Tipperary.
1977	Syntex locates at Clarecastle, Co. Clare.
1979	Premier Periclase starts producing magnesia from seawater at Drogheda.
1982	Last sulphuric acid plant in the Republic closes at NET’s Arklow plant.
1983	Aughinish Alumina starts production at Aughinish Island, Co. Limerick.
1988	Supreme Court decides against Merck, Sharp & Dohme and for John Hanrahan.
1989	Merrell Dow withdraws from plans to locate a new pharmaceutical plant at Killeagh, Co. Cork after strong local opposition.
1989	Sandoz lodges planning application for a £250 million plant at Ringaskiddy.
1990	Sandoz granted planning permission by Cork County Council, subject to 77 stringent conditions.
1991	Work starts on Sandoz plant in Ringaskiddy.
1993	Fires at Hickson and ADM plants in Cork. (ADM was incorrectly given as Pfizer in the printed text.)
1994	Environmental Protection Agency (EPA) set up.
1995	Sandoz starts full-scale production.

treble production in future. Other chemical industries outside the pharmaceutical and fine chemicals sector include Mitsui Denman at Little Island, Co. Cork which produces refined manganese(IV) oxide for dry batteries, and Henkel, also in Co. Cork, which makes ion exchange reagents for copper extraction as well as additives for phosphate-free detergents. In addition, Loctite makes adhesives and sealants at Tallaght, Co. Dublin.

It would certainly be no exaggeration to say that the growth of the chemical industry in this country during the past twenty-five years has been meteoric. In terms of percentage annual growth, both in turnover and in output, the Irish chemical industry has for many years been the fastest growing chemical industry in Europe. In recent years, Ireland has been a substantial net exporter of pharmaceuticals and also a big net exporter of other organic chemicals.

The Irish chemical industry today has little or no historical connection, either in terms of ownership or of technology, with such chemical industry as existed in Ireland prior to the Second World War. We owe our present industry very much to the incentive policies developed by successive Irish governments from the 1960s onwards, which have been implemented with enthusiasm and persistence by the IDA. The effective selling by the IDA of the attractions of Ireland as a manufacturing base, especially for export-oriented projects, has persuaded many multi-national firms of the highest reputation to establish major investments here in chemical and pharmaceutical manufacture.

At this point one must acknowledge the important decision taken by the Irish government in 1960 to set up the state-owned company NET with a view to relieving the severe nitrogen deficiencies experienced by Irish agriculture during the 1930s and 1940s.

In 1987 the new company, IFI, was formed from the amalgamation of NET, ICI and Richardsons (Belfast), resulting in a 51% shareholding by the Irish state and 49% by the private sector. IFI now produces 1.4 million tonnes of fertiliser each year, more than sufficient to meet the needs of Irish agriculture.

The turnover of each of the three plants operated by IFI depends on sales and can change depending on various markets. Overall, IFI has an approximate turnover of £150 million per annum. It must be borne in mind of course that the gradual decline in demand and usage of fertilisers both in Ireland and across Europe throughout the ’80s and ’90s has placed pressure on IFI to become cost effective and economical in a very competitive market.

1.4 Why Study Industrial Chemistry in School?

The chemical industry is an important factor in the modern Irish economy, a source of many jobs and an illustration of the importance of chemistry in our lives. As chemistry teachers, we need to have a knowledge of Ireland’s chemical industry. What products are being manufactured? Which companies are manufacturing these products? Where are these companies located? What raw materials are being used? What are the uses of these products? These are the questions we ought to ask and try to answer. By keeping abreast of what is going on, one can use the information to illustrate many aspects of the syllabus or when discussing careers in the chemical industry.

If we are not familiar with Ireland’s chemical industry, our chemistry courses can become too academic, out of touch with economic reality, irrelevant to most of the pupils, and inadequate as a preparation and as a stimulus to a career in chemistry or a career using chemistry. The quotation below from the Journal of Chemical Education makes the case for studying industrial chemistry very well.

> ‘All the existing high school curricula try to show how a chemist works in a research laboratory, emphasising practical work, and concept formation. This approach usually does not show how these chemical concepts are applied outside the school laboratory or that we live in a world which is increasingly dependent on the chemical industry and on industrial research and its applications. The teaching of chemistry without discussing this industry omits a most important aspect of modern life and, by implication, indicates that industrial applications are not important.

> One result of this omission is the well-publicised negative attitude of the general public towards chemistry as a whole with a consequent over-emphasis in the media on the hazards of pollution, carcinogenesis, chemical warfare, radioactive waste disposal, etc. These issues are indeed part of the facts and problems of daily life, but the publicity that they attract gives an unbalanced picture of the nature of science in general, and of chemistry, in particular.'
>
> N. Nae, A. Hofstein, D. Samuel,
>
> *J. Chemical Education* 57, pp. 366–368, 1980.

1.5 What is the Chemical Industry?

There is some problem defining what we mean by the chemical industry in Ireland as the different bodies concerned – the IDA, FICI and FÁS – all have slightly differing definitions. The chemical and allied industries can include some or all of the following industries.

Chemicals

Basic organic chemicals

Basic inorganic chemicals

Oil refining

Fertiliser manufacture

Agrochemicals (pesticides, etc.)

Adhesives, sealants, mastics

Perfumes, toiletries, soaps and detergents

Miscellaneous chemicals, e.g. candles, dental chemicals, explosives, matches, lime, etc.

Pharmaceuticals

Bulk pharmaceutical manufacture

Finished pharmaceuticals

Diagnostic/biotechnology chemicals

Distribution

Distribution of pharmaceuticals

Distribution of chemicals

Distribution of fertilisers, detergents, garden chemicals, etc.

Plastics and Rubber

Healthcare plastics

Other plastics used in packaging, houseware, engineering, etc.

Rubber

Ceramics

Crystal glass

Other glass abrasives

Pottery/ceramics

Allied Products

Photographic and film processing

Leather tanning

The chemical and allied products industry in Ireland is currently made up of 619 companies, employing over 37 000 people.

The regional distribution of companies within this industry is not uniform. There are 231 companies located in the Greater Dublin region, accounting for almost 30% of the industry's total workforce. The South East and South West regions, with 65 and 100 companies respectively, account for a further 15.3% and 14.3% of employment. The remaining 223 companies are dispersed throughout the remaining regions.

1.6 Future Prospects for the Chemical Industry in Ireland

According to a detailed study of the chemical and allied products industry in Ireland by Price Waterhouse for FÁS in 1993, the prospects are both positive and interesting.

Overall employment was forecast to grow in the period 1993 to 1997 by 20%. This forecast included new company start-ups, which were expected to come on stream during the forecast period. The overall growth in employment varied significantly between the different sectors of the industry. The pharmaceutical sector was set to grow by 42%, whereas there was expected to be a fall of 9% and 4% in the bulk chemicals and the glass and ceramics sectors, respectively.

Employment was set to grow in all regions with growth rates ranging from 37% in the Midlands to just 14% in the South East. While all categories of employment were set to grow, the demand for engineers/scientists was expected to increase most.

A major issue facing the industry throughout Europe as well as Ireland is the challenge of meeting ever higher standards of pollution control and environmental protection. It is estimated that the proportion of the industry's total investment devoted to combating various forms of pollution will rise from its present level of 10% to 20% during the 1990s.

The prospects for the industry in Europe are reasonably encouraging. It was identified in the Cecchini Report as one of the industries most likely to benefit from the completion of the Single Market. The recent decline in real oil prices also favours the industry. Recovery in the European economy is likely to generate a growth rate in excess of 3% per annum in the consumption of chemicals. International trade in chemical products is likely to continue to expand more rapidly than consumption.

There is a generally optimistic view of the prospects for further rapid growth and trade in the industry, assuming a resumption of growth in the global economy.

Note: a very valuable resource for teaching industrial chemistry is 'The Chemical Industry in Ireland', by P. E. Childs and M. Walsh. (See Bibliography, p. 38).

CHAPTER 2

THE MANUFACTURE OF AMMONIA AND UREA BY IFI AT COBH, CO. CORK

2.1 Introduction

Irish Fertilizer Industries, Cobh, Co. Cork has been producing ammonia since 1979 and is one of Ireland's largest chemical plants. Ammonia is the basis of all nitrogenous fertilisers and 1500 tonnes of ammonia are produced daily at the above plant.

From Cobh, ammonia goes to IFI's Arklow and Belfast factories for processing into the company's well-known range of fertiliser products, including NET Nitrate which is calcium ammonium nitrate (CAN), *pasture sward,* etc. The ammonia is also supplied to Cobh's own urea plant, producing 1000 tonnes of urea daily, one third of it for the home market and two thirds for export.

Ammonia from Cobh is sought by many countries for use in the manufacture of ammonium sulphate, nitric acid, ammonium phosphate and ammonium nitrate, just a few products in which ammonia is the main constituent. Since IFI came into existence in 1988, all of the ammonia produced at Cobh is used in IFI's three factories at Cork, Arklow and Belfast. The factory at Belfast produces *pasture sward* and *cut sward*.

2.2 Feedstock

The source of the hydrogen is natural gas, while the nitrogen comes from compressed air.

The natural gas comes from Ireland's offshore gas field at Kinsale Head, which was discovered and developed by Marathon Petroleum. It is estimated that IFI will use 40% of the gas field at a rate of 1.5 million cubic metres per day. The gas is piped underwater to Inch Beach in East Cork, from where Bord Gáis supplies it by underground pipeline to IFI.

Natural gas is odourless and for safety reasons Bord Gáis must give it a recognisable odour. Sulphur in the form of a mixture of mercaptans is added at a concentration of 9 ppm to the gas which is delivered to the IFI plant. The first step in the IFI process is to remove these sulphur compounds as they are poisonous to the catalysts used later in the process. The removal is brought about by mixing the feed gas with hydrogen and passing it over a cobalt/nickel/alumina catalyst. The hydrogen sulphide produced is removed by zinc oxide.

$$RSH\,(g) + H_2(g) \longrightarrow RH + H_2S$$

$$ZnO(s) + H_2S(g) \longrightarrow ZnS + H_2O(g)$$

The effluent gas should now contain less than 0.25 ppm of sulphur.

2.3 Rates and Conditions of Reactions

(a) Primary Steam Reforming

This is the stage at which hydrogen is obtained from the natural gas. The following two reactions take place:

(i) $$CH_4\,(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \qquad \Delta H = +\,210\text{ kJ mol}^{-1}$$

(ii) $$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

Since reaction (i) is an endothermic reaction, a high temperature will favour the formation of product, (Le Chatelier's principle). A low pressure will favour the formation of the product (2 moles on left but 4 moles on right).

In practice the reaction is carried out by passing the steam/methane mixture over a nickel oxide catalyst at 825 °C contained in tubes at 900 °C in a furnace at 1050 °C. Although a low pressure favours the formation of the product a pressure of 30 atm is employed since the later stages operate at high pressure. The high temperature is produced by burning the natural gas outside the tubes containing the catalyst and through which the methane is passing. There are 520 tubes containing 22 tonnes of catalyst (which lasts for about 2 years). Ideally, all the methane would be converted to carbon dioxide, but this has never been achieved and the reformed gas output consists of approximately H_2 = 70%, CO = 10%, CO_2 = 10%, CH_4 = 10%.

(b) Secondary Reforming

In the *Secondary Reforming* reaction, the methane content of the gas is reduced from 10% to approximately 0.5%. This is done by injecting air into the gas from the primary reforming stage. This has two purposes:

(1) the oxygen reacts with the residual methane using a nickel catalyst according to

$$CH_4 + 2O_2 \xrightarrow{Ni} CO_2 + 2H_2O;$$

(2) the nitrogen content of the original air is used later for the ammonia synthesis.

The gas leaving this stage contains the nitrogen and hydrogen in the required ratio, but along with carbon monoxide (12.5%) and carbon dioxide (7.5%).

These latter gases must be removed as they are both catalyst poisons at the ammonia synthesis stage.

(c) Shift Reaction

The carbon monoxide is converted to carbon dioxide (which is easily removed at this stage) by the *Shift reaction:*

$$CO + H_2O \longrightarrow CO_2 + H_2$$

which should be carried out at a low temperature. The gas, mixed with steam, is first passed over an iron oxide catalyst at 355 °C (this reduces the CO concentration from 12.5% to 3%) and then over a copper catalyst at 200 °C (which reduces the CO concentration down to 0.2%). (The Shift reaction was introduced by Bosch and was an improvement on the original process, hence the name Haber-Bosch Process is sometimes used instead of Haber Process.)

The carbon dioxide now remaining is removed as described in Section 5 on the co-products.

(d) Methanation

The small remaining quantities of oxides of carbon (0.5% total CO and CO_2) must now be removed as they would poison the catalyst during the ammonia synthesis. This is achieved by means of a reaction called *methanation* which involves reacting them with hydrogen in the presence of nickel or nickel oxide catalyst at 300 °C.

$$CO + 3H_2 \xrightarrow{Ni} CH_4 + H_2O$$

$$C0_2 + 4H_2 \xrightarrow{Ni} CH_4 + 2H_2O$$

This is a reverse of the steam reforming process and is exothermic. The gas composition at this stage is N_2 = 24.7%, H_2 = 74%, CH_4 = 1.0%, Ar = 0.3%, He = 0.0%, at a pressure of 25 atm.

(e) Compression

To increase the ammonia yield in the synthesis reaction, it needs to be compressed to the highest practicable pressure. Compression takes place in two stages:

(1) from 25 to almost 100 atm, during which it becomes heated and after which it is cooled to 8 °C and

(2) from 100 to about 200 atm. (The actual operating pressure is 185 atm.)

(f) Synthesis

The catalyst for the ammonia synthesis is finely divided iron oxide. The activity of this catalyst is promoted by the inclusion of small quantities of the oxides of aluminium, potassium and magnesium throughout the catalyst particles. The reaction is highly exothermic and the heat produced is extracted by heat exchangers and used to raise the temperature of the incoming gases to 350 °C. The temperature reaches a maximum of 500 °C during the formation of ammonia. (The catalyst will be damaged at 550 °C.) The exit gas is cooled in two stages, first to 43 ^{o}C and then to –23 °C. At this temperature and at a pressure of 178 atm the ammonia liquefies and thus it is easily separated. Some of the ammonia goes directly to the urea plant and the rest is cooled to –33 °C for storage at atmospheric pressure. The unreacted nitrogen and hydrogen are recompressed and recycled. The composition of the gas mixture (including fresh gas and recycled gas) entering the converter is N_2 = 21.1%, H_2 = 63.3%, NH_3 = 1.7%, Ar = 3.15%, CH_4 = 10.2%, He = 0.05%.

The main stages are summarised in Fig. 2.1, p. 12.

2.4 Product Yield

During the steam reforming process, in which methane is converted to hydrogen, there is a 91% conversion in the primary phase, while by the secondary phase only about 0.25% of methane remains in the gas mixture of hydrogen, nitrogen, carbon monoxide and carbon dioxide.

To facilitate the removal of oxides of carbon (which are catalyst poisons for the synthesis reaction) carbon monoxide must first be converted to carbon dioxide in the Shift reactions. In the high-temperature Shift reaction at 355 °C, carbon monoxide is reduced from 12.5% to 3.0% and in the low-temperature Shift reaction at 200 °C, the final concentration of carbon monoxide is 0.2%

In the actual Haber reaction to produce ammonia from the reaction of hydrogen and nitrogen, the yield has been improved recently from 13% to 17%. This was brought about by modifying the ammonia synthesis converter. The flow of gas was changed from axial to radial by the insertion of a stainless steel mesh basket to retain the catalyst. The particle size of the catalyst was reduced which gave a much greater surface area for the same mass of catalyst without causing a significant pressure drop across the catalyst bed.

The use of stainless steel gauzes is now known to make the catalyst more effective, possibly as it helps to maintain the temperature at a more constant level.

The annual production of ammonia in the world at present is 1.4×10^8 tonnes. The Marino Point plant, which is one of the world's technologically most advanced fertiliser plants, produces 1500 tonnes of ammonia each day. This production represents almost 0.4% of the world's production.

2.5 Co-products

The major co-product is carbon dioxide. This may be reduced from an initial value of about 17% down to 0.1% by spraying the gas with hot concentrated potassium carbonate solution under a pressure of 27 atm. The acidic carbon dioxide will react with the alkaline potassium carbonate according to:

$$CO_2 + H_2O + K_2CO_3(aq) \longrightarrow 2KHCO_3(aq)$$

When the pressure on the solution is released, the hydrogencarbonate dissociates back into carbon dioxide and potassium carbonate.

The carbon dioxide can be used later to manufacture urea on the same site or may be sold to soft drinks manufacturers and breweries. IFI, which manufactures 17 000 tonnes of carbon dioxide per annum, is the largest supplier of carbon dioxide in Ireland.

2.6 Waste Disposal and Effluent Control

As with all chemical plants, great attention and care have to be taken in this area. Very strict regulations are now being enforced for the monitoring of all emissions and effluents from chemical plants.

IFI has to obtain a licence for liquid and gaseous emissions from the local council which limits all daily emissions and effluents from the plant. For example, the plant is allowed to lose 600 kg of nitrogen as nitrogenous compounds each day into the harbour. The local authority carries out its own monitoring of the emissions while the company itself uses independent third party accredited procedures covering tests on environmental emissions and quality control of products. The air emissions are monitored stringently for the presence of ammonia, oxides of nitrogen and urea dust.

Effluent treatment at IFI is carried out within the process plants to allow recycling of the ammonia and carbon dioxide back into the production stream.

Urea plant effluent is treated with steam to hydrolyse urea to ammonia and carbon dioxide at 180 °C. The ammonia and carbon dioxide are condensed into concentrated solution and pumped back to the high-pressure synthesis section of the urea plant.

Ammonia plant effluent treatment is the recovery of process condensate and condensed steam from turbines. The treatment is by ion exchange resins where ammonia is replaced by hydrogen ions and carbon dioxide is replaced by hydroxide ions. A total of 255 m^3 per hour of water is recovered, treated and re-used in this way.

Emissions to Atmosphere

Approximately 350 000 m^3 of air per hour is used to cool the urea produced at IFI. This air contains small traces of ammonia and urea which are monitored by IFI, the local authority and by Forbairt at IFI's request. Forbairt also, at IFI's request, operates five monitoring stations measuring ground-level concentrations of ammonia and deposit rates of urea at selected sites in the local community. All emissions are carried out under licence.

2.7 Quality Control

The laboratory in Cobh devotes much of its time to detailed analyses of gas mixtures at various stages of the process. This is achieved with the aid of gas chromatography and infrared spectroscopy. This on-going gas analysis is used to accurately reflect the performances of the various catalysts.

In addition to the laboratory, a fully-computerised control room is manned around the clock. This monitors temperatures, pressures, pH, and flow rates, etc., throughout the plant. As in all modern chemical plants this is indeed the nerve centre of the entire plant, and has obviously contributed to a reduction in the workforce and the incidence of human error on the site.

2.8 Safety

The entire area encompassing the plant site has to satisfy a Division 1, or Division 2 level of safety. This means that all equipment operating on the site, or brought on to the site must be intrinsically safe, e.g. must not be capable of creating a spark.

Everyone working on the site is trained in the use of breathing apparatus and First Aid. A fully trained and equipped fire-fighting team is on twenty-four hour standby on the site.

2.9 Costs

The main costs involved in the Cobh plant are the following.

(a) Natural Gas.

(b) Electric power – the total power demand of the plant is in excess of 60 MW, of which a large proportion is required to drive the turbines for the compressors. However, up to 80% of the total power requirement is recovered from the plant because of the highly exothermic nature of many of the reactions involved at various stages, e.g. the purification processes and the ammonia synthesis reaction. In addition, the flue gases from the burning of natural gas in the primary reformer reduce in temperature from 1050 °C to 130 °C with a series of heat recovery coils, while the temperature of the gases leaving the secondary reformer reduces from 1000 °C to 350 °C. This is the correct temperature for the Shift reaction to take place. In this latter case, the heat is recovered by three waste heat boilers which are linked directly to the main steam drum. Therefore, the use of heat exchangers plays a very important role in reducing the overall running costs of the plant.

(c) The cost of fresh water with a requirement of 4.5 million litres per day.

(d) The labour cost of a 200-strong workforce on the site.

2.10 Site Location

The Cobh complex is located in a very favourable position for the following reasons.

(1) It is adjacent to a deep-water harbour and jetty which can accommodate ships of 25 000 tonnes used for the transport of ammonia and urea to the home and export markets.

(2) The site is adjacent to the Cork-Cobh rail line which can deliver 2-3 train loads of ammonia to Arklow daily.

(3) It is convenient to the supply of natural gas coming from the gas field off Kinsale Head.

(4) Availability of skilled personnel in the area, from graduate engineers and chemists to technicians and craftsmen to plant operatives who are trainees on-site.

(5) There is a seawater cooling system available, which is capable of utilising 25 000 tonnes of water per hour.

2.11 Construction Materials

The overall contractor for the Cobh project was the Kellogg International Corporation of London, and the ammonia process used is that developed by Pullman Kellogg of the United States. As with any chemical plant, great care and attention have to be paid to materials used in its construction. For the main part, mild steel is used on a deep solid concrete foundation. Stainless steel with a very high specification is used in certain parts of the plant, such as compressors and reaction chambers, which can only be allowed to corrode at a slow rate. The stainless steel used in the plant is purpose designed and custom made for the plant. The reaction chamber has a mass of 400 tonnes, contains 185 tonnes of catalyst and has a wall thickness of 17 cm.

Two 15 000 tonne refrigerated tanks are used to store anhydrous ammonia at –33 °C at the plant.

2.12 Urea Plant – Marino Point

The manufacture of urea is based on two chemical reactions. The first of these reactions is the reaction of ammonia and carbon dioxide to produce ammonium carbamate, NH_2COONH_4.

The feedstock is anhydrous ammonia and carbon dioxide, both of which are supplied by the ammonia plant.

The following reactions occur.

$$CO_2 + 2NH_3 \longrightarrow NH_2COONH_4$$

(exothermic)

This reaction releases heat which can be used to produce steam later in the plant. It is followed by the elimination of a molecule of water from the carbamate to give urea.

$$NH_2COONH_4 \longrightarrow NH_2CONH_2 + H_2O$$

(endothermic)

The second of these reactions is slow and in order to make it proceed at a practical rate, it must be carried out at a high temperature. This in turn means carrying out the process under pressure to prevent ammonium carbamate from dissociating back to ammonia and carbon dioxide. In the process used by IFI the ammonia and carbon dioxide are reacted together at a pressure of 140–150 atm.

Under these conditions not all the carbon dioxide and ammonia are converted to urea, and it is necessary to separate and recover them for re-use. This is done by passing the solution from the reactor through a stripper in counter current with the incoming carbon dioxide at the synthesis pressure.

This has the effect of sweeping out most of the ammonia and returning it to the reactor. After stripping, the solution contains approximately 60% urea and as little as 8% carbon dioxide, and 3% ammonia. The pressure is now reduced to about 3 atm and the solution is passed through a rectification column, where most of the remaining carbon dioxide and ammonia is removed. The pressure is finally reduced to atmospheric pressure and any remaining vapours flashed off to leave a 75% urea solution. All of the ammonia and carbon dioxide removed are recycled.

The urea solution obtained is next concentrated under vacuum in a two-stage evaporation unit to give a urea melt with a concentration of 99.8%.

To produce a solid product, the molten urea is then sprayed downwards from the top of a tall prill tower against an upward flow of air. As the melt sprays down through the tower, it breaks into small spherical particles or prills about 1.0–2.4 mm in diameter. These prills are constantly removed from the bottom of the prilling tower, screened and passed to bulk storage.

IFI has pioneered the process by which prilled urea may be fattened to form granular urea. IFI can now make 500 tonnes of prills per day and, using a spray of molten urea and an air cooling system in a rotation drum, convert the prills into 1000 tonnes of granules which are 1.7–4.0 mm diameter in size.

The output of urea is 1000 tonnes per day and is stored in bulk, mainly in a 15 000 tonne store. The urea prills can be exported either directly in bulk or in bags, depending on the market.

The urea bagging operation is completely automated, starting with a roll of printed plastic and finishing with neatly stacked pallets of fertilisers for movement by road and rail.

Urea prills destined for the export market, both bulk and bagged, are distributed from the plant by sea and are loaded on to the ships by an adjustable spiral shiploader.

Bagged and palletised product (1.5 tonne loads) is stored in the open before distribution to the domestic market, for which polythene pillow-type bags will usually be used. The pallets can be moved by either road or rail; by rail the bags will be loaded onto trains of 360-400 tonne capacity.

Summary of the Urea Process

(1) The synthesis of aqueous urea solution.

(2) The recovery and recycling of unconverted reactants.

(3) The concentration of the aqueous urea to a melt.

(4) The prilling of the urea melt.

(5) The fattening of prills to form granules of urea.

Uses of Urea

(1) It is used as a fertiliser (46% N). It is the most concentrated straight fertiliser, and has been particularly popular in the tropics.

(2) It is used to produce urea-formaldehyde resins and to produce melamine for the production of melamine-formaldehyde resins.

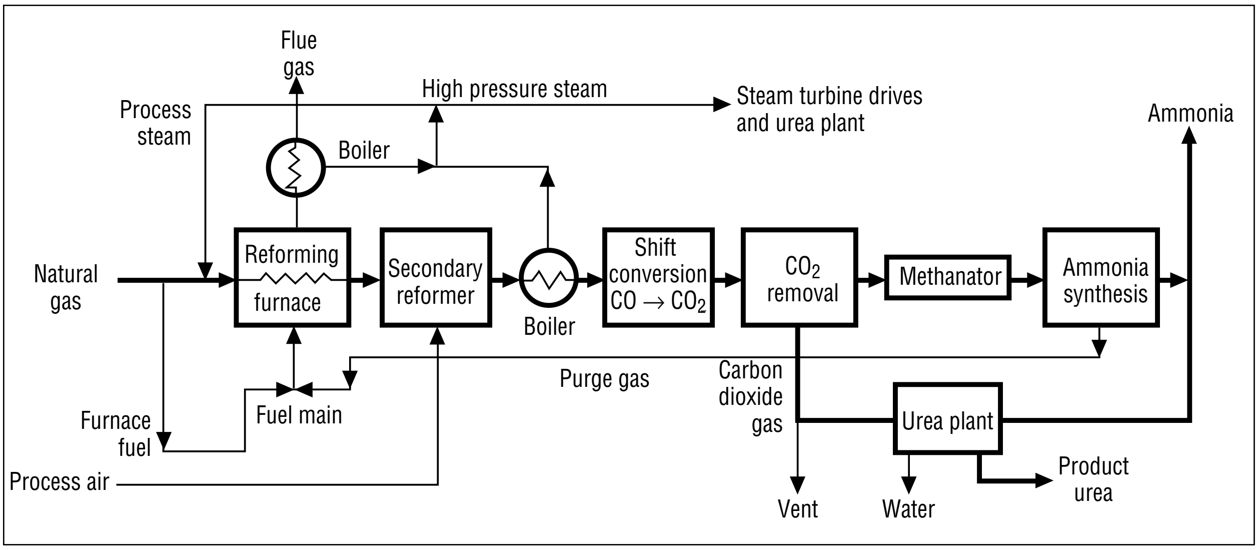

Fig. 2.1 *Block flow diagram of IFI Cobh ammonia–urea plant*

CHAPTER 3

THE MANUFACTURE OF NITRIC ACID AND CALCIUM AMMONIUM NITRATE BY IFI AT ARKLOW

3.1 Introduction

Irish Fertilizer Industries is a joint venture company involving the State Company Nítrigin Éireann Teoranta (NET) and Richardsons Fertilizers Ltd., ICI's Northern Ireland subsidiary. These two companies were combined in 1987 to service the whole of Ireland. The company is the only fertiliser manufacturer in Ireland and operates three plants:

Marino Point, Cork	– Ammonia and Urea
Arklow, Co. Wicklow	– Calcium Ammonium Nitrate
Belfast	– Compound Fertilisers

The Arklow factory is located on a 40 hectare site approximately 3 kilometres from the town of Arklow and has been in operation since 1965. At present 200 people are employed, making the factory the largest employer in the area.

The factory manufactures 565 000 tonnes per annum of calcium ammonium nitrate (CAN) in two CAN plants and two nitric acid plants. Three ingredients are necessary to manufacture CAN: ammonia, nitric acid and limestone. The ammonia is transported by rail to Arklow from Cobh in pressurised tankers. The train of six tankers runs two or three times per day with a cargo of 250 tonnes. The ammonia is stored in two pressurised spheres of capacity 1000 tonnes and 2000 tonnes, respectively. The intermediate, nitric acid, is made by combustion of ammonia and absorption of the resulting gas to make 57% acid. CAN is made by neutralising the acid with ammonia, adding limestone or dolomite and forming the end-product either by the granulation or the prilling process.

The product is bagged in 50 kg bags, palletised in two tonne units and shrink-wrapped in a fully automatic bagging plant which has a capacity of 120 tonnes per hour. There is also a big-bag filling unit which can handle 0.5 tonne and 1 tonne big bags and the new IFI Four-Pak of 4 × 0.5 tonne bags on a pallet. CAN is supplied in bulk to blenders and exported in bulk through the port of Arklow to most of the North-Western European countries.

3.2 Feedstock

To manufacture calcium ammonium nitrate (CAN) three ingredients are necessary; ammonia which comes from IFI, Cobh by direct train link, nitric acid which is produced in the plant itself, and dolomite/limestone which comes from Kilkenny.

3.3 Rates and Conditions of Reactions

There are a number of different chemical reactions which have to be considered in this section. The first three are concerned with the manufacture of nitric acid and are:

(A) Oxidation of ammonia to nitrogen oxide

$$4NH_3(g) + 5O_2(g) \xrightarrow[900\ ^\circ C]{Pt/Rh} 4NO + 6H_2O$$

$$\Delta H = -900 \text{ kJ mol}^{-1}$$

(B) Oxidation of nitrogen oxide to nitrogen dioxide

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

$$\Delta H = -115 \text{ kJ mol}^{-1}$$

(C) Absorption of nitrogen dioxide in water

$$3NO_2(g) + H_2O \longrightarrow 2HNO_3(aq) + NO(g)$$

$$\Delta H = -16 \text{ kJ mol}^{-1}$$

Reaction (A) is very rapid and gives a conversion of 95-96% when an ammonia/air mixture containing 10.2% ammonia is passed over the Pt/Rh catalyst. The excess air reduces the risk of explosion and limits the temperature to between 800 °C and 900 °C. A maximum of 11.5% NH_3 by volume in air is considered safe at pressures up to 20 atm.

However, it is not possible to operate at this pressure, because of the high temperature which develops, not only on the catalyst itself, but on vessels below the burner chamber. Construction materials limit the catalyst operating temperature to around 950 °C.

For the oxidation of ammonia (A) a pressure of 3–4 atm is used at the burner in the Arklow plant.

The temperature and contact times must be just right to give good yields – if contact time is too high or too low, side reactions can occur which reduce the yields. For example it is possible for NH_3 to react as follows.

$$4NH_3 + 3O_2 \longrightarrow 2N_2 + 6H_2O$$

Here the ammonia is wasted. Certain impurities in the catalyst, particularly oxides of the transition metals, could encourage this reaction, and so must be avoided.

To ensure that reaction (A) takes place as fully as possible, the following measures are taken.

(1) Absolutely pure ammonia and air (the ammonia and air are filtered to remove any oily impurities) are used.

(2) The combustion temperature is controlled between 880 °C and 890 °C.

(3) A pure specified catalyst of 95% Pt and 5% Rh woven in a fine mesh gauze is used. The platinum gauze, which may be obtained from PGP in Shannon, is enriched with 5% rhodium to give it extra strength.

The Pt/Rh catalyst is prepared under conditions that ensure a close control on impurity limits, particularly for those contaminants which act as catalyst poisons. The total content of specific impurities should not exceed 100 ppm.

Catalyst gauzes are now generally replaced every sixteen weeks.

In reaction (B) the nitrogen oxide reacts with the oxygen remaining in the air after the ammonia combustion. This reaction occurs as the gases pass from the burner through the boiler and heat exchangers to the cooler condenser. By the time the gases reach the cooler condenser about half the nitrogen oxide, NO, has been converted to nitrogen dioxide, NO_2.

In the cooler condenser, the water which was formed in (A) condenses and absorbs some of the nitrogen dioxide which has been formed up to that point to produce nitric acid – reaction (C).

The acid formed here is dilute (about 35%). It is pumped into the absorption tower at the point where the acid is at the same concentration.

It can be seen that more nitrogen oxide is formed by reaction (C) – one mole for every three moles of nitrogen dioxide absorbed. Nitrogen oxide cannot be absorbed, it must be converted to nitrogen dioxide first. Extra oxygen is provided by the introduction of secondary air after the gas cooler. The remaining nitrogen oxide is then converted to nitrogen dioxide. This takes place at the bottom of the primary tower. The nitrogen dioxide is then absorbed in water to form nitric acid. As before, some nitrogen oxide is formed in the absorption process. As the gases pass through the tower, the oxidation of nitrogen oxide and the absorption of nitrogen dioxide to form nitric acid and a smaller amount of nitrogen oxide is repeated. It is vital to have sufficient oxygen remaining in the gas for the successive oxidations.

The gases leaving the top of the secondary tower should therefore contain at least 3% oxygen.

The absorption efficiency is normally 99.9%. The amount of water used is controlled to give a product acid strength of 55 to 58%.

Both the oxidation and absorption reactions are made more efficient by keeping the temperature as low as possible and the pressure as high as possible. The gas temperature at the inlet to the primary tower should not exceed 50 ^{o}C, while the pressure will be between 9 and 10 atm.

Manufacture of Calcium Ammonium Nitrate

The factory manufactures 565 000 tonnes per annum of calcium ammonium nitrate in two CAN plants – a granulation plant and a prilling plant.

Both plants can be considered as two sections, a dry section and a wet section. The wet section produces a concentrated aqueous solution of ammonium nitrate by neutralising 56% w/w nitric acid with gaseous ammonia in a stainless steel column according to the following reaction:

$$\underset{\text{gas}}{NH_3} + \underset{\text{liquid}}{HNO_3} \longrightarrow NH_4NO_3$$

$$\Delta H = -92 \text{ kJ mol}^{-1}$$

The heat evolved from the reaction is used to concentrate the ammonium nitrate by evaporation of water which originated from the nitric acid to give a solution containing 96%–99% ammonium nitrate. The solution is concentrated by heating with steam in a heat exchanger operating at reduced pressure.

For granulation, 96% ammonium nitrate is mixed with ground limestone and recycled product in a granulator in the correct ratio to yield a product containing 27.5% N. The granulator causes agitation of the mixture and the formation of imperfectly shaped granules.

These are then fed to a rotary dryer for drying and conditioning of the granules by heating in a current of hot air flowing co-currently with the product. After drying, the product is screened to obtain the required product size. The oversize product is crushed and mixed with the undersize product which is returned as recycle to the mixing vessel.

The product, size 2–4 mm, is cooled in a fluid bed cooler to approximately 35–40 ºC and is then coated with oil and china clay before passing into storage.

In the prilling plant the ammonium nitrate is concentrated to 99.8% by extra evaporation. The concentrated solution is then mixed with limestone and recycled product in a mixing vessel prior to prilling. Again, the ratio of limestone added is such that the finished product contains 27.5% nitrogen.

The prilling process consists of spraying the ammonium nitrate/limestone mixture from nozzles located in the top of the prilling tower. As the droplets fall through the tower, from a height of approximately 50 metres, they are cooled by a stream of counter-current ambient air, which causes the droplets to solidify into typically spherical particles.

The prills collected at the base of the tower are then screened and cooled in a manner similar to the granular product and are of size 2–4 mm at a temperature of 30 °C to 40 °C. These are also coated with oil and china clay for protection and to ensure good handling characteristics.

Prilling is a general method and it can be used for compound fertilisers. It is also used in Marino Point in the manufacture of urea.

The percentage of nitrogen in CAN made at Arklow over the years has varied. Initially, it was 20.5% N. It has increased over the years through 23% to 26% to its current 27.5% N.

The product is bagged in 50 kg polythene sacks and palleted in 8 layers of 5 bags to give a 2 tonne pallet. The pallet is then shrink-wrapped with a white plastic hood, which reflects the heat from the sun and prevents thermal degradation of the product. 500 kg bags are now also used to transport the fertiliser. The overall processes are summarised in Fig. 3.1 – Fig. 3.4, pp. 19–21.

3.4 Product Yield

To determine the yield of nitric acid from the process described above, we need to take into account the exact percentage conversion of ammonia to nitrogen oxide in (A) above, say 95%, and the percentage absorption of nitrogen dioxide to nitric acid in (C), say 99.9%. To calculate the overall yield here we must multiply the yields from each stage, i.e. overall yield = 95 × 0.999 = 94.9%.

Therefore, it can be concluded that the process is very efficient with very little wastage of reactants and very little formation of co-products or possible loss or NO_x emissions to the atmosphere.

To calculate the overall yield of CAN from the process (or rather to state the overall efficiency of the plant), we must consider the percentage conversion of nitric acid and ammonia to ammonium nitrate by neutralisation.

This is a highly efficient reaction, and therefore final yields of CAN from ammonia at the end of the process will generally be quite high – in the region of 94%.

3.5 Co-products

There are no co-products formed.

3.6 Waste Disposal and Effluent Control

The two major offending waste materials resulting from the Arklow plant are the nitrogen oxides released into the atmosphere and any liquid effluents containing ammonia and nitrates in the condensates.

Since NO does not react with water, it follows from (C) that, however large an absorption system is, it cannot be 100% efficient and some NO will be lost from it.

Older nitric acid plants, and indeed Arklow in the past, would have been responsible for emitting waste gases containing 2000 – 3000 ppm of NO_x gases clearly visible as brown plumes from the stacks. However, the Arklow plant has been able to reduce these levels of NO_x greatly to well below 200 ppm by the replacement of older plant and equipment with more modern plant that operates on the best available technology.

In addition, very efficient and sophisticated equipment is now in operation to measure all gaseous emissions from the stacks and at ground level.

In accordance with its air pollution licence, IFI has installed analysers to continuously measure the concentration of oxides of nitrogen (NO_X) in the exhaust gas from the nitrogen acid production plants and also at ground level.

The analysis is based on the chemiluminescence reaction between nitrogen oxide (NO) and ozone (O_3) as follows:

$$NO + O_3 \longrightarrow NO_2^* + O_2$$

$$NO_2^* \longrightarrow NO_2 + hf$$

The NO_2 produced in the reaction is in an electronically excited state which quickly decays, giving a light output *hf* which is proportional to the NO concentration.

Similarly, automatic analysers are installed in the final effluent discharge for the continuous measurement of levels of ammonia, nitrates, pH, suspended solids and dissolved solids. This is in accordance with the effluent licence.

The analysis of ammonia and nitrate is based on ion-selective and gas-sensing probe techniques. Analysis of total dissolved solids is based on a measure of the electrical conductivity using a conductivity probe.

The pH is measured using a typical pH electrode housed in a continuous flow cell. The measurement of turbidity gives a value for the quantity of suspended solids in the effluent. Turbidity measurement is based on the absorption of light which is focused through a sample stream. The absorption of light is proportional to the quantity of suspended solids present in the sample.

The plant has just introduced the Ammonia Recovery Unit which strips ammonia from the process condensate originating in the wet section of the two CAN plants. These ammonia-rich condensates enter at the top of the upper section of the tower and 99% of the ammonia is recovered by a counter-current stream of air, Fig. 3.5, p. 21. The ‘clean’ condensate at the bottom of this section is sent to the nitric acid plants for re-use as process water in the absorption towers. However, the air which exits at the top of the tower is now laden with ammonia, so it is recirculated to the lower section of the tower where it is scrubbed by contact with nitric acid. Thus, all of the ammonia in the air forms a weak solution of ammonium nitrate, leaving the cleaned air available once more for its duty in the upper section of the tower. The ammonium nitrate solution is sent to the CAN plants for recycling into the process. In this way, this process generates no problem wastes to the air or water media. By tackling the problem streams at source this system is a much more effective way of reducing environmental impacts than by an end-of-pipe treatment process for the total site effluent.

3.7 Quality Control

The laboratory at Arklow operates continuously, providing analysis of feedstock and products. Samples are taken at various stages of the production processes to ensure products meet the required specification while operating at maximum efficiency.

The main analytical requirements for the fertiliser product are the nitrogen content and size analysis. It is important that these values meet the specification and provide the farmer with a free-flowing product with good spreading characteristics at the correct nutrient level.

The gas streams at the nitric acid plants are analysed to determine the combustion and absorption efficiencies.

The site operates boilers and cooling towers which require comprehensive water analysis to determine the necessary chemical treatment.

3.8 Safety

Safety in operation is of vital importance to IFI, whose policy it is to train their staff to a high degree of Safety Awareness. The highest standards are inherent in all aspects of their work.

Maintenance arrangements and operating and emergency procedures are continually under review to ensure best practice. Because of the large quantities of ammonia stored on-site for use in the manufacture of nitric acid and fertiliser, the plant comes under the European Communities (Major Accident Hazards of Certain Industrial Activities) Regulations 1986. These required the company to submit to the Health and Safety Authority a SAFETY CASE, i.e. a comprehensive document, outlining their operation, with details of RISK ASSESSMENT and arrangements for management of SAFETY.

Other legislation under which the factory operates is the SAFETY, HEALTH AND WELFARE AT WORK ACT 1989, the SAFETY, HEALTH AND WELFARE AT WORK (GENERAL APPLICATION) REGULATIONS 1993, the FACTORIES ACT 1955 and a host of regulations made under the acts.

3.9 Economics of Fertiliser Manufacture

The manufacture of nitrogenous fertiliser is highly capital intensive and, assuming equal cost of feedstock, the technical design of the plant is the most important factor in determining the cost of the product. For existing plants certain modifications can be implemented economically to improve performance, e.g. for nitric acid plants debottlenecking to increase plant output and modifications to the heat exchanger train to improve energy recovery.

For an operating plant the various technical factors affecting the economics of nitric acid production are shown in the extract from a Fertilizer Society paper given in the Appendix on p. 22.

For a fertiliser factory making nitric acid and CAN the cost breakdown for one tonne of product, including bagging and handling, is approximately as follows.

(1)	Ammonia and other direct materials	70%.
(2)	Labour – operations, maintenance, site management, etc.	20%.
(3)	Maintenance materials/services plus factory overheads	10%.

In addition to improving cost efficiency by plant modifications and additions, considerable improvements have been achieved in recent years by the automation of packaging and the application of advanced process control technology.

3.10 Costs

The main elements in the manufacturing cost of nitric acid are the cost of ammonia feedstock, the cost of the catalyst, the cost of utilities, power and steam, and the price of stainless steel. The first three factors directly affect the operating cost, while the fourth affects the initial capital investment.

The cost of dolomite/limestone has also to be taken into consideration for the production of CAN.

Generally, in order to minimise the cost per tonne of product, efforts have to be made to maximise the annual rate of production while minimising the cost of materials.

The maximum rate of nitric acid production is set by the amount of air which can be supplied; it is assumed that the air compressor capacity is the ultimate limitation. Therefore, for maximum utilisation of this unit, one requires infrequent gauze changes and so the minimum lost time in shutdown. Also for maximum rate, one requires the highest ammonia concentration practicable in the converter and the minimum air to the absorber.

Obtaining the cost per tonne of product is not straightforward, because so many operational factors interact. For example, extending the period between gauze changes reduces the conversion efficiency. Steam/power costs are improved by a higher gauze temperature. However, this increases the loss of catalyst and reduces the length of time between shutdowns.

Considerable savings in the cost of heating the burner can be made because of the exothermic nature of the three reactions in the nitric acid process. With the specified ratio of ammonia to air in the burner the heat released by the combustion of ammonia maintains the burner temperature at 880 °C to 890 °C. The heat is recovered in the waste-heat boiler to generate steam and the steam turbine drives the air compressor.

Heat released by the oxidation and absorption reactions should also be removed quickly, as both reactions are more efficient at lower temperatures. The heat is removed in the various gas coolers and by the cooling coils in the absorption towers.

3.11 Site Location

The site location for the Arklow plant has many advantages for a variety of reasons. Among these are the convenient and close access to the Avoca river for fresh water, the local harbour, the direct rail link into the plant and the improving road network in the area.

Another reason for the original siting in 1965 of the plant in Arklow was the close availability of the raw material, pyrites (FeS_2), which was a by-product from the nearby Avoca mines. This was used to make sulphuric acid and ammonium sulphate in the plant but was discontinued in 1982 when the mines closed down.

3.12 Construction Materials for the Plant

Specialised stainless steel constitutes most of the vital material used in the construction of this plant. This is due to the very corrosive and reactive nature of the reactants and products being contained here.

ARKLOW FACTORY

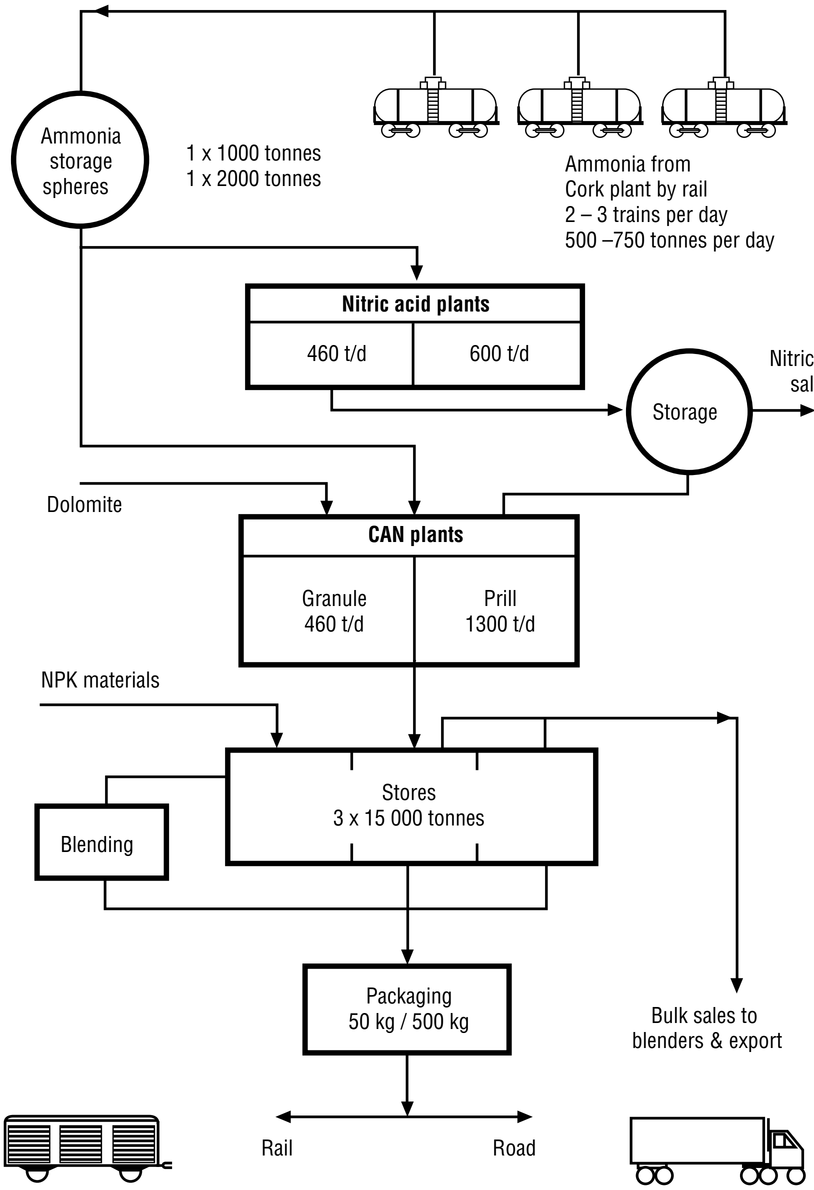

Fig. 3.1

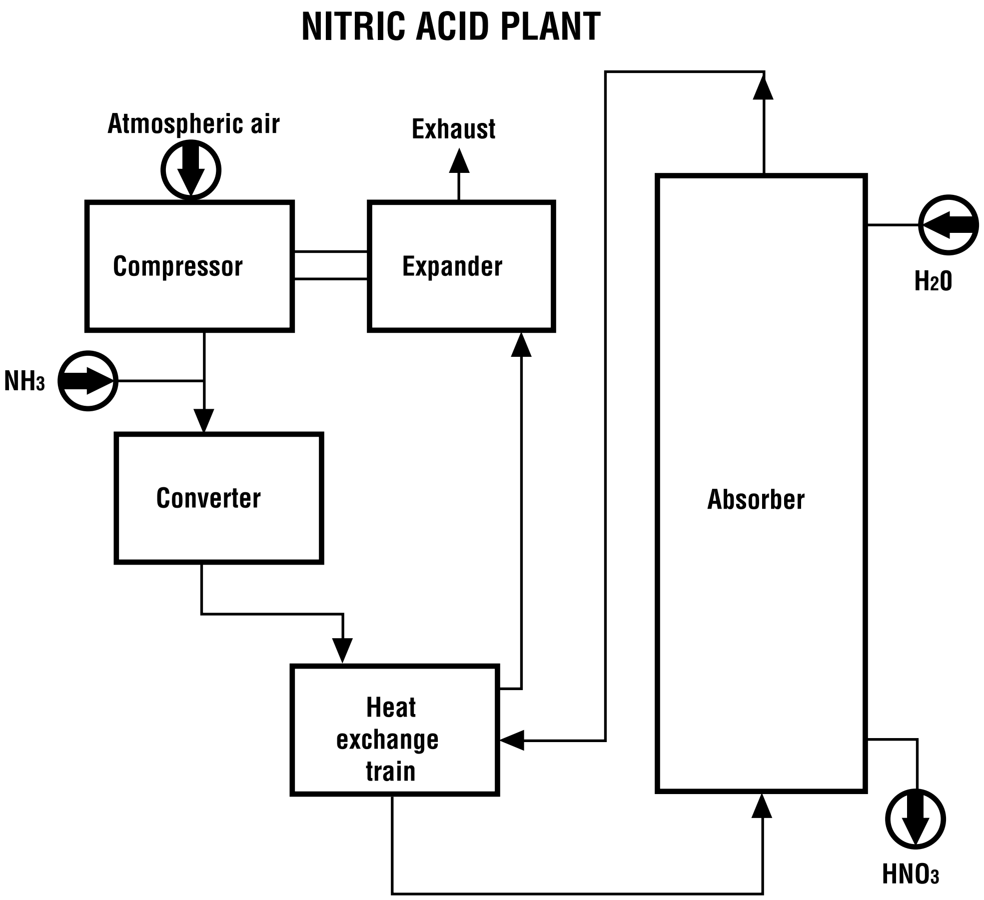
NITRIC ACID PLANT
Atmospheric air
Exhaust
Compressor
Expander
NH_3
H_2O
Converter
Absorber
Heat exchange train
HNO_3

Fig. 3.2

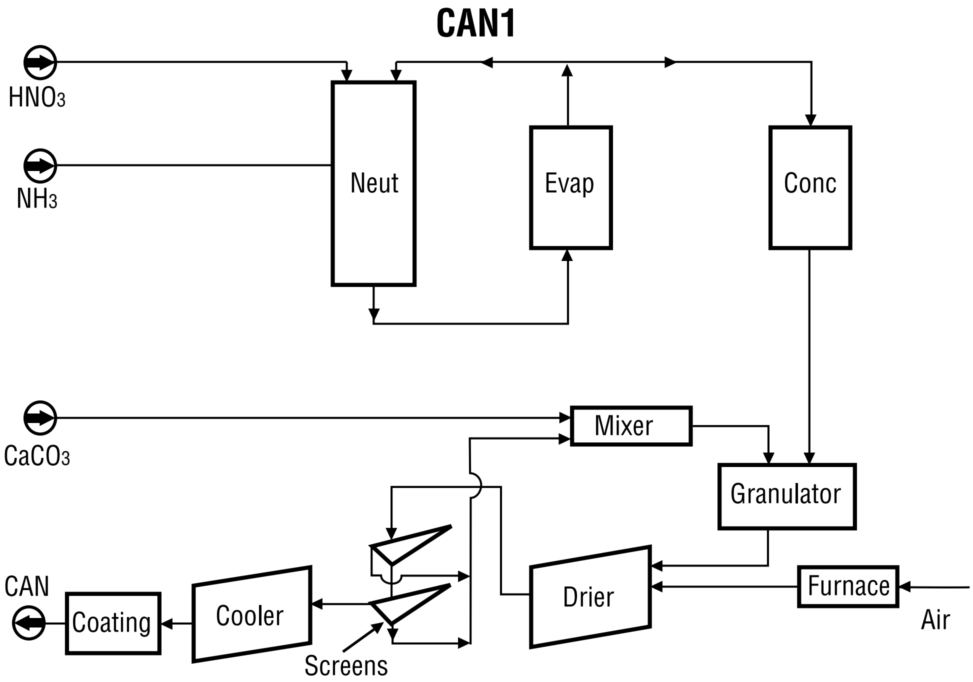
CAN1
HNO_3
NH_3
Neut
Evap
Conc
$CaCO_3$
Mixer
Granulator
CAN
Coating
Cooler
Screens
Drier
Furnace
Air

Fig. 3.3

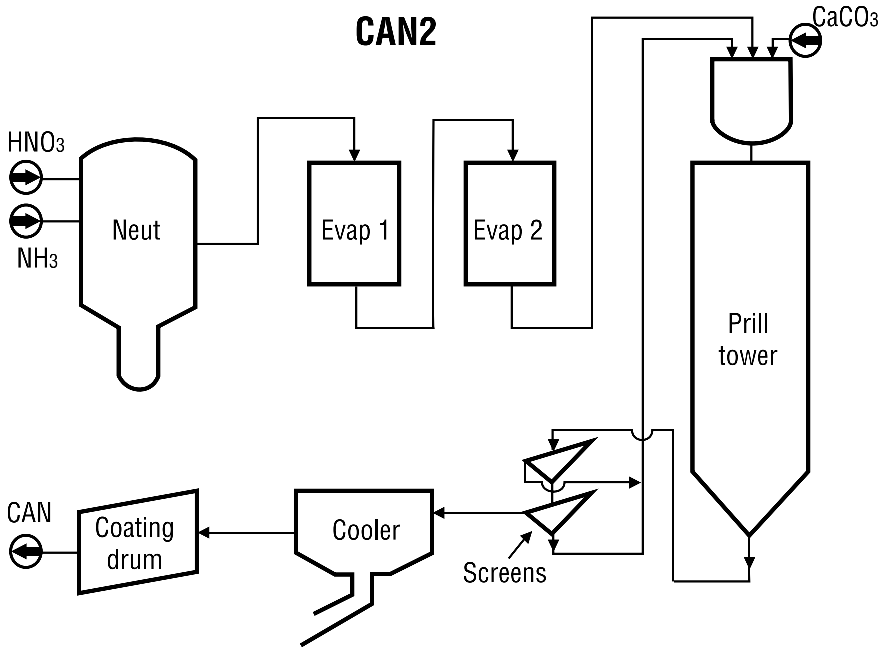

Fig. 3.4

THE AMMONIA RECOVERY UNIT

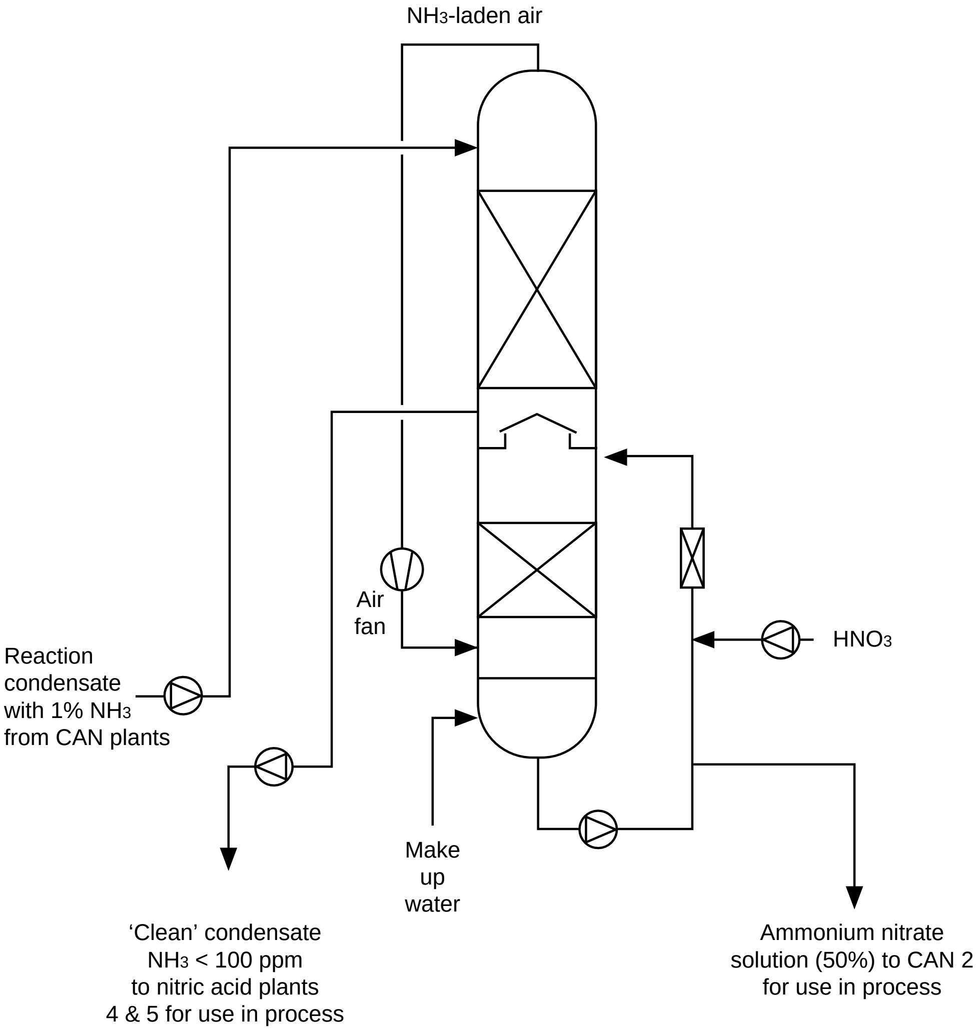

Fig. 3.5

APPENDIX ECONOMIC OPERATION*

Economic Operation

A company operating a number of plants which are essentially variations of the same basic flowsheet will find that different plants have good and bad features. The basic question is how to bring such plants to operate to give the best profits giving due regard to the variables of ammonia price, platinum price and market demand for the product. Our company has done a lot of work developing its nitric acid plants towards an optimum economic performance. From the technical point of view this means concentrating on those factors which affect the operation of the two main stages of the process, the converter and the absorber.

Fig. I, p. 23 illustrates how technical factors are related to economic factors. If one is looking to minimise cost/tonne of the product this will be done by maximising the annual rate of production and minimising the cost of materials. The maximum rate of production of nitric acid on a given plant is set by the amount of air which can be supplied; it is assumed in Fig. I that the air compressor capacity is the ultimate limitation. The annual rate factor can then be broken down into the utilisation of the unit and the instantaneous rate: likewise the cost of materials and utilities consists principally of the cost of ammonia, platinum, power and steam.

These are broken down further in Fig. I into operational aspects of the absorber and converter. For example, for maximum utilisation one requires infrequent gauze changes and the minimum lost time at the shutdown. For maximum rate one requires the highest ammonia concentration practicable in the converter and the minimum bleach air to the absorber, – and so on. Factors not associated with the operation of the converter and absorber have been omitted: for instance whilst utilisation is obviously dependent on the number of times a year a plant has to shut down for a gauze change, it is also very much dependent on the mechanical integrity of the plant and the standard of maintenance, etc., but these have been excluded.

Obtaining the cost/tonne of acid is not straightforward because these operational factors interact. For example, extending the period between gauze changes reduces the conversion efficiency. Minimising Pt losses by employing a recovery system adversely affects both the production rate and the absorber efficiency. The conversion efficiency and steam/power costs are improved by a higher gauze temperature – but this increases the Pt loss and reduces the campaign length. Higher bleach air rates improve absorption but reduce rate, and so on.

The minimum cost per tonne occurs when all these conflicting factors are evaluated and given their correct economic weighting, and models have been developed to do this, offline. Three technical models are used for ammonia oxidation, Pt recovery and nitrous gas absorption respectively, and an economic optimisation is performed as a separate model linking the three.

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*Extract from paper by Bradley J. K. and Drake G., *Proc. Fertilizer Society, Oct. 1981.*

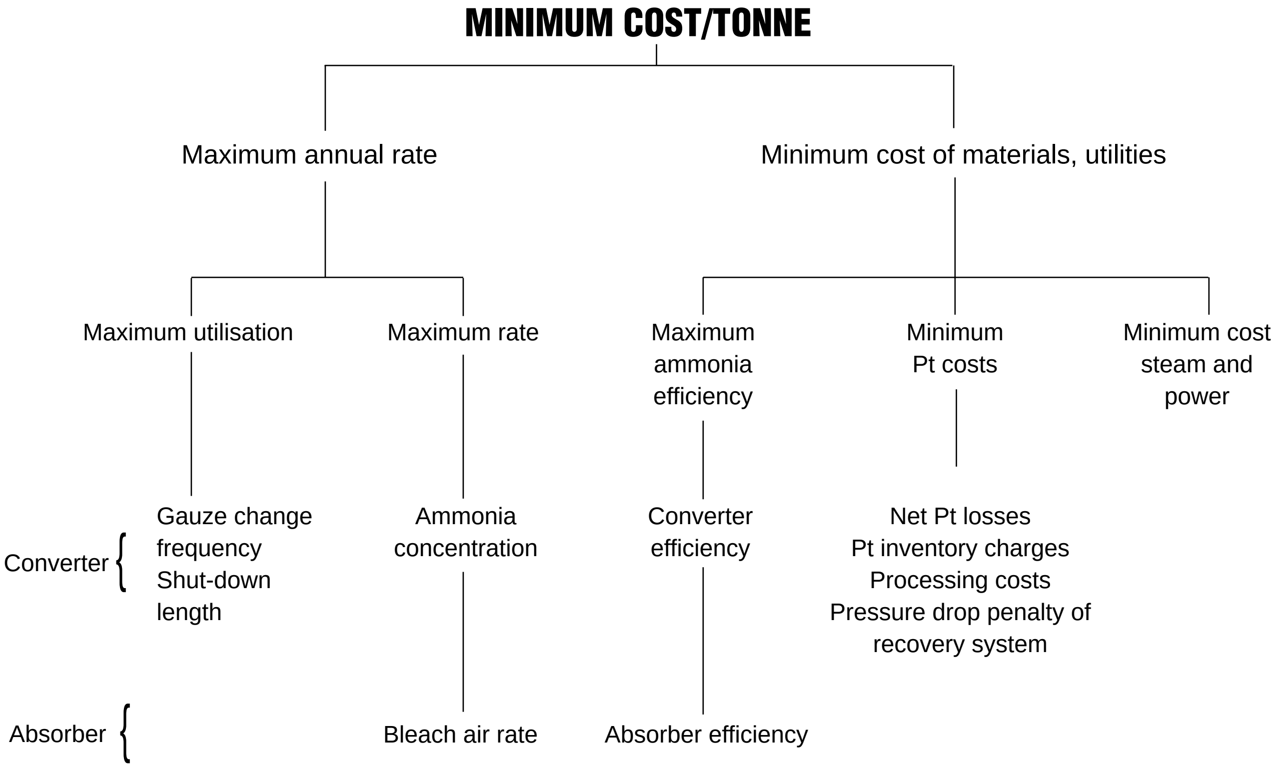

Fig. I *Technical factors affecting the economics of nitric acid production*

CHAPTER 4

MANUFACTURE OF MAGNESIUM OXIDE BY PREMIER PERICLASE AT DROGHEDA, CO. LOUTH

4.1 Introduction

Chemically, periclase is the compound magnesium oxide. The magnesium oxide product manufactured by Premier Periclase has two properties which make it useful.

(a) It has a very high melting point. Pure periclase melts at a temperature of 2800 °C.

(b) Pure periclase, hard burned (see section 4.4) is chemically unreactive.

These two properties combine to make periclase the ideal material for lining high-temperature furnaces which are used in the steel, cement, glass and other high-temperature industries.

Non-metallic materials for use at high temperatures (such as periclase) are called refractories.

4.2 History

The first recorded use of seawater for the production of magnesia was at a place called Sète on the Mediterranean coast of France in 1885. Lime was also used in the precipitation but it was not a commercial process.

In 1935, a company called the Marine Chemical Company, based near San Francisco, started producing magnesium hydroxide (precipitate) from seawater using oyster shells as a source of lime. Their process stopped at the precipitate stage with no effort being made to further process the magnesium hydroxide to refractory-grade periclase. In 1936/37 a company called Steetley at Hartlepool on the North East coast of England started the first full-scale commercial process for the production of periclase from seawater. The plant at that stage had an annual production of 10 000 tonnes per annum.

The industry received a large boost during the Second World War, when the demand for periclase increased at the same time as supplies of natural periclase/magnesite from Austria became unavailable. By the early 1970s, there were 27 factories using seawater or brine (a concentrated salt water found underground) to produce more than 3.73 million tonnes of magnesia/periclase per annum.

By 1985, four new factories, including Premier Periclase had come into operation. However, seven of those operating in the early 1970s had closed down. These closures were for economic rather than technical reasons, confirming that the periclase business is not an easy one. During the early 1970s, Irish Cement decided to close down its oldest cement plant at Drogheda and replace it with a new dry-process plant at its nearby Platin factory. A task force was set up to find an alternative industry to use the staff and site equipment that were about to become redundant. The production of magnesia from seawater was an obvious choice, especially as the Drogheda plant lay only 3 miles from the sea, on the tidal Boyne, and also contained, amongst other essential equipment, three large rotary kilns (3.6 m × 160 m), ideal for the process.

A decision was therefore made to undertake a feasibility study for a 100 000 tonne (approx.) per year plant and a pilot plant was set up. Work on the site started in September 1977, quarry operations (for limestone) started in early 1979 and lime burning in May 1979. The furnaces and kilns were started up towards the end of 1979, building up to full production at the end of 1980. After a difficult start due to international recession, full production capacity was reached in 1983 and has been maintained ever since.

An otherwise obsolete plant has been transformed into an efficient and highly productive industry, successfully utilising valuable capital plant and a trained labour force.

The high quality product is exported to customers generally located in the major steel-making countries. The periclase product is then made into refractory bricks by these companies.

4.3 Feedstock

The main feedstocks for the process are seawater and limestone.

Seawater is taken from the Boyne estuary for approximately eight hours per day, around high tides, and stored in a large reservoir. About 150 000 m^3 of seawater are used each day and are pumped through large underground pipelines to the magnesia plant, four miles upstream.

Limestone is quarried near Drogheda at Mullaghcrone, Co. Meath. This limestone is very pure calcium carbonate (over 98%) and 300 000 tonnes of crushed, washed and graded limestone are produced annually. Approximately 1000 tonnes of limestone are required each day, which necessitates 50 truckloads being brought from the quarry to the plant per day. Up to six million litres of fresh water per day are also required for washing and slaking the calcium oxide (‘burned lime’).

Sulphuric acid is also required for degassing both the seawater and the fresh water.

4.4 Rates and Conditions of Reactions

Theoretically, the chemistry of the process is quite simple; however, complex chemical engineering is required to carry out the process in a way that produces a product of the desired purity that settles, washes and filters easily.

The chemistry of the process to produce pure magnesium oxide (magnesia) from the seawater can be divided up into 4 main reactions as follows.

(1) Limestone calcination

$$\underset{\text{limestone}}{CaCO_3(s)} \xrightarrow[1450\ ^{o}C]{\text{heat}} \underset{\text{lime}}{CaO\ (s)} + CO_2(g) \uparrow$$

(2) Lime slaking

$$CaO(s) + H_2O \longrightarrow \underset{\text{slaked lime slurry}}{Ca(OH)_2\ (aq)}$$

(3) Seawater reaction to produce magnesium hydroxide

$$\underset{\text{from seawater}}{MgCl_2\ (aq)} + \underset{\text{slaked lime}}{Ca(OH)_2(aq)} \longrightarrow$$

$$\underset{\substack{\text{magnesium}\\ \text{hydroxide}}}{Mg(OH)_2(s)} + CaCl_2\ (aq)$$

(4) Magnesium calcination

$$Mg(OH)_2(s) \xrightarrow[900\text{–}950\ ^\circ C]{\text{heat}} \underset{\text{magnesia}}{MgO\ (s)} + H_2O\ (g)$$

In **Reaction 1** limestone is burned and calcined in a rotary kiln at 1450 °C to give extremely pure calcium oxide (lime). Pure limestone contains 44% carbon dioxide and 56% lime. In order to have the highest degree of purity in the final product, it is essential to eliminate as much of the carbon dioxide as possible. Any carbon dioxide not removed goes to the wet end of the plant as limestone. It does not react with seawater but settles out on the precipitate as an undesirable impurity.

The lime is stored in large concrete silos to minimise recarbonation.

Reaction 2 shows the slaking of the lime which produces a slurry of ‘milk of lime’ – calcium hydroxide. The fresh water necessary to do this is decarbonated by adding sulphuric acid to lower the pH to around 4. The sulphuric acid dissociates any $CaCO_3$ in the water to calcium sulphate, water and carbon dioxide gas. The calcium sulphate is soluble in water and flows back into the sea. The acidified water is then passed downwards through a tower against a rising current of air which strips off carbon dioxide.

A similar process of acidification and aeration to remove dissolved carbon dioxide is also carried out on the seawater. The decarbonated seawater is reacted with the slaked lime according to **Reaction 3** in a large, circular, 30.5 metre diameter, concrete reactor. The conditions for this reaction must be carefully controlled to produce coarse crystals of magnesium hydroxide which will settle and filter more easily. These conditions are (a) to dilute the incoming seawater with spent seawater (minus its magnesium content), and (b) to seed the seawater with a heavy slurry of magnesium hydroxide from the primary thickener. The combination of (a) and (b) produces large particles of magnesium hydroxide which settle and filter well. Fine precipitates are usually gelatinous and cannot be handled easily.

From the reactor the precipitate and used seawater overflow into two 99 m diameter primary thickener tanks. The purpose of these primary thickeners is to separate the precipitate from the spent seawater. They allow the precipitate to settle to the bottom of the tanks with the spent seawater overflowing at the top. The settling is helped by the addition of a flocculant which causes the precipitate crystals to stick together and thereby settle faster.

Part of the slurry goes back to the reactor and part goes on to two secondary thickeners, where the precipitate is further thickened before filtration and washing.

The precipitate is now filtered and washed before being pumped to the multi-hearth furnaces where **Reaction 4** – the final stage, the production of magnesia – is carried out.

The first step in this process is filtration. This is carried out on three large drum filters and two belt press filters. These filters remove water from the precipitate. At best the precipitate contains about 20% solids and 80% water. The ‘cake’ leaving the drum filters contains 50–55% solids and is fed to the belt press filters. The final ‘cake’ leaving here contains about 70% solids, i.e. 30% water.

A second feature of this filter operation is that the cake is washed with clean, fresh water, resulting in improved final product purity. From the filtration stage the cake goes to one of two multi-hearth furnaces which operate in parallel.

The furnaces have three functions:

(a) to remove the rest of the water associated with the precipitate;

(b) to convert the precipitate, which is magnesium hydroxide, into magnesium oxide (caustic magnesia);

(c) to produce this caustic magnesia with the required fineness for briquetting prior to sintering in the periclase kiln.

Each furnace has 16 hearths or floors – one on top of the other. In the top 5–7 hearths, the remaining 45 to 50% of excess water is boiled off.

In the middle 5 or 6 hearths, the now dry powdery precipitate is heated further to a maximum temperature of 900 °C. This brings about **Reaction 4** which changes the magnesium hydroxide precipitate to caustic magnesium oxide.

In the bottom 3 or 4 hearths, the caustic magnesium oxide is cooled down, finally leaving the hearths at a temperature of 300 ^{o}C to 350 ^{o}C. Caustic magnesium oxide is a very fine powder and can be called ‘chemical grade magnesium oxide’.

This fine powder is now converted into stick-shaped pellets by being pressed a number of times through five briquetting machines. Pressures of around 17 MPa are applied to the machine rollers to form sound briquettes of good density. The pelletised caustic magnesium oxide with a density of about 2.0 g cm^{-3} is fed into one of two periclase shaft kilns. In these kilns the pellets are heated to as high a temperature as possible, which is normally 2200 ^{o}C to 2400 ^{o}C. Due to the intense heat the magnesium oxide crystallites grow and the pellets shrink, causing the density to increase beyond 3.4 g cm^{-3}.

In brief, the kilns transform reactive low density caustic MgO into unreactive high density sintered MgO, otherwise known as ‘periclase’.

The sintered pellets are stored in a building capable of holding up to 20 000 tonnes, ready for shipment from a wharf on the Boyne. The product is a buff-brown colour and is a chemically unreactive granular material.

4.5 Product Yield

Rather than concentrating on product yield, perhaps it is more appropriate to consider percentage purity or impurity of the product. The main factors influencing purity of the finished product are the purity of the raw materials, particularly limestone. Limestone contains impurities such as silica (SiO_2), usually in the form of quartz, and also small amounts of iron oxide (Fe_2O_3) and aluminium oxide (Al_2O_3).

Another factor influencing final product purity is the extent to which underliming or overliming takes place in the reaction:

$$Ca(OH)_2 + MgCl_2 \longrightarrow Mg(OH)_2 + CaCl_2$$

In the case of underliming, where less $Ca(OH)_2$ is supplied giving a resultant pH of around 10, then a very pure product (98.5% MgO containing 0.3% B_2O_3) is obtained.

B_2O_3 is an impurity which reduces the melting point of the periclase, thus reducing the performance/quality of the final product. Hence, as low a level as possible of B_2O_3 is desired.

With overliming, where extra $Ca(OH)_2$ is supplied giving a resultant pH of about 12, a pure product (97.5% MgO) is also obtained but, due to the higher pH, it contains only about 0.06% B_2O_3. After sintering, the B_2O_3 level is reduced to 0.01% (by volatilisation of the boron) which gives a higher quality product than in the case of underliming. A 10% overliming factor will generally produce this preferred product.

Yield

Seawater yields only about 2 g of magnesia (as MgO) in every litre. Hence, to meet the company’s daily production requirement of 300 tonnes, 150 million litres of seawater has to be available.

(Incidentally, the salt present in the highest concentration in seawater is common table salt, sodium chloride, at about 30 g per litre.)

4.6 Co-Products

While no significant or commercial co-products are generated during the process of manufacturing periclase, extensive research and development efforts are continually being made to establish magnesia-based secondary products. Magnesia is already used in a wide range of pharmaceutical, animal feed and miscellaneous industries.

4.7 Environmental Control

Extensive environmental monitoring is carried out as part of the overall process control, e.g. stack emission monitoring for dust and sulphur; quarry blast vibration measurements; effluent pH and suspended solids monitoring; factory and quarry noise monitoring; etc. The high-temperature exhaust gases are passed through electrostatic precipitators (EPs) and scrubber systems which remove the dust and sulphur produced during the burning processes. The electrostatic precipitators work by electrostatically charging the dust particles which are then attracted to, and collected on, oppositely charged plates. This fine dust material can be recovered and recycled into the process.

The scrubber system works by spraying the dust particles contained in the exhaust gas with a fine water spray and then collecting the magnesia in slurry form.

All spent seawater from the process goes to the effluent clarifier where fresh seawater is used to neutralise the excess lime. A floating bed of precipitate is used as the final filter before returning the spent seawater back to the Irish Sea. These processes reduce the pH and suspended solids of the spent seawater which now contains calcium chloride instead of magnesium chloride, (Reaction 3). The spent seawater is pumped out to sea 1500 m from the shore.

4.8 Quality Assurance

In order to ensure control over every step in the process, from seawater to sintered magnesia, a detailed chemical analysis is carried out by the laboratory at every stage in the process marked L on the accompanying flow sheet, Fig. 4.1, p. 31. A team of chemists and technicians work in shifts to carry out these wide-ranging analyses every hour. In this way, if any problem arises, it can quickly be detected and rectified.

The carbonate (as measured by the amount of CO_2 produced) content of both the seawater, fresh water and lime samples must be carefully checked to ensure that calcium is not precipitated out as calcium carbonate and carried through with the magnesium hydroxide. Two methods are used for this analysis: an automatic acid-base titration and a carbon analyser which measure the residual carbonate in samples.

The calcium balance in the reactor is checked hourly and the composition of all the solid products – limestone, lime, $Mg(OH)_2$, filter cake, calcined magnesia and sintered magnesia are also checked hourly, using X-ray fluorescence analysis. This is a multi-element automatic method which uses a pressed solid sample or samples dissolved in lithium borate glass, and gives a printout of the percentages of calcium, magnesium, silicon, iron, manganese, etc., in the samples. This is also a very rapid method so that a continuous check of the process can be maintained.

Boron is another important element which must be monitored, but boron is too light an element to be analysed by X-ray fluorescence. An Inductively Coupled Plasma Emission Spectrometer (ICP) is used instead.

The company's Quality Management System has been independently audited and accredited to the International Standard I.S. EN ISO 9002.

4.9 Safety

Premier Periclase has a safety policy statement which conforms to all safety statute regulations.

In general terms, this policy sets out to identify all possible hazards and risks on the plant site. It implements controls throughout the plant to reduce all risks and eliminate any hazards.

The policy follows the well-proven strategy of hazard elimination/substitution/reduction/isolation/warning/personal protection/equipment/review of progress.

To a large extent the primary mechanism for reducing risks in most areas of the plant is engineering, e.g. dangerous or moving machinery can be adequately guarded.

Safety makes up a very significant and considerable element in the company's overall annual budget. An on-going safety training programme is provided for all personnel working on the site by outside safety consultants.

In addition, a comprehensive Health/Safety team, comprising safety officer, electricians, fitters and nurse, operates throughout the entire plant. The company has a definite policy of inviting other companies in the area into their own safety courses on a regular basis. A contractual safety procedure also exists for all contractors and temporary workers entering the site whereby they are all brought through, and instructed on, all safety procedures before commencing work.

A hearing conservation programme is operated in areas of the plant that have high noise levels; for example due to the stone crushing in the quarry or the combustion air fans in the shaft kilns and multi-hearth furnaces. This emphasises the need for, and effectiveness of, wearing ear muff protectors in these areas. As excessive noise can cause hearing loss, prevention of this form of induced hearing loss is most important.

4.10 Cost

One of the major cost factors for the process is energy. However, depending on economic circumstances, this energy may be derived from a variety of sources, including heavy fuel oil, natural gas or petroleum coke.

Other major costs include plant maintenance, materials, labour, marketing and administration.

4.11 Site Location

The location of the plant is favoured by the following factors.

(1) Close proximity to a plentiful supply of limestone.

(2) Close proximity to the seawater reservoir at Baltray and a plentiful supply of fresh water.

(3) A convenient road and sea link to the plant for transport and export purposes.

(4) The presence of a great deal of production facilities in place when the process was being set up in 1977/’78. The present site and a substantial amount of equipment and machinery were originally used by Irish Cement Ltd until it was decided to replace the old wet cement process plant by a new dry process plant at the nearby Platin factory. For example, the large rotary kilns (3.6 m × 160 m) required to convert the raw materials to form cement clinker for the manufacture of cement were ideal for the production of magnesia.

(5) The presence of a highly skilled and trained workforce.

4.12 Construction Materials for Plant

Many of the external buildings on the site consist of mild steel structures with cladding on the surface. Large silos of concrete construction are also used. However, a variety of different materials are used throughout the plant. Due to the hard-wearing and high-temperature nature of the process, quite an amount of these materials have to be replaced and updated from time to time. There is a continual search for new and more efficient materials with longer life spans in certain critical regions of the plant.

The lime rotary kiln consists of a steel outer tube which gives it good structural properties and resistance to all weather conditions. Internally, it contains refractory bricks capable of withstanding high temperatures (over 1500 ^{o}C).

The shaft kilns, which are used in the sintering process, utilise higher quality refractory bricks. Insulation material (rock wool/fibre glass) is also used in the building which helps in noise reduction as well as providing heat insulation.

In the quarry, high-wear steel has to be used in the crushers and washers because of the close and continued contact with stones. Also in the quarry, strong rubber belts are used for transporting the stones and rocks.

All acid-handling equipment used within the plant has to be made of stainless steel, while a high grade of steel is necessary in all water-handling systems and equipment because of grit problems in the water.

In many high-wear situations, ceramic-lined ducts, which have prolonged life spans, are now used to prevent wear.

The latest additions as part of an energy saving project are new belt presses used to dry the filter cake before it enters the multi-hearth furnaces. These incorporate the use of stainless steel with new high-quality polymer belts imported from Austria.

As has been mentioned elsewhere, the original rotary kilns and concrete silos were inherited from the old cement works previously on the site. However, the multi-hearth furnaces, the briquetting plant and tank farms all had to be purpose-built for the periclase process.

The accompanying summary sheets, Figs. 4.1–4.7, pp. 31–37, may be found useful in teaching about the process at Premier Periclase.

PROCESS SUMMARY

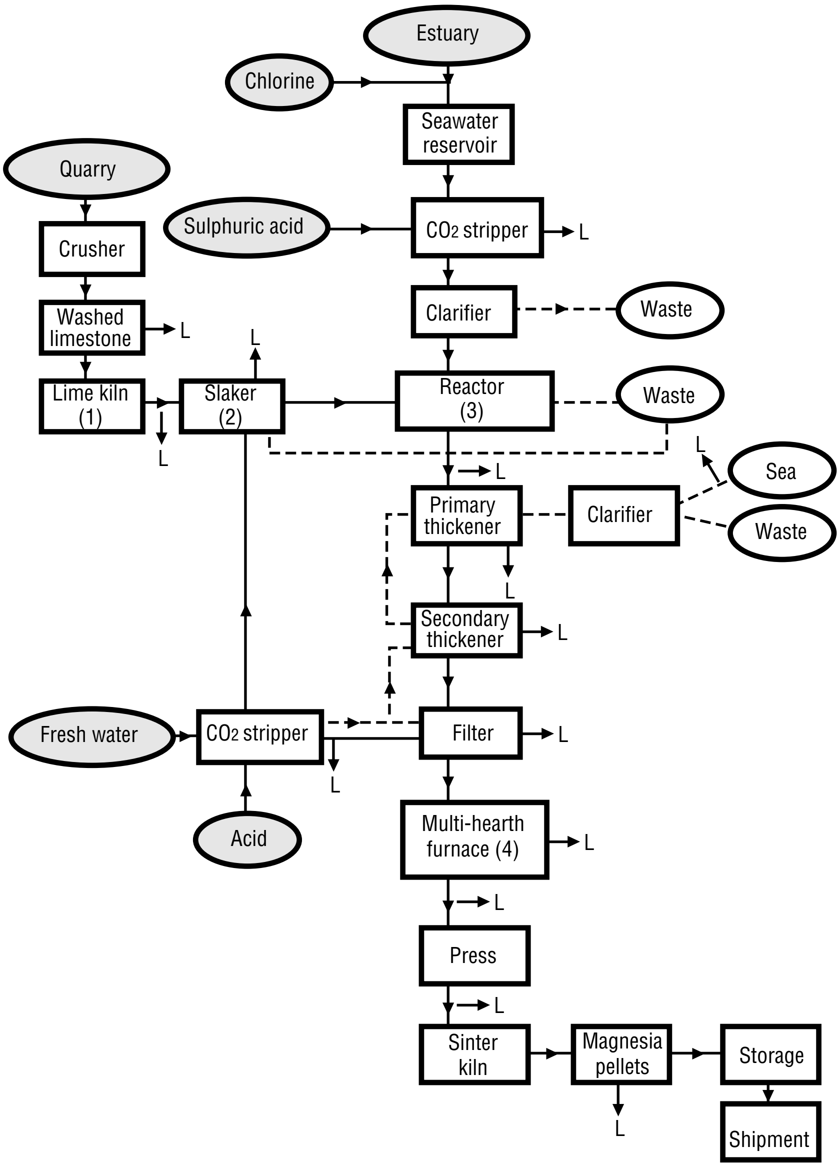

Fig. 4.1

THE CHEMISTRY OF MAGNESIA PRODUCTION FROM SEAWATER

1) Limestone calcination

$$\underset{\text{limestone}}{CaCO_3(s)} \xrightarrow[\text{1400 °C}]{\text{heat}} \underset{\text{lime}}{CaO(s)} + CO_2(g)$$

(2) Lime slaking

$$CaO(s) + H_2O \longrightarrow \underset{\text{slaked lime slurry}}{Ca(OH)_2(aq)}$$

(3) Seawater reaction to produce magnesium hydroxide

$$\underset{\text{from seawater}}{MgCl_2\ (aq)} + \underset{\text{slaked lime}}{Ca(OH)_2(aq)} \longrightarrow \underset{\text{magnesium hydroxide}}{Mg(OH)_2(s)} + CaCl_2(aq)$$

(4) Magnesium calcination

$$Mg(OH)_2(s) \xrightarrow[\text{900–950 °C}]{\text{heat}} \underset{\text{magnesia}}{MgO(s)} + H_2O(g)$$

Fig. 4.2

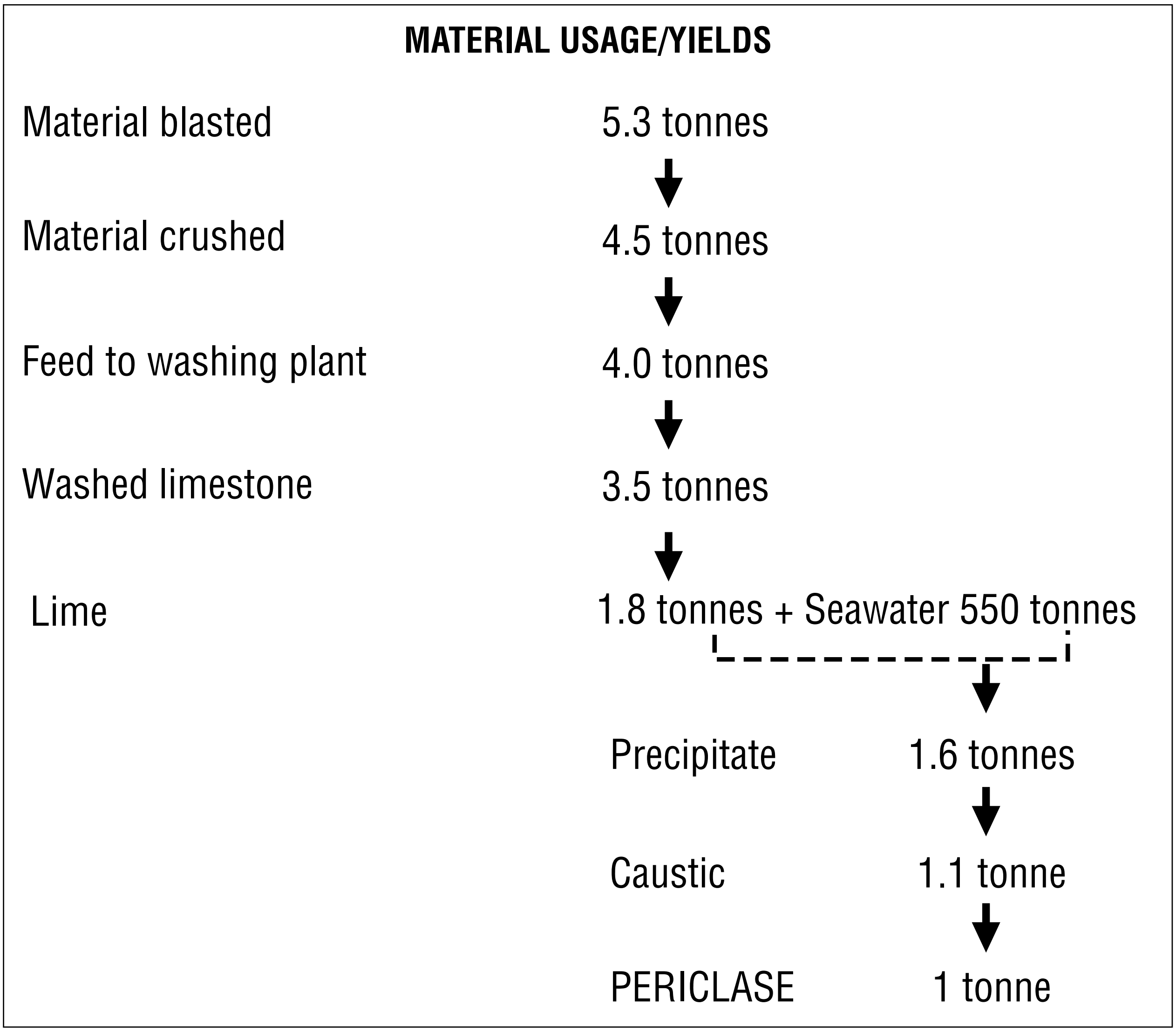
MATERIAL USAGE/YIELDS
Material blasted
5.3 tonnes
Material crushed
4.5 tonnes
Feed to washing plant
4.0 tonnes
Washed limestone
3.5 tonnes
Lime
1.8 tonnes + Seawater 550 tonnes
Precipitate
1.6 tonnes
Caustic
1.1 tonne
PERICLASE
1 tonne

Fig. 4.3

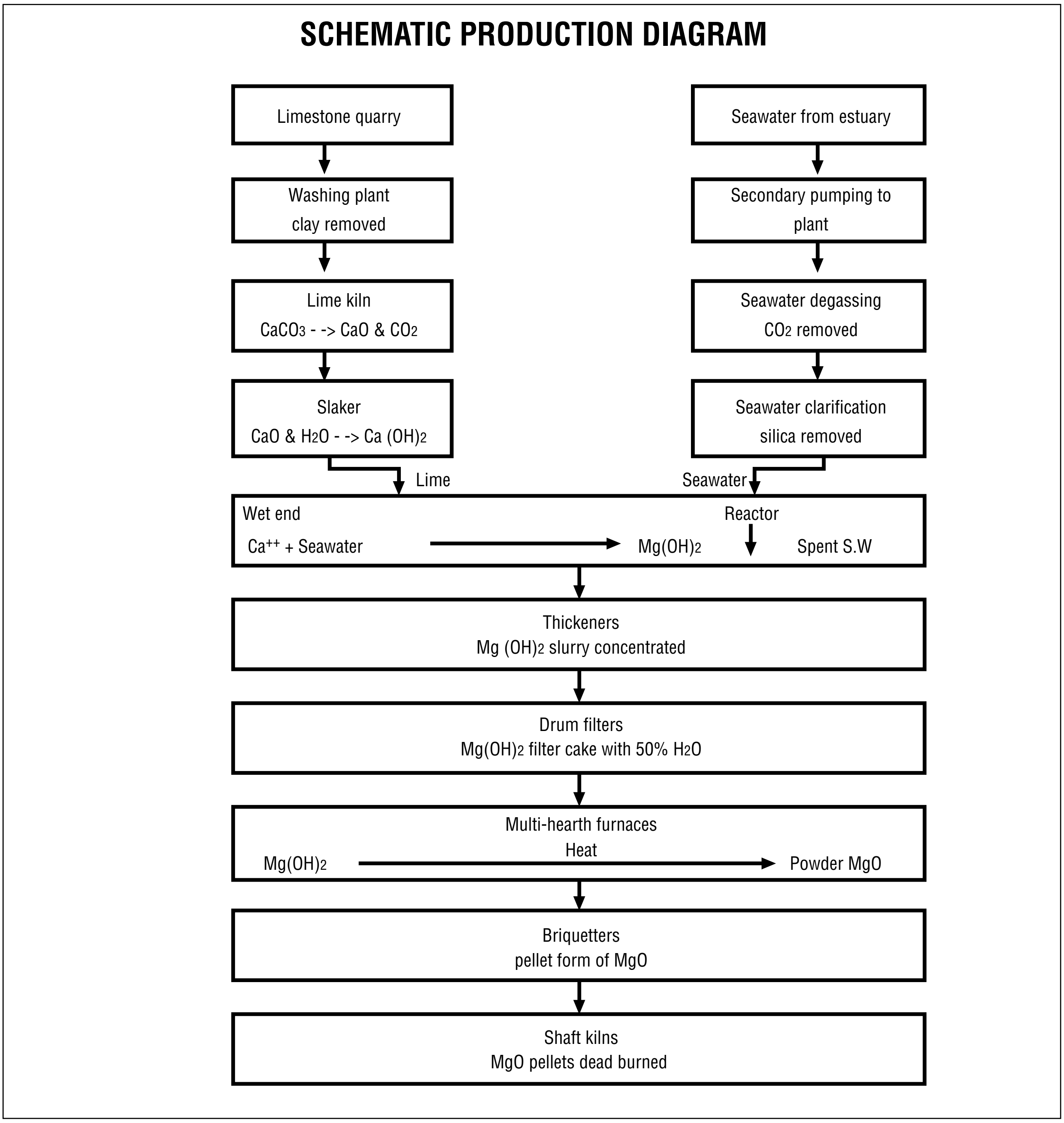
SCHEMATIC PRODUCTION DIAGRAM
Limestone quarry
Washing plant
clay removed
Lime kiln
$CaCO_3$ - -> CaO & CO_2
Slaker
CaO & H_2O - -> Ca $(OH)_2$
Lime
Seawater from estuary
Secondary pumping to plant
Seawater degassing
CO_2 removed
Seawater clarification
silica removed
Seawater
Wet end
Reactor
Ca^{++} + Seawater
$Mg(OH)_2$
Spent S.W
Thickeners
Mg $(OH)_2$ slurry concentrated
Drum filters
$Mg(OH)_2$ filter cake with 50% H_2O
Multi-hearth furnaces
Heat
$Mg(OH)_2$
Powder MgO
Briquetters
pellet form of MgO
Shaft kilns
MgO pellets dead burned

Fig. 4.4

ELEMENTS IN SEAWATER

The elements in seawater are listed in order of decreasing average concentration. These are average concentrations as there are variations in composition depending on the location where the sample was collected.

Element	Concentration (mg/l)
Oxygen	8.57 x 10^{3}
Hydrogen	1.08 x 10^{3}
Chlorine	1.90 x 10^{4}
Sodium	1.06 x 10^{4}
Magnesium	1.27 x 10^{3}
Sulphur	8.85 x 10^{2}
Calcium	4.00 x 10^{2}
Potassium	3.80 x 10^{2}
Bromine	6.5 x 10^{1}
Carbon	2.8 x 10^{1}
Strontium	8.1 x 10^{0}
Boron	4.6 x 10^{0}
Silicon	3 x 10^{0}
Fluorine	1.3 x 10^{0}
Argon	6 x 10^{-1}
Nitrogen	5 x 10^{-1}
Lithium	1.8 x 10^{-1}
Rubidium	1.2 x 10^{-1}
Phosphorus	7 x 10^{-2}
Iodine	6 x 10^{-2}
Barium	3 x 10^{-2}
Aluminium	1 x 10^{-2}
Iron	1 x 10^{-2}
Indium	<2 x 10^{-2}
Molybdenum	1 x 10^{-2}
Zinc	1 x 10^{-2}
Nickel	5.4 x 10^{-3}
Arsenic	3 x 10^{-3}
Copper	3 x 10^{-3}
Tin	3 x 10^{-3}
Uranium	3 x 10^{-3}
Krypton	2.5 x 10^{-3}
Manganese	2 x 10^{-3}
Vanadium	2 x 10^{-3}
Titanium	1 x 10^{-3}
Caesium	5 x 10^{-4}
Cerium	4 x 10^{-4}
Antimony	3.3 x 10^{-4}
Silver	3 x 10^{-4}
Yttrium	3 x 10^{-4}
Cobalt	2.7 x 10^{-4}
Neon	1.4 x 10^{-4}
Cadmium	1.1 x 10^{-4}
Tungsten	1 x 10^{-4}
Selenium	9 x 10^{-5}
Germanium	7 x 10^{-5}
Xenon	5.2 x 10^{-5}
Chromium	5 x 10^{-5}
Thorium	5 x 10^{-5}
Gallium	3 x 10^{-5}
Mercury	3 x 10^{-5}
Lead	3 x 10^{-5}
Zirconium	2.2 x 10^{-5}
Bismuth	1.7 x 10^{-5}
Lanthanum	1.2 x 10^{-5}
Gold	1.0 x 10^{-5}
Niobium	1 x 10^{-5}
Thallium	<1 x 10^{-5}
Hafnium	<8 x 10^{-6}
Helium	6.9 x 10^{-6}
Tantalum	<2.5 x 10^{-6}
Beryllium	6 x 10^{-7}
Protactinium	2 x 10^{-9}
Radium	6 x 10^{-11}
Radon	6 x 10^{-16}

Fig. 4.5

A DESCRIPTION OF SOME OF THE MATERIALS USED/PRODUCED AT PREMIER PERICLASE LIMITED

NAME	NAME-CHEMICAL	FORMULA	COMMENTS
LIMESTONE	Calcium Carbonate	$CaCO_3$	A naturally-occurring rock found in great abundance in Ireland. Chalk is a particularly pure form of calcium carbonate.
LIME	Lime	CaO	Formed by burning limestone to remove the carbon dioxide (CO_2) which is present in naturally-occurring limestone.
SLAKED LIME	Calcium Hydroxide	$Ca(OH)_2$	Formed by the reaction of lime and water.
PRECIPITATE	Magnesium Hydroxide	$Mg(OH)_2$	Precipitated when slaked lime is added to water.
CAUSTIC	Magnesium Oxide	MgO	Formed by burning (calcining) precipitate to remove the water contained in the precipitate crystal.
PERICLASE	Magnesium Oxide	MgO	Formed by hard burning of caustic to rearrange the crystal structure.

Fig. 4.6

SCHEMATIC FLOW CHART

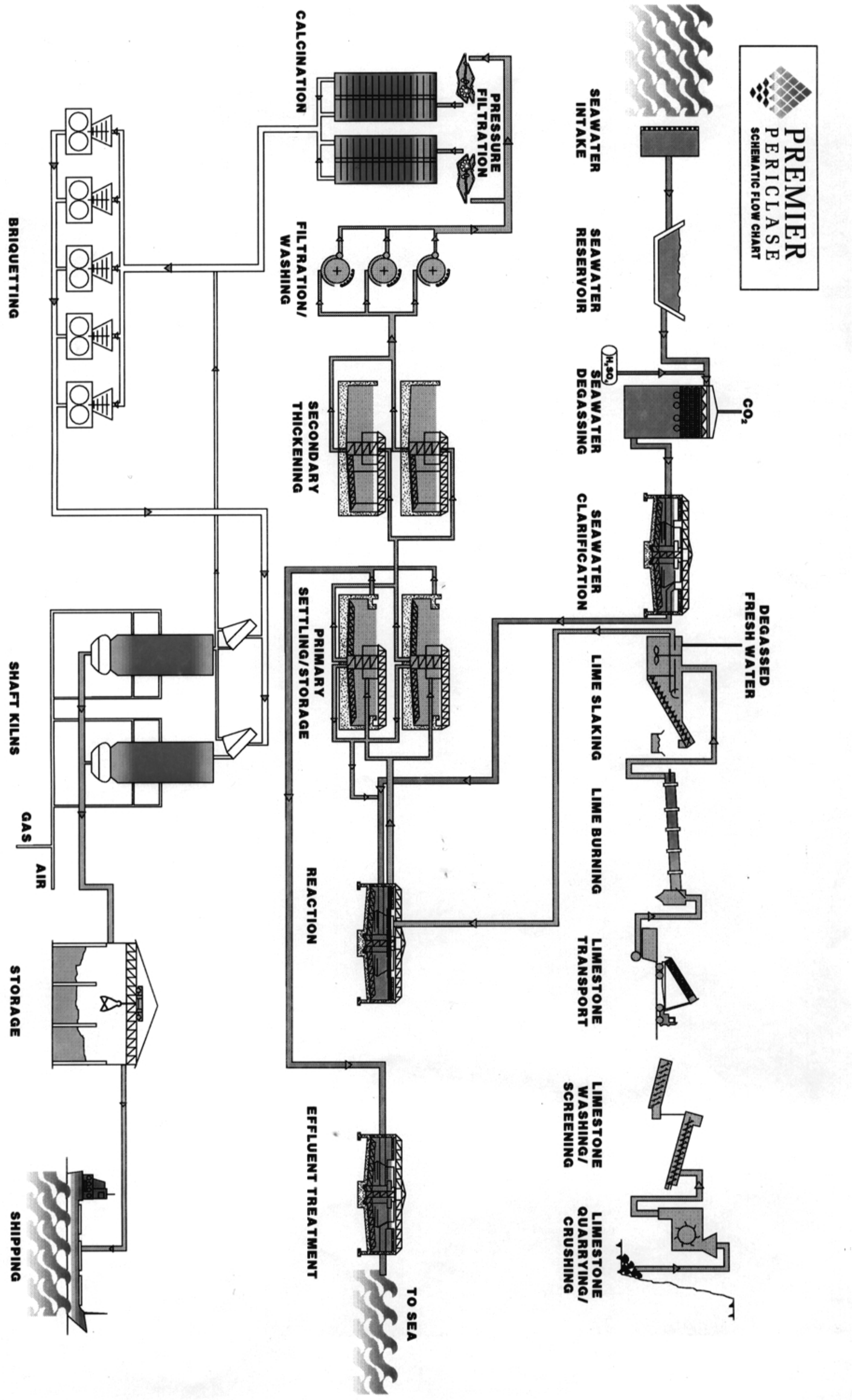

Fig. 4.7

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MODULE 4

Environmental Chemistry – Water

CONTENTS

Chapter 1 **pH**

Chapter 2 **Hardness in Water**

Chapter 3 **Water and Water Treatment**

CHAPTER 1 pH

1.1 Self-Ionisation of Water

When water is purified by repeated distillation and any ions or solutes are completely removed, its electrical conductivity falls to a very low but definite constant value, which can be measured by very sensitive instruments. This can only be explained by the fact that water produces ions as a result of its own self-ionisation or dissociation according to

$$H_2O \rightleftharpoons H^+ + OH^-$$

However, this is somewhat simplified because it is well established that H^+ ions (or protons) cannot exist independently in aqueous solution. Therefore, it is more correct to write the above equation as

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

The species H_3O^+ is called the hydronium (or oxonium) ion. Both names are in common use. At equilibrium as much water is being reformed as is breaking down. We can write an equilibrium expression based on the equation above as follows.

$$K_c = \frac{[H_3O^+]\,[OH^-]}{[H_2O]^2}$$

or

$$K_c\,[H_2O]^2 = [H_3O^+]\,[OH^-]$$

The concentration of water $[H_2O]$ may be taken as constant since the proportion dissociated is very small, i.e. $[H_2O] >> [H_3O^+]$. A constant multiplied by another constant is also constant. Therefore, we can take $K_c\,[H_2O]^2$ as constant at any given temperature and write $K_c\,[H_2O]^2 = K_w = [H_3O^+]\,[OH^-]$.

$$K_w = [H_3O^+]\,[OH^-]$$

At 298 K the value of K_w has been found to be 1×10^{-14} mol^2 l^{-2}. The quantity K_w is often referred to as the ionic product of water.

It is also possible to derive an expression for K_w containing the hydrogen ion, H^+, rather than the hydronium ion, H_3O^+. Such an expression is less correct than that given above, since hydrogen ions are known not to exist in solution. Nevertheless, such an expression is often accepted since it leads to the same arithmetic conclusions because the self-ionisation of water would generate the same number of hydrogen ions, if they could exist in solution, as hydronium ions.

In pure water all the H_3O^+ and OH^- must come from the dissociation of water molecules and so must be present in equal concentrations.

$$\begin{aligned} [H_3O^+] &= [OH^-] \\ [H_3O^+]^2 &= 1 \times 10^{-14}\ \text{mol}^2\ \text{l}^{-2} \\ [H_3O^+] &= 1 \times 10^{-7}\ \text{mol l}^{-1} \\ \text{and}\quad [OH^-] &= 1 \times 10^{-7}\ \text{mol l}^{-1} \end{aligned}$$

Therefore, in 1 litre of pure water at 298 K there are 1×10^{-7} mole of H_3O^+ ions and 1×10^{-7} mole of OH^- ions.

Now, since only a minute trace of the water is ionised, each litre of water will contain virtually 1000 g of H_2O, and as 1 mole of water has a mass of 18 g we can say that the concentration of water in moles per litre is 1000/18 = 55.55 moles per litre, i.e. a constant value. At 298 K there are 1 x 10^{-7} mole of dissociated molecules to every 55.55 moles of undissociated water molecules or one H_3O^+ ion and one OH^- ion for every 5.555 x 10^8 molecules of water.

1.2 The pH Scale

Since concentrations of H_3O^+ ions in water are very small yet spanning a large range of orders of magnitude, a negative logarithmic scale was found to be useful. Such a scale, called the pH scale, was devised by **Sørensen** in 1909. Sørensen worked for Carlsberg on problems associated with the brewing of beer. The ‘p’ in pH comes from the German word ‘potenz’ meaning power and the H originally came from $[H^+]$.

The pH of a solution is the negative logarithm to the base 10 of the hydronium ion concentration measured in moles per litre.

$$pH = -\log_{10} [H_3O^+]$$

Similarly, the pOH of a solution is defined as

$$pOH = -\log_{10} [OH^-]$$

Neither pH nor pOH has units.

The pH scale provides a convenient and effective means of communication of the relative acidity and basicity of a particular solution. Sørensen's idea avoids awkward exponents like 10^{-4} and provides a scale of positive numbers going from zero upwards as the solution becomes less acidic. The pH scale is most useful when considering solutions where the concentrations of ‘free’ hydrogen ions in the form H_3O^+ is less than 1.0 mole per litre and greater than 1 x 10^{-14} mole per litre. Consequently we normally consider the scale as limited to the range 0 to 14. It is emphasised that the higher the hydronium ion concentration (the more acidic the solution), the lower the pH. Conversely, the lower the hydronium ion concentration the higher the pH. This definition also indicates that a change of one pH unit represents a change in the concentration of H_3O^+ ions by a factor of 10. For example, when the pH decreases from 5 to 4, the H_3O^+ concentration increases by a factor of 10 from 1 x 10^{-5} mol per litre to 1 x 10^{-4} mol per litre, Table 1.1.

$[H_3O^+]$/mol l^{-1}	pH	$[OH^-]$ /mol l^{-1}	pOH	K_w/mol^2 l^{-2}
1 x 10^{0}	0	1 x 10^{-14}	14	1 x 10^{-14}
1 x 10^{-1}	1	1 x 10^{-13}	13	1 x 10^{-14}
1 x 10^{-2}	2	1 x 10^{-12}	12	1 x 10^{-14}
1 x 10^{-3}	3	1 x 10^{-11}	11	1 x 10^{-14}
1 x 10^{-4}	4	1 x 10^{-10}	10	1 x 10^{-14}
1 x 10^{-5}	5	1 x 10^{-9}	9	1 x 10^{-14}
1 x 10^{-6}	6	1 x 10^{-8}	8	1 x 10^{-14}
1 x 10^{-7}	7	1 x 10^{-7}	7	1 x 10^{-14}
1 x 10^{-8}	8	1 x 10^{-6}	6	1 x 10^{-14}
1 x 10^{-9}	9	1 x 10^{-5}	5	1 x 10^{-14}
1 x 10^{-10}	10	1 x 10^{-4}	4	1 x 10^{-14}
1 x 10^{-11}	11	1 x 10^{-3}	3	1 x 10^{-14}
1 x 10^{-12}	12	1 x 10^{-2}	2	1 x 10^{-14}
1 x 10^{-13}	13	1 x 10^{-1}	1	1 x 10^{-14}
1 x 10^{-14}	14	1 x 10^{0}	0	1 x 10^{-14}

Table 1.1 *pH scale at 25 °C*

The pH scale can accommodate solutions having acidities between approximately 1 mol per litre hydronium ion (pH = 0) to approximately 1 mol per litre hydroxide ion (pH = 14). Of course solutions which have a higher H_3O^+ ion concentration than 1 mole per litre and a lower H_3O^+ ion concentration than 1 x 10^{-14} mole per litre both exist. However, the pH scale is not very useful outside the range 0 - 14 since, in more concentrated solutions of acids and bases, the acid or base behaves as if it were not fully dissociated in solution (see overleaf). This makes it difficult to perform pH calculations and generates results which are of little use. It is nonetheless possible to have pH values less than zero and greater than 14.

In pure water the [H_3O^+] and the [OH^-] are equal to 1×10^{-7} mol per litre at 298 K. A pH of 7 represents a neutral solution at 298 K. The pH of pure (neutral) water deviates from this value at other temperatures, as the value of K_w is strongly temperature-dependent. Experiment has shown that the value of K_w increases as temperature increases, Table 1.2.

T/K	θ/°C	K_w/mol^2 l^{-2}	pH of pure water	pH of 1 mol l^{-1} H_3O^+ soln.	pH of 1 mol l^{-1} OH^- soln.
273	0	1.14×10^{-15}	7.47	0	14.94
283	10	2.93×10^{-15}	7.27	0	14.53
293	20	6.81×10^{-15}	7.08	0	14.17
298	25	1.01×10^{-14}	7.00	0	14.00
303	30	1.47×10^{-14}	6.92	0	13.83
313	40	2.92×10^{-14}	6.77	0	13.53
323	50	5.48×10^{-14}	6.63	0	13.26
373	100	5.13×10^{-14}	6.14	0	12.29

Table 1.2 *Ionic product and pH of pure water, 1 mol* l^{-1} H_3O^+ *and 1 mol* l^{-1} OH^- *solutions at temperatures between 273 K and 373 K*

Thus, a greater proportion of water molecules undergo self-ionisation as temperature rises. Furthermore, it may be concluded, from Le Chatelier's principle, that since the self-ionisation reaction tends to occur to a greater extent as the temperature rises, this reaction must be endothermic. The pH scale therefore shrinks, and the pH of pure water drifts downwards, as temperature increases. Fig. 1.1 illustrates this temperature-dependence of pH.

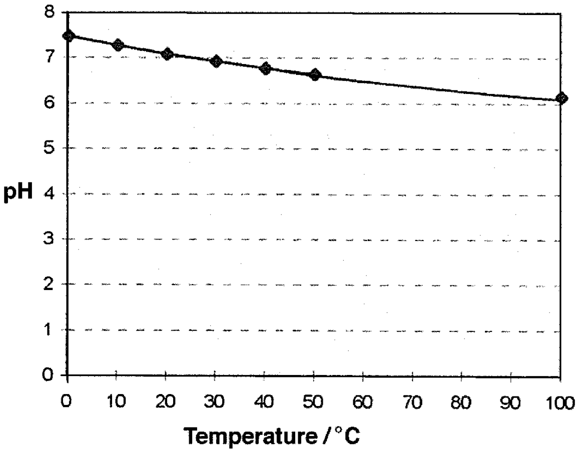


Fig. 1.1 *Temperature dependence of pH*

A knowledge of the molar hydrogen ion concentration in aqueous solution is of the greatest importance in chemistry, biology and medicine because it helps to explain the occurrence of many reactions. The pH scale is now used throughout chemistry, geology, medicine, agriculture, etc. The pH of our blood must be maintained at a particular value to ensure the proper functioning of many biological processes. This is discussed in more detail in section 1.3.

The pH scale is used by the Environmental Protection Agency (EPA) to define waste as corrosive if its pH is either lower than 3 (highly acidic) or higher than 12.5 (highly alkaline).

Sørensen's definition of pH has been modified somewhat as a result of G.N. Lewis's concept of activity of ions in solution. Owing to the fact that ions in solution interact with similar ions in that solution and with other ions in that solution, they do not exert their full effects and their 'effective concentration' is reduced. The revised definition of pH takes this into account and defines pH in terms of hydrogen ion activity or the effective concentration of hydrogen ions in solution.

However, this revised view or definition of pH need not be considered at Leaving Certificate level as it does not significantly affect pH values and certainly not in dilute aqueous solutions. The idea of activity, or effective concentration, is important where pH values are above 14 or below zero, as ion concentrations are high and interaction of ions plays a significant role in determining the overall ion activity or effective concentration.

1.3 Experimental Methods of Determining pH

One of the simplest methods of measuring pH is to use Universal Indicator, which is available absorbed onto paper or as a solution. Universal Indicator is a mixture of indicators that shows a gradual change of colour over a pH range. It turns different colours depending on the pH of the solution. Each shade of universal indicator colour corresponds to a pH value. A colour reference chart is used to read the pH.

Acidity/Basicity	**pH**	**Typical Colour**
Strongly acidic	0 1 2	Red
Weakly acidic	3 4 5 6	Yellow
Neutral	7	Green
Weakly alkaline	8 9 10	Blue
Strongly alkaline	11 12 13 14	Violet

Table 1.3 *The colour of universal indicator (range 1-12) in different solutions*

Short-range Universal Indicators are also available, including ranges 4-11, 0-6, 5-9, 9-12. Universal Indicator strips or sticks are also available (though expensive) which offer an accuracy of 0.5 pH units within their given test range.

More precise measurements of pH can be made with a pH meter. This instrument, its calibration and operation, are described in more detail in section 1.6. However, since buffer solutions are used in the calibration of pH meters it is convenient to refer briefly to buffer solutions at this point. A buffer solution is one which will resist changes in pH caused by the addition of small amounts of acid or alkali. The pH of a solution can be held relatively constant if it contains a buffer.

It takes just a small amount of a strong acid or strong base to cause a large change in the pH of an unbuffered solution.

The addition of 0.05 cm^3 of 2 molar hydrochloric acid, i.e. half the quantity measured by the smallest graduation on a standard school laboratory burette, to a litre of pure water reduces the pH of the solution from 7 to 4. This is a change of three units in pH but a 10^3 or 1000-fold increase in acidity. If such a change occurred in your blood stream you would die. The pH of blood cannot be allowed to change by more than 0.2 - 0.3 pH units from its normal pH of 7.35.

An effective buffer can be made by preparing a solution containing both a weak acid and one of its salts formed with a strong base, e.g. ethanoic acid and sodium ethanoate. A salt is fully dissociated in aqueous solution but the weak acid dissociates only to a slight extent, i.e. it remains largely associated.

The action of the ethanoic acid/sodium ethanoate buffer can be explained by considering how the ethanoic acid/ethanoate ion equilibrium

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$

responds to the addition of acid of base.

If H_3O^+ ions from an aqueous acid are added to a system containing the above buffer, the equilibrium is disturbed and H_3O^+ ions will combine with the CH_3COO^- ions which are present in large excess to form CH_3COOH, shifting the position of the equilibrium to the left until equilibrium is restored. When equilibrium is re-established the hydrogen ion concentration will have been raised only very slightly in comparison with the actual amount of hydrogen ions added. Thus the pH change is suppressed. Similarly, if a base containing OH^- ions is added the OH^- ions will combine with H_3O^+ ions to form water. More CH_3COOH will dissociate, providing H_3O^+ ions until equilibrium is restored. Again the change in H_3O^+ ion concentration is small compared with the quantity of H_3O^+ ions removed from solution by the base and the pH change is small. Owing to the shifting of the equilibrium in the buffer neither additions of small quantities of acid nor of small quantities of base will significantly change the overall pH of the buffered system.

Liquids that contain buffers are said to be ‘buffered’ against the changes in pH that the H_3O^+ or OH^- ions otherwise cause.

The blood and other body fluids include buffers and many of them work to maintain an appropriate acid-base balance. The maintenance of the pH of the blood is so critical that a special vocabulary exists to describe small shifts away from its normal value. If the pH becomes lower, i.e. the acidity of the blood is increased, the condition is called acidosis. Acidosis is characteristic of untreated diabetes and emphysema and other conditions. If the pH of the blood increases, which means that the blood becomes more alkaline, the condition is called alkalosis. An overdose of hydrogencarbonate (bicarbonate), exposure to low partial pressure of oxygen at high altitudes, or prolonged hysteria can cause alkalosis. In their more advanced stages, acidosis and alkalosis are medical emergencies because they interfere with the smooth working of respiration. Both acidosis and alkalosis are greatly restrained, and in a healthy person usually totally prevented, by buffers.

The body uses several buffer systems, among which the carbonic acid/hydrogencarbonate system is of the greatest importance. The body controls the concentrations of the two components of the H_2CO_3/HCO_3^- buffer system in different ways. Blood carbonic acid concentration is controlled by varying respiration, the amount of CO_2 being exhaled being proportional to the rate and depth of breathing. Breathing more quickly and more deeply increases the amount of CO_2 exhaled and lowers the carbonic acid concentration in the blood. The concentration of the hydrogencarbonate is controlled by varying the rate of excretion of this ion in the urine. The normal ratio of the HCO_3^- to the H_2CO_3 in the blood is 20:1. When the concentration of the HCO_3^- increases relative to that of the H_2CO_3, blood pH rises. If this increase is sufficient to cause blood pH to exceed the normal range alkalosis results. Conversely, acidosis is found when the pH decreases because the above ratio decreases.

1.4 Calculation of the pH of Dilute Solutions

When calculating the pH of an acidic or basic solution it is essential to know if the acids or bases involved are strong or weak. Confusion often arises between the words concentration and strength when referring to acids or bases. Concentration refers to the number of moles of acid or base per litre, while strength refers to the proton donating/accepting power of the acid or base. Strong acids or bases include HCl, H_2SO_4, HNO_3, NaOH and KOH, etc. All of these will be fully ionised in solution regardless of whether they are present in moderately concentrated or dilute aqueous solutions. However, at high concentrations the activity may be less than the actual concentration due to interaction/interference between ions. The pH of a strong acid or base can be quite easily calculated once its concentration is known.

Example 1
What is the pH of a 0.02 M HCl solution?

$$\underset{0.02\ M}{HCl} + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

HCl is a strong acid and it is in dilute solution, thus, we have 100% dissociation to ions.

$$\begin{aligned} \text{Therefore } [H_3O^+] &= 0.02\ M \\ pH &= -\log_{10} [H_3O^+] \\ &= -\log_{10} 0.02 \\ &= 1.7 \end{aligned}$$

Similarly, for strong bases the molar concentration of hydroxide ions is equal to the molar concentration of the base multiplied by the number of OH^- ions per formula unit. The conversion to $[H_3O^+]$ from $[OH^-]$ is made by using the relationship

$$[H_3O^+]\ [OH^-] = 1 \times 10^{-14}\ mol^2\ l^{-2} \text{ at } 298\ K\ (25\ ^\circ C)$$

Alternatively, the idea of pOH, where
$pOH = -\log_{10} [OH^-]$ can be used.

Then

$$pH + pOH = 14 \quad \text{at 298 K } (25^\circ \text{ C})$$

or

$$pH = 14 - pOH \quad \text{at 298 K } (25^\circ \text{ C})$$

Example 2

Calculate the pH of a 0.01 M solution of the strong base $Sr(OH)_2$ at 298 K.

$Sr(OH)_2$ is a strong base and is therefore fully dissociated as follows in solution.

$$Sr(OH)_{2(aq)} \xrightarrow{\text{100\% dissociation}} Sr^{2+} + 2OH^-$$

$$0.01 \text{ M} \rightarrow 0.02 \text{ M } OH^-$$

$$[OH^-] = 0.02 \text{ M}$$

$$pOH = -\log_{10} 0.02$$

$$= 1.7$$

$$pH = 14 - pOH$$

$$= 14 - 1.7$$

$$= 12.3$$

Note

All hydroxides of Group II elements are strong bases except $Be(OH)_2$. However, some of these hydroxides have very limited solubility in water.

When calculating the pH of weak acids and bases a slightly different approach must be taken. It must be remembered that weak acids produce a lower concentration of H_3O^+ ions in aqueous solution than do strong acids of the same concentration as they do not dissociate fully in solution. For example, a 0.01 M HCl solution has a pH of 2.0; however a 0.01 M CH_3COOH solution has a much lower concentration of H_3O^+ ions and its pH is 3.4.

The concentration of hydronium ions (oxonium ions, H_3O^+) in a solution of weak acid must be calculated by taking into account the concentration of the undissociated acid. It is often useful to use dissociation constants in calculating pH values for solutions of weak acids and bases.

If we consider a weak acid, HA which dissociates according to the equation

$$HA_{(aq)} + H_2O \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

we can write an equilibrium expression for this process in the form

$$K_c = \frac{[H_3O^+][A^-]}{[H_2O][HA]}$$

and rearrange to

$$K_c [H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

As when we derived an expression for K_w earlier, the concentration of water is taken as constant and the product of two constants is a constant. We can therefore define a new constant, the dissociation constant, K_a, for the weak acid HA as

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

The relationship between K_a and pH for a dilute solution can be derived as follows.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

This can be rearranged to

$$K_a [HA] = [H_3O^+][A^-]$$

The weak acid produces H_3O^+ and A^- in a 1:1 ratio.

Thus

$$K_a [HA] = [H_3O^+]^2$$

and

$$[H_3O^+] = \sqrt{K_a[HA]}$$

but

$$pH = -\log_{10}[H_3O^+]$$

therefore

$$pH = -\log_{10}\sqrt{K_a[HA]}$$

The dissociation process can be viewed as the acid of concentration, c_o, dissociating to an equilibrium mixture as follows.

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

	HA	H_2O	H_3O^+	A^-
Initially	c_o	55.5	0	0
at equilibrium	$c_o - x$	$55.5 - x$	x	x

The extent of the dissociation of the acid is small because a weak acid is involved. This means that the approximations of

$$c_o - x \approx c_o$$

and

$$55.5 - x \approx 55.5$$

are valid and the initial concentration of the acid rather than the concentration of the acid present at equilibrium can be used in the above expressions.

Example 3

Calculate the pH of 0.1 M CH_3COOH given that K_a for ethanoic acid is 1.8×10^{-5} mol l^{-1}.

It is noted that ethanoic acid is a weak acid and we can therefore expect the molar concentration of H_3O^+ ions to be less than 0.1 M and so its pH should be greater than 1 (because $-\log_{10} 0.1 = 1.0$).

$$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$$

$$pH = -\log_{10}\sqrt{K_a[HA]}$$

$$= -\log_{10}\sqrt{1.8 \times 10^{-5} \times 0.1}$$

$$= 2.87$$

One limitation of this approach to pH calculation is that it ignores the concentration of hydrogen ion in water which results from the self-ionisation of water. When the acid is in such low concentration that the calculation predicts a hydronium ion concentration of less than 1×10^{-7} mol per litre, we cannot say that its pH is higher than 7 because the self-ionisation already provides hydrogen ions at a concentration of 1×10^{-7} mol per litre. For example the pH of 1×10^{-8} M HCl solution is not 8, because the self-ionisation of water already provides hydrogen ions at a concentration of 1×10^{-7} mol per litre, which is ten times greater than the concentration produced by the acid and gives rise to a pH of 7. We can safely ignore the contribution of the self-ionisation of water only when the calculated hydronium ion concentration is substantially (two orders of magnitude) higher than 1×10^{-7} mol per litre.

The pH of such a solution can be calculated as follows. 1×10^{-8} mol of HCl dissociates fully in solution.

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

However, this is very small and only serves to disturb the dissociation in pure water slightly. We consider this disturbance.

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

The water self-ionises to give one H_3O^+ ion and one OH^- ion.

$$K_w = [H_3O^+][OH^-]$$

$$K_w = 1 \times 10^{-14}$$

$$1 \times 10^{-14} = [H_3O^+][OH^-]$$

The hydrogen ion concentration contains a small contribution from the HCl and so will be greater than the hydroxyl ion concentration by this amount. Let x be the equilibrium concentration of OH^- ions in the solution.

$$1 \times 10^{-14} = (x + 1 \times 10^{-8})\, x$$

$$1 \times 10^{-14} = x^2 + 1 \times 10^{-8} x$$

$$x^2 + 1 \times 10^{-8} x - 1 \times 10^{-14} = 0$$

Solving this quadratic equation gives

$$x = \frac{-1 \times 10^{-8} \pm \sqrt{1 \times 10^{-16} + 4 \times 10^{-14}}}{2}$$

The one positive solution for x is

$$x = 9.5 \times 10^{-8}$$

$$\text{and} \quad [H^+] = [x + 1 \times 10^{-8}]$$

$$= 1.05 \times 10^{-7} \text{ mol l}^{-1}$$

$$\text{pH} = -\log_{10} [H_3O^+]$$

$$\text{pH} = 6.98$$

A weak base has a lower pH than a strong base of the same molar concentration. A weak base in solution establishes a dynamic equilibrium with its conjugate acid and therefore produces less OH^- than a comparable strong base. It is useful to define the dissociation constant, K_b, for a weak base and to derive an expression for the pH of a solution of a weak base in terms of this constant.

If we consider a weak base, B, which dissociates according to the equation

$$B_{(aq)} + H_2O_{(l)} \rightleftharpoons HB^+_{(aq)} + OH^-_{(aq)}$$

The equilibrium expression for the process is

$$K_c = \frac{[HB^+]\,[OH^-]}{[H_2O]\,[B]}$$

This can be rearranged to

$$K_c\,[H_2O] = \frac{[HB^+]\,[OH^-]}{[B]}$$

As was the case in the discussion of dissociation constants for weak acids the value of the water concentration is taken as a constant. We define the dissociation constant, K_b, for the weak base as

$$K_b = \frac{[HB^+]\,[OH^-]}{[B]}$$

An expression for the pH of an aqueous solution of a weak base can be easily derived from this equation.

The expression for K_b rearranges to

$$K_b\,[B] = [HB^+]\,[OH^-]$$

The weak base produces HB^+ and OH^- in a 1:1 ratio.

Thus

$$K_b\,[B] = [OH^-]^2$$

and

$$[OH^-] = \sqrt{K_b[B]}$$

Hence

$$\text{pOH} = -\log_{10} \sqrt{K_b[B]}$$

But

$$\text{p}K_w = \text{pH} + \text{pOH}$$

and

$$\text{pH} = \text{p}K_w - \text{pOH}$$

This gives the expression

$$\text{pH} = \text{p}K_w + \log_{10} \sqrt{K_b[B]}$$

At a temperature of 25 °C,

$$\text{p}K_w = \text{pH} + \text{pOH}$$

$$= 14$$

Therefore, also at a temperature of 25 °C,

$$\text{pH} = 14 + \log_{10} \sqrt{K_b[B]}$$

Example 4

Calculate the pH of a 0.20 M solution of the weak base methylamine, CH_3NH_2, at 25 °C, given that K_b for CH_3NH_2 is 3.6×10^{-4} mol l^{-1}.

$$CH_3NH_2 + H_2O = CH_3NH_3^+ + OH^-$$

$$[CH_3NH_2] = 0.20 \text{ mol per litre}$$

$$pOH = -\log_{10}\sqrt{K_b[B]}$$

$$= -\log_{10}\sqrt{3.6 \times 10^{-4} \times 0.20}$$

$$pOH = 2.1$$

At 25 °C the value of $pK_w = 14$

Hence $pH = 14.0 - 2.1$

$$= 11.9$$

The method recommended for calculating the pH of aqueous solutions of weak acids and bases for the Leaving Certificate uses the formulae derived above, i.e.

$$pH = -\log_{10}\sqrt{K_a[HA]}$$

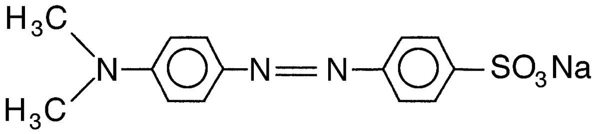
$$pH = pK_w + \log_{10}\sqrt{K_b[B]}$$

1.5 Indicators

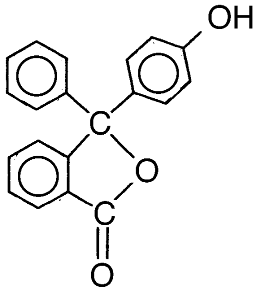
Acid-base indicators are substances which change colour according to the pH of the solution in which they are placed. Consequently, they are used to test for acidity or alkalinity and are very often used to detect the end-point (also known as the stoichiometric point) in acid-base titrations.

Most indicators are weak acids or bases and are, therefore, only slightly dissociated in solution. They have to have one distinct colour when present in the undissociated acid or base form and another distinct colour when present in the dissociated conjugate base or conjugate acid form.

Two common examples of indicators are methyl orange and phenolphthalein, Fig. 1.2.



Methyl orange



Phenolphthalein

Fig. 1.2 *Two common indicators*

To understand how indicators work, methyl orange is taken as an example. Consider the undissociated form of the molecule as HIn and the dissociated form as In^-. The dissociation of the weak acid can be written as follows.

$$HIn + H_2O \rightleftharpoons H_3O^+ + In^-$$

Red Colourless Yellow

On the addition of some aqueous acid (containing H_3O^+ ions) the above equilibrium will be shifted to the left in accordance with Le Chatelier's principle, and so the solution becomes RED. On the other hand when a base is added to the methyl orange it removes H_3O^+ from the solution, thus shifting the equilibrium to the right in an effort to replace the lost H_3O^+. This results in the YELLOW colour of the In^- dominating the solution.

The dissociation constant for the weak acid indicator can be written as

$$K_{In} = \frac{[H_3O^+][In^-]}{[HIn]}$$

This expression can be rearranged to

$$\frac{K_{In}}{[H_3O^+]} = \frac{[In^-]}{[HIn]}$$

If we consider the two species HIn and In^- to have similar efficiencies of light absorption in the visible region (i.e. similar extinction coefficients) then when

$$[HIn] \approx [In^-]$$

neither the colour of HIn or In^- is dominant but an intermediate colour is observed. This corresponds to the condition that

$$K_{In} \approx [H_3O^+]$$

or

$$pK_{In} \approx pH$$

It is assumed that for the colour of one of the species, HIn or In^-, to dominate in solution, that species must be present in greater than ten–fold excess over the other. It can, therefore, be concluded that for the red colour of the associated indicator to dominate

$$\frac{K_{In}}{[H_3O^+]} = \frac{[In^-]}{[HIn]} < \frac{1}{10}$$

or

$$K_{In} < \frac{[H_3O^+]}{10}$$

i.e. the pH is more than one unit lower than the value of the pK_{In} of the indicator.

Conversely, if the colour of the dissociated ion In^- is to be dominant the condition which must be fulfiled is that

$$\frac{K_{In}}{[H_3O^+]} = \frac{[In^-]}{[HIn]} > \frac{10}{1}$$

or

$$K_{In} > [H_3O^+] \times 10$$

i.e. the pH is more than one unit higher than the pK_{In} of the indicator.

As a rough guide we can take the range of an indicator (i.e. the pH range over which the colour change is observed) as (pK_{In} - 1) to (pK_{In} + 1).

Example 5

Calculate the pK_{In} and estimate the colour change range of methyl orange indicator given that the value of the K_{In} for methyl orange is 2 x 10^{-4} mol per litre.

The value of pK_{In} is given by

$$pK_{In} = -\log_{10} K_{In}$$

$$= -\log_{10} (2 \times 10^{-4})$$

$$= 3.7$$

And we would therefore expect the colour change to be observed as the pH of the solution changes from 2.7 to 4.7. In fact the range over which one observes a change in colour for methyl orange is much narrower than this (3.2 to 4.4).

The values of the dissociation constants and corresponding pK_{In} values for a number of indicators are given in Table 1.4.

Indicator	**K_{In}/mol l^{-1}**	**pK_{In}**
Methyl orange	2×10^{-4}	3.7
Litmus	3×10^{-7}	6.5
Bromothymol blue	8×10^{-8}	7.1
Phenolphthalein	7×10^{-10}	9.1

Table 1.4 *K_{In} and pK_{In} values for some common indicators*

The pigment (dye) responsible for colour in both the poppy (RED) and the cornflower (BLUE) is the same chemical compound. However, it can be said to behave as an acid-base indicator because the acidic sap of the poppy produces the RED colour while the basic sap of the cornflower produces the characteristic BLUE of the cornflower.

Table 1.5 gives a list of common acid-base indicators, the colour change observed and the pH range over which the colour change is observed.

Indicator	Colour change	pH range
Methyl orange	Red - yellow	3.2 - 4.4
Litmus	Red - blue	4.7 - 8.2
Bromothymol blue	Yellow - blue	6.0 - 7.6
Phenolphthalein	Colourless - pink	8.0 - 10.0

Table 1.5 *Colour change ranges for some common indicators*

The colour change of an indicator is often due to the change in colour of a molecule to the colour of an ion derived from that molecule or vice-versa. Near the end-point both coloured forms will be present in appreciable quantities and it is not possible to say exactly when the two forms are at equal concentrations. The eye cannot judge the exact end-point, and indicators effectively change colour over a range of two pH units.

The range of an indicator is the pH range over which it changes colour. Tables 1.4 and 1.5 above clearly show that the K_{In} values and pH ranges at the end-points for different indicators differ widely.

Many indicators, like phenolphthalein, are only slightly soluble in water (remember phenolphthalein is an organic molecule of high molecular mass), and are therefore prepared for use by dissolving the indicator in an alcohol or in a mixture of an alcohol and water. Because of this, the colour of the indicator solution may be unfamiliar until it is added to an aqueous solution.

When an indicator is used to locate the end-point of a titration, the pH at the end-point will be near the middle of the indicator's pH range, and may be well away from 7. This is an important point as many students misunderstand the use of indicators and expect them all to change colour at pH 7. In fact, it is because different indicators change colour at different pHs that they have such a wide application in acid-base titrations in industry and in the laboratory.

Another point that needs to be borne in mind by students is the amount of indicator used in titrations. Ideally the minimum quantity necessary to produce a clearly visible colour change should be used. Remember the indicator itself is usually a weak acid or base and is itself capable of participating in acid-base reactions, consuming titrant and influencing the titration results.

Since an indicator changes colour over a pH range, it can be sometimes difficult to know just which colour to take as the end-point. Where this problem arises, one solution is first to do an acid-base titration (with an indicator present) using a pH meter and then to determine the colour of the indicator at the end-point. Subsequently, samples can be titrated to exactly this colour. Sometimes a colour standard is prepared and the titration is carried out until the indicator colour matches that of the standard.

1.6 The pH Meter

pH Measurement Using a pH Meter

A pH meter is an electrical device used to measure accurately the pH of a solution. It consists of two electrodes immersed in separate solutions and connected to a voltmeter calibrated to read in pH units. The pH of a test solution is determined from the difference in electrical potential between the two electrodes when they are dipped into the solution.

One of these electrodes is called the external reference electrode, and is usually a standard Hg/Hg_2Cl_2 (calomel) or Ag/AgCl electrode filled internally with a strong Cl^- ion solution, usually 3 M KCl. The potential of this external reference electrode is determined by its internal filling solution and is thus constant, i.e. it is independent of any or all solutions into which it may be immersed.

The other electrode is the so-called glass electrode used for H_3O^+ detection. The glass electrode is the most widely used ion-selective electrode, i.e. an electrode used to preferentially detect and measure a particular ion. It normally consists of a glass tube upon which is grafted a special glass bulb which is very thin (50 - 100 μm thick). This is filled by the manufacturer with an acid solution, usually 0.1 M HCl, and it also contains an internal reference electrode, usually an Ag wire coated with AgCl.

Nowadays, for convenience and ease-of-use, the two electrodes, i.e. the external reference electrode and the glass electrode, are combined as two separate compartments within one overall probe. The glass electrode compartment makes contact with the test solution through the glass bulb, while the reference electrode compartment makes contact through a ceramic frit or plug known as a liquid junction, Fig. 1.3(a).

A thin hydrated 'gel' layer (about 1 μm thick) is formed on the inside and on the outside of the special glass bulb upon contact with solution. (**Note:** the membrane must be kept immersed in solution to maintain the gel layer - if this dries out it will shrink and crack and the electrode will lose its activity.) Through a complex set of ion-exchange reactions involving the gel layers and alkali metal and hydronium ions, both in the glass and in the solutions in contact with the glass, equilibrium potentials are established at the internal and external membrane surfaces. Since the internal filling solution is constant the potential established at the internal membrane surface is constant, while the potential of the external membrane surface depends on the H_3O^+ concentration of the test solution. Thus, the potential of the outer membrane surface, as measured with respect to the potential of the external reference electrode, can be used to determine the pH of a test solution.

A simpler, but not quite accurate, explanation of the phenomenon is to picture the outer hydrated gel layer as a kind of 'sponge' for H_3O^+ or H^+ ions. The more H_3O^+ ions there are in a test solution the greater the number that are absorbed by the gel layer 'sponge', and consequently the greater the positive potential of the membrane, and vice versa.

The relationship between potential and H_3O^+ concentration (or pH) is given by the Nernst equation as follows.

$$E_g = E^\circ + \frac{2.303\,RT}{F}\log_{10}[H_3O^+] \text{ at } 25\ ^\circ\text{C} \quad (1)$$

where

E_g = potential of glass electrode (outer membrane) in millivolts,

E° = a constant whose value depends on electrode make, age, etc.,

R = universal gas constant,

T = temperature,

F = faraday,

$[H_3O^+]$ = molar concentration of hydronium ions.

Since, by definition,

$$\text{pH} = -\log_{10}[H_3O^+]$$

by substitution, equation (1) becomes

$$E_g = E^\circ - 59\ \text{pH} \quad \text{at } 25\ ^\circ\text{C} \quad (2)$$

Equation (2) is clearly the equation of a straight line. Therefore, a graph of potential/mV against pH gives a straight line graph with a slope of -59 mV, Fig. 1.3(b).

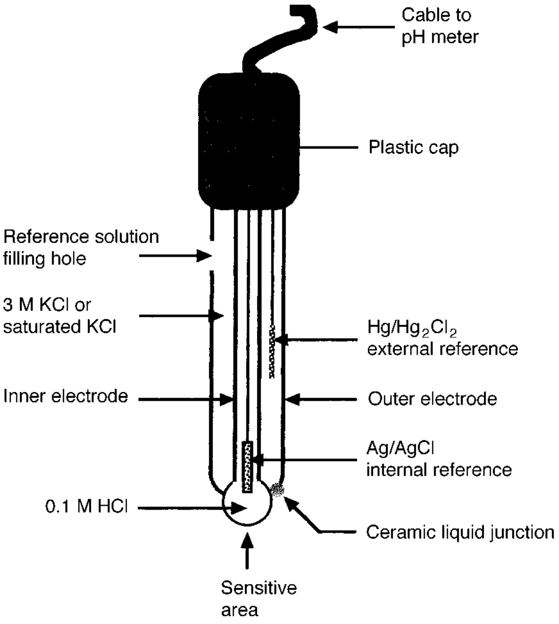


Fig. 1.3(a) *Common pH electrode system*

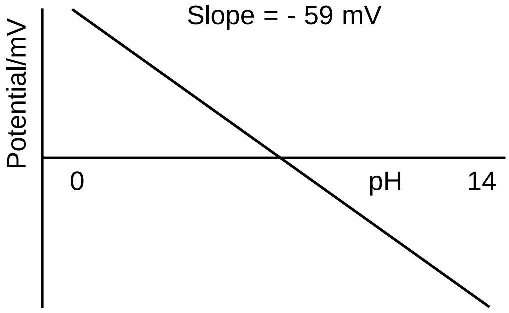


Fig. 1.3(b) *Potential against pH for a glass electrode at 25 °C*

Adjustments to a pH Meter

A set of guidelines is presented here for the adjustment, calibration and use of a pH meter. Probably the single most important and obvious instruction is to first read the instructions accompanying the instrument. While the instructions vary from meter to meter it is still possible to give a general guide to the operation of a pH meter.

(a) Never touch the tip of the glass electrode with your fingers.

(b) Never tap the glass electrode against the wall of the beaker. These electrodes are delicate.

(c) When not in use, clamp the probe in distilled water and set the meter to the ‘stand by’ setting.

(d) Follow the storage procedure between use. Different pH electrodes have different storage conditions, so it is important to follow the instructions accompanying the pH electrode. The lifetime of the probe depends on its careful storage.

(e) Check the level of the reference electrolyte.

(f) There are specific procedures for cleaning the reference junction of a pH probe which has become contaminated. For example, to remove inorganics, soak the probe in 0.1 M disodium edta; to remove oil or grease, clean the probe with mild detergent; to remove highly resistant deposits, clean with hydrogen peroxide solution. After cleaning return the probe to pH = 7 buffer overnight.

Calibration of a pH Meter

Many modern pH meters are calibrated at two of the following pH values: pH = 4, pH = 7 and pH = 10. Usually, pH = 7 is chosen initially and then pH = 4 if the acid region is under investigation or pH = 10 if the solution under test is alkaline. A general calibration procedure is given here.

(a) Switch on the pH meter. Adjust the temperature setting to room temperature. Press the pH key.

(b) Remove the probe from the distilled water and allow any excess water to drip off the probe.

(c) Immerse the probe in the pH = 7 buffer and reset the meter reading to the exact pH of the buffer solution at that temperature. This is done using the ‘OFFSET’ knob. Remove the probe and wash with distilled water.

(d) Immerse the probe in the pH = 4 buffer or the pH = 10 buffer and reset the meter reading to the exact pH of the buffer solution at that temperature. This is done using the ‘SLOPE’ knob. Remove the probe and wash with distilled water.

(e) Wash the probe using distilled water before transferring it to the solution under test.

Testing the pH of an Unknown Sample

(a) Test the sample first with pH paper to get a rough idea of the pH of the sample under test. Then, depending on the result of this test, calibrate the pH meter using buffer pH = 4 or pH = 10. In addition, some pH meters operate over the pH (0-10) range and the pH (4-13) range on separate settings. The universal indicator test also allows one to select the correct setting.

(b) Having calibrated the pH meter and selected the correct setting, remove the pH probe from the distilled water. Allow excess water to drain from it. Dry off any water adhering to the sensitive area by touching it with a piece of filter paper.

(c) Immerse the probe in the solution under test. Allow the pH reading to 'settle' and note the reading.

(d) Remove the probe from the test solution. Wash down with distilled water. Replace the probe in distilled water.

1.7 Titrations: Choosing an Indicator, and pH Curves for Titrations

pH Curves for Titrations

The equivalence point of an acid-base titration is that point when the stoichiometrically equivalent quantities of acid and base are present in solution, i.e. the amount of acid present is exactly the stoichiometric quantity which reacts with the amount of base present. The end-point on the other hand is a point in a titration where it is considered that the stoichiometrically equivalent quantities of acid and base are present. This is usually detected using a suitably chosen indicator, i.e. one which undergoes a readily identifiable colour change at a pH as close as possible to the pH at which the equivalence point occurs. The objective is that, where possible, the equivalence point and the end point coincide.

One of the best ways to follow the course of an acid-base titration is to measure the pH as the titration progresses, and to plot a titration curve of pH versus millilitres of titrant added (usually it is the base that is added to the acid in pH titrations). During the greater part of an acid-base titration, the pH changes gradually as the titrant is added. Near the equivalence point, however, the pH changes dramatically. The rate of pH change is greatest at the equivalence point. Data for a titration curve may be obtained experimentally with a pH meter. Experiments where the data to produce these curves are collected are described in section 1.6. The co-ordinates of the graph are pH on the vertical axis and volume of titrant on the horizontal axis.

To illustrate their usefulness, pH curves for a number of acid-base titrations are considered below.

A strong acid versus a strong base, e.g. HCl versus NaOH

The titration curve observed for an HCl versus NaOH titration is shown in Fig. 1.4.

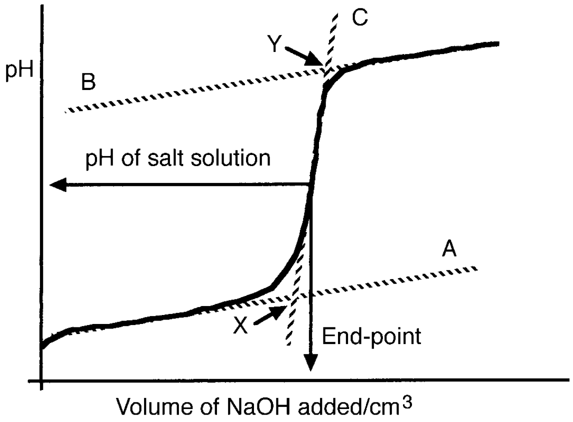


Fig. 1.4 *Titration curve for HCl versus NaOH*

The equivalence point can be determined by extrapolating straight lines on the approximately linear region before and after neutralisation (lines A and B) followed by extrapolating a straight line along the approximately linear neutralisation region of the curve (line C). The mid-point of the segment X-Y as indicated is the equivalence or neutralisation point.

In the case of a hydrochloric acid/sodium hydroxide titration this occurs at around pH = 7. This is due to the fact that at the equivalence point only sodium chloride and water are present. Sodium chloride is the salt of a strong acid and a strong base (HCl and NaOH) and does not give rise to a difference in the activities of H_3O^+ or OH^- ions in the solution. The pH at which the equivalence point of this titration occurs can be compared to the pH obtained when a solution of sodium chloride of the same concentration is tested. The two results should be equal.

A weak acid versus a strong base, e.g. CH_3COOH versus NaOH

The titration curve observed for a CH_3COOH versus NaOH titration is shown in Fig. 1.5.

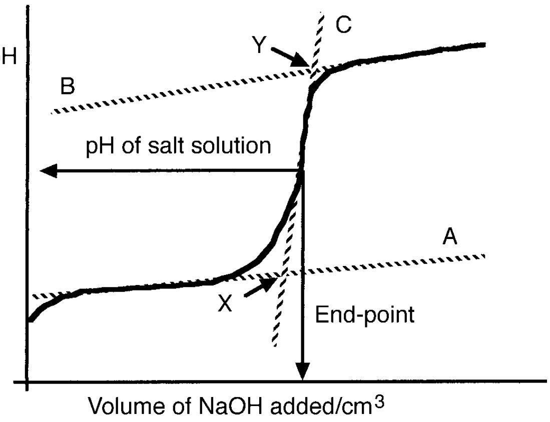


Fig. 1.5 *Titration curve for CH_3COOH versus NaOH*

Again the equivalence point can be determined by extrapolating straight lines on the approximately linear region before and after neutralisation (lines A and B) followed by extrapolating a straight line along the approximately linear neutralisation region of the curve (line C). The mid-point of the segment X-Y as indicated is the equivalence or neutralisation point.

In this case the equivalence point occurs at a pH greater than 7. This can be easily explained. At the equivalence point sodium ethanoate and water are present. The sodium ethanoate can undergo hydrolysis and this forms ethanoic acid and sodium hydroxide. The sodium hydroxide is a strong base and it dissociates completely. The ethanoic acid is a weak acid and only undergoes slight dissociation. Thus, the activity of OH^- ions exceeds the activity of H_3O^+ ions in solution and a pH of greater than 7 results. The pH at which the equivalence point has been estimated can be checked against the pH of a solution made up by dissolving sodium ethanoate in deionised water.

In the case of this experiment further information in addition to the equivalence point and the pH at which it occurred can be obtained from the titration curve. Firstly, the titration produces sodium ethanoate and so a mixture of ethanoic acid and sodium ethanoate is present during the titration. When these concentrations are approximately equimolar a buffer solution is produced and a 'buffering zone' is evident in the titration curve. This is a region where no substantial change is occurring in pH despite the continued addition of base, Fig. 1.6.

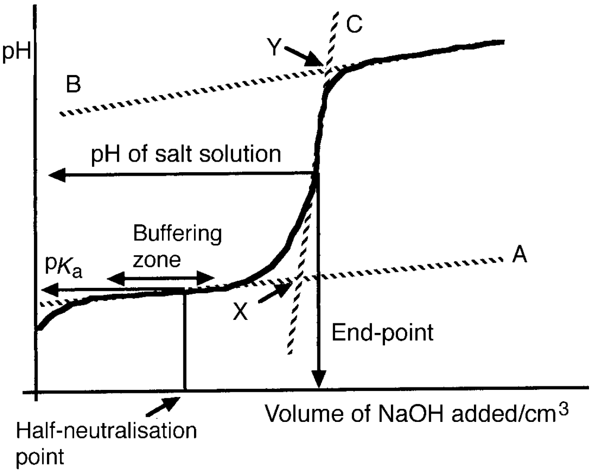


Fig. 1.6

Secondly, the pK_a of ethanoic acid can be read from the titration curve. The expression for the dissociation constant K_a, is

$$K_a = \frac{[H_3O^+]\,[CH_3COO^-]}{[CH_3COOH]}$$

At the 'half-neutralisation point' half the total amount of sodium hydroxide required to neutralise the ethanoic acid has been added. Thus, half the ethanoic acid is converted to sodium ethanoate and so

$$[CH_3COOH] = [CH_3COO^-]$$

This means that at the half-neutralisation point

$$K_a = [H_3O^+]$$

and

$$pK_a = pH$$

A strong acid versus a weak base, e.g. HCl versus NH_4OH

When a strong acid is titrated against a weak base the equivalence point occurs at a pH below 7. The titration of hydrochloric acid versus ammonia solution shows this. Simply dissolving ammonium chloride in water and testing the pH of the resulting solution verifies this. Again this is readily explained by considering the hydrolysis of the salt. Hydrolysis of ammonium chloride produces ammonia, a weak base, and hydrochloric acid, a strong acid. The strong acid dissociates completely and the weak base does not. The activity of H_3O^+ ions in the resultant solution is greater than the activity of the OH^- ions. Consequently, the pH is lower than 7.

A weak acid versus a weak base

When a weak acid is titrated with a weak base the equivalence point would be reached at a pH of approximately 7. However, there is no sharp change in pH at any stage, so the exact equivalence point of the titration cannot be shown by any indicator. For this reason, this type of titration is not carried out, as such titrations could not possibly yield any accurate or reliable results.

Choosing an Indicator for a Particular Titration

In order that the end–point indicated by the indicator correlates well with the equivalence point of the titrated species the pH at the equivalence point should be in the colour change range of the indicator. Ideally, the pH at the equivalence point should be close to the pK_{In} for the indicator (see Table 1.4, p. 10).

Examination of the ranges of pH over which some indicators change colour were given in Table 1.5 (p. 11). These should be studied in the context of the pH curves and the pH of the mixtures at the equivalence points and the suitability of each indicator considered.

Experimentally Examining pH Titrations HCl/NaOH

(a) Pipette 25 cm^3 of the HCl solution (0.1 M) into a 250 cm^3 beaker and add 75 cm^3 of distilled water. Add a small magnetic stirring pellet.

(b) Remove the pH probe from the distilled water. Wash down with distilled water using a wash bottle. Place the probe in the acid solution as shown and gently clamp it in position, Fig. 1.7. Record the pH of the solution.

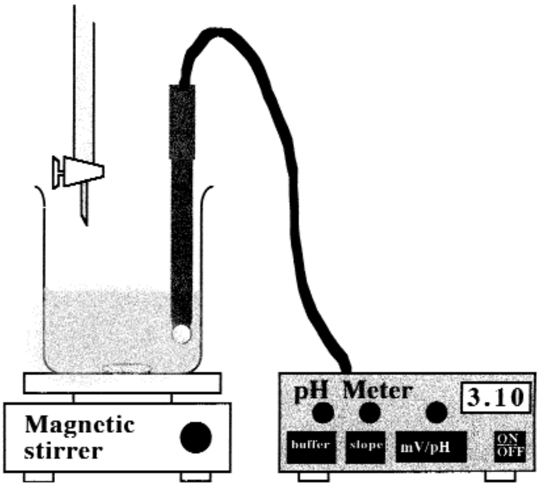


Fig. 1.7 *pH titration*

(c) Add the NaOH solution (0.1 M) from the burette 1 cm^3 at a time, allowing the pH reading to 'settle' before recording its value and adding the next portion of NaOH.

(d) As the end-point approaches the pH changes rapidly - add the NaOH in 0.1 cm^3 portions at this stage.

(e) Continue until the pH is about 11. Tabulate as shown below.

(f) Plot pH versus volume of NaOH added. The analysis of pH curves has been detailed on p.14.

Volume of NaOH/cm^3															
pH															

CH_3COOH/NaOH

Repeat as for HCl/NaOH, except using 0.1 M ethanoic acid instead of HCl.

HCl/NH_4OH

Repeat as for HCl/NaOH, except using 0.1 M ammonia solution instead of NaOH.

CH_3COOH/NH_4OH

Repeat as for HCl/NaOH, except using 0.1 M ethanoic acid and 0.1 M ammonia solution. Note that while the pH may rise from about 3.5 to 10 in this experiment, the change in pH is very gradual, with no vertical part to the pH curve at any stage.

CHAPTER 2 HARDNESS IN WATER

2.1 Introduction

Water which does not form a lather easily with soap has always been regarded as hard, while water which produces a good lather is considered as soft. The ions most commonly responsible for this undesirable interaction with soap have been clearly identified as calcium(II) and magnesium(II). Strontium(II), iron(II) and manganese(II) ions can also cause water hardness but their contribution to total hardness is usually very small and they are therefore normally ignored. In addition, aluminium(III) and iron(III) ions can also give rise to water hardness, but the concentrations in which these ions arise is so small that their contribution is also normally taken as negligible.

In hard water, a reaction between the dissolved calcium and magnesium ions and soap occurs. The product is an insoluble scum or precipitate. An example of the type of reaction that takes place is

$$\underset{\substack{\text{stearate ions}\\\text{in soap}}}{2C_{17}H_{35}COO^{-}} + \underset{\substack{\text{calcium ions}\\\text{in hard water}}}{Ca^{2+}} \rightarrow \underset{\substack{\text{'insoluble scum'}\\\text{(calcium stearate)}}}{(C_{17}H_{35}COO)_2Ca}$$

Soaps are the sodium or potassium salts of fatty acids (long-chain organic acids) such as octadecanoic acid (stearic acid). The soap will only form a lather when all the Ca^{2+} ions have been precipitated and so the soap used in doing this is wasted.

As water is such a good solvent, all water supplies will contain a wide range of dissolved substances, including the hardness-causing metal ions mentioned above. These dissolved substances may be solids, liquids or gases. One of these gases, carbon dioxide, which is present in all rain water actually enhances the dissolving capacity of water because of its acidic nature. This is of great importance when rain water is flowing over rocks containing compounds of the Group II elements calcium and magnesium. Examples of these rocks include gypsum (calcium sulphate), limestone, marble, calcite, etc., (calcium carbonate) and dolomite (magnesium carbonate and calcium carbonate). The result of water flowing over these rocks is the presence of calcium and magnesium ions in the water which imparts the property of hardness to it.

Since limestone rock is very widespread in this country its solution and deposition are the most important processes to take into account when considering hardness in water in Ireland. As limestone, $CaCO_3$, is not very soluble in pure water, its saturation concentrations vary from about 13 p.p.m. at 16 °C to about 15 p.p.m. at 25 °C. This level of solubility does not account for the much higher concentrations of Ca^{2+} ions which are common in natural waters. Other solvents, especially carbonic acid, have been shown to be responsible for this increased solubility of $CaCO_3$. The presence of organic acids, for example lactic acid which can result from rotting vegetation, can also play a significant part in the solution of $CaCO_3$. Processes of this type make a major contribution to the dissolution of $CaCO_3$ in Ireland, where peaty water is regularly in contact with limestone rock. Chelating agents are other organic compounds which bind to calcium and have a similar effect to that of acids on limestone. Sulphuric acid is an effective solvent of limestone. The sulphuric acid may originate from the burning of fossil fuels or may be produced by the weathering of sulphide minerals such as pyrites. It is generally accepted that nitric acid in rainwater as a result of lightning storms makes a negligible contribution as a limestone solvent.

The role played by carbonic acid is complex, as it involves the carbon dioxide-water-calcium carbonate equilibrium systems. It is not a matter of one simple reaction to produce more soluble hydrogencarbonate and less soluble carbonate, but of a series of reversible reactions and ionic equilibria. Dissolved calcium carbonate is in an ionic state

$$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$$

Natural waters have some carbon dioxide in solution. The equilibrium amount increases with rising partial pressure of carbon dioxide in the air in contact with the water and falls with rising water temperature. A little of the dissolved CO_2 reacts very rapidly with the water to produce carbonic acid according to the following equilibrium reactions.

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+ \rightleftharpoons H_2CO_3$$

Calcium carbonate then reacts with the carbonic acid to produce soluble calcium hydrogencarbonate:

$$CaCO_3 + HCO_3^- + H^+ \rightleftharpoons Ca(HCO_3)_2$$

This last reaction disturbs the equilibria represented in the first two equations and increases the concentration of dissolved Ca^{2+} in the water quite significantly.

For convenience hardness is always quoted in p.p.m. of $CaCO_3$ despite the fact that (i) calcium carbonate rock may not be the origin of all or any of the hardness present, and (ii) even where calcium carbonate rock is present, the calcium carbonate itself is only very sparingly soluble in water and most of the hardness present would be actually attributable to the compound calcium hydrogencarbonate. This allows direct comparison of the hardness of different water samples and benefits from the fact that $CaCO_3$ has a relative formula mass of 100 which is convenient in calculations.

Typical hardness values for water running over limestone would be around 200 - 300 p.p.m. of $CaCO_3$. Comparing these figures with the solubility of calcium carbonate in pure water given above clearly demonstrates the effect of dissolved CO_2 on limestone solubility. Ground water may have even higher values of hardness, e.g. in excess of 400 p.p.m.

2.2 Temporary and Permanent Hardness

Temporary hardness is referred to as hardness in water which can be removed by boiling, while permanent hardness cannot be removed by boiling.

Temporary hardness is caused by the presence in the water of calcium hydrogencarbonate and magnesium hydrogencarbonate, the former being far more common than the latter in Irish waters, again because of the prevalence of limestone rock.

This form of hardness arises when rain water, containing the weak acid carbonic acid (H_2CO_3), runs over limestone rocks dissolving out Ca^{2+} according to

$$CaCO_3 + HCO_3^- + H^+ \rightleftharpoons Ca(HCO_3)_2$$

The dissolved $Ca(HCO_3)_2$ is now responsible for the temporary hardness.

When this hard water is boiled a reaction occurs which results in the calcium ions being precipitated out of solution in the form of $CaCO_3$ which is almost insoluble. This precipitate forms the deposit called ‘scale’ or ‘fur’ which is often clearly visible on the inside of kettles and boilers in hard-water regions.

$$Ca(HCO_3)_{2(aq)} \xrightarrow{\text{heat}} CaCO_{3(s)} + H_2O_{(l)} + CO_{2(g)}$$

Any process which removes or reduces the degree of hardness of a water sample is termed water softening. Boiling a sample of water which has temporary hardness is an example of a water softening method.

Permanent hardness is caused by the presence of dissolved calcium and magnesium sulphates and calcium and magnesium chlorides. An example of how this type of hardness can be acquired by water is where water is flowing through, or over, gypsum rocks (calcium sulphate). The calcium sulphate is slightly soluble in water and so the water contains dissolved calcium sulphate after passing through the rocks, giving a hardness of up to about 500 p.p.m., again recorded as 500 p.p.m. $CaCO_3$.

Permanent hardness cannot be removed by boiling and therefore alternative methods must be used to soften the water where that is necessary.

The sum of the temporary hardness and the permanent hardness is referred to as the total hardness.

2.3 Methods of Removing Hardness from Water - Water Softening

A number of methods are used for removing hardness.

Distillation

This removes all dissolved substances, including gases, from water, and produces very pure water, particularly if the distillation is repeated a number of times. However, due to high energy costs it is very expensive and is generally only used when very high purity water is required for analytical laboratory work and production of pharmaceuticals. Often car batteries are topped up with distilled water.

Addition of Washing Soda

Washing soda is essentially a crystalline sodium carbonate hydrate. The sodium ions undergo an exchange reaction with the calcium ions present in the hard water causing the formation of insoluble calcium carbonate which can precipitate out as follows.

$$Ca^{2+}_{(aq)} + Na_2CO_{3(aq)} \rightarrow CaCO_{3(s)} + 2Na^{+}_{(aq)}$$

The use of inexpensive washing soda in this way was a traditional wash-day technique for economising on soap which was quite an expensive commodity. Water softened in this way is very suitable for washing but not suitable for drinking or most other purposes.

Other substances, e.g. calcium hydroxide and sodium sesquicarbonate, work in a similar way by precipitating the ions which cause hardness. Sodium sesquicarbonate, $Na_2CO_3.NaHCO_3.2H_2O$, is better than sodium carbonate for household use because it is less alkaline.

Bath salts, e.g. Radox, contain crystals of sodium carbonate, colourings and perfumes. The function of the sodium carbonate is simply to soften the water, thus allowing soap to be as effective as possible in producing a luxurious foamy lather.

Ion-exchange Resins and Deionisers

Ion-exchange is a process by which water is passed through a column of a material which replaces one kind of ion with another. The ions come from the solid phase (ion-exchange resin) and are exchanged with ions in the water. Some naturally-occurring materials may be used for ion exchange, e.g. zeolite - a type of clay. These clays are complex sodium aluminium silicates. In this type of ion-exchange resin the hardness-causing calcium and magnesium ions are replaced by sodium ions from the zeolite as the water flows through the material. The water is softened but not deionised.

However, synthetic ion-exchange resins, manufactured in the form of small insoluble beads, are now more commonly used. Ion-exchange resins are compounds with a very open molecular structure that can capture positive ions, including Mg^{2+} and Ca^{2+}, and exchange them for H^+ ions, which become H_3O^+ in solution; negative ions such as Cl^- or SO_4^{2-} can be exchanged for OH^- ions. The H_3O^+ ions react with the OH^- ions and form water. Thus, any dissolved ionic substances, including those responsible for hardness, are completely removed from the water by a combination of cation-exchange material and anion-exchange material. The water is completely deionised in the process.

The cation-exchange material generally consists of three parts. The main bulk of the material does not take part in the ion exchange but acts as a support and is usually labelled R, the active site which contains a group such as SO_3^- or CO_2^- and the cation which is to be exchanged, i.e. H^+ ions.

The following equilibrium is established when the exchange resin comes in contact with a solution containing ions as it passes through the resin.

$$Na^+_{(aq)} + RSO_3^- H^+_{(resin)} \rightleftharpoons RSO_3^- Na^+_{(resin)} + H^+_{(aq)}$$

Positive ion exchange can be demonstrated in the laboratory by packing some cation-exchange resin into a column and passing deionised water through the column first. The solution exiting the column is neutral to universal indicator. If dilute sodium chloride solution is then passed through the column the solution exiting the column is acidic. It also gives a positive test for chloride ions showing that it is most likely dilute hydrochloric acid solution. To produce a better visual effect, if a solution of copper(II) sulphate, $CuSO_4$, is passed through cation-exchange resin the blue colour is removed because the hydrated copper(II) ions are removed from solution and the colourless liquid exiting the column is acidic (sulphuric acid solution).

The cation ion-exchange resin can be regenerated by washing the column with dilute hydrochloric or sulphuric acid. This is done until the solution exiting the column is acidic and then the column is washed with deionised (or distilled) water until the solution exiting the column is neutral to universal indicator.
Many anion-exchange resins are synthetic resins containing quaternary ammonium groups R_4N^+. As a solution containing chloride ion is passed through a column of anion-exchange resin the following equilibrium is set up.

$$Cl^-_{(aq)} + R_4N^+OH^-_{(resin)} \rightleftharpoons R_4N^+Cl^-_{(resin)} + OH^-_{(aq)}$$

The ion-exchange resin may be regenerated by passing a solution of sodium hydroxide through it. This is done until the solution exiting the column is basic and then the column is washed with deionised (or distilled) water until the solution exiting the column is neutral to universal indicator.

If tap water is run slowly through an ion-exchange resin containing cation and anion-exchange material, deionised water of low conductivity can be obtained. This type of ion exchange is a convenient and relatively economical method used in school and college laboratories to supply deionised water. This type of ion-exchange is also the method most favoured by industry for the production of very large quantities of low-conductivity water. Again the method is convenient, reliable and economical. Very pure water is needed industrially for use in high pressure boilers, because even very small quantities of impurities can lead to the formation of sediment. Industrial boiler water is probably the purest high-tonnage chemical used, for it must have no more than 0.02 p.p.m. of impurity (approximately 2 g of impurity in 100 t of water).

Domestic water softeners, which are attached to the water supply not intended for drinking but rather connected to the central heating system, immersion heater, hot water supply, etc., contain zeolite-type cation ion-exchange resins which exchange Ca^{2+} ions in the water supply for Na^+ ions. These resins are regenerated by passing a solution of sodium chloride through them. This process of regeneration can be automated with the regeneration solution being passed through the resin at suitable intervals as required.

A second type of domestic ion-exchange unit has recently become quite popular. These may be connected to the drinking water supply or can be added as cartridges to jugs of water from the tap and are used to ‘purify’ the water. They contain burnt coconut shell and ion-exchange material to reduce the non-ionic and ionic content of water.

They are intended to improve the taste and quality of water which has been pre-treated. However, the pleasant taste and health benefits of dissolved calcium ions are actually reduced in the process. Fluoride ion, which is the cause of some controversy, is also removed.

Calgon

Another way of softening water involves the use of ‘Calgon’, the trade name for sodium tripolyphosphate. This substance works by forming complexes with the calcium and magnesium ions, leaving them in solution but unable to react with soap. Again the water is softened but not fit for drinking.

2.4 Soaps and Detergents

It has been mentioned already that soaps are the sodium and potassium salts of long-chain fatty acids. The cleaning action of soap is due to the attraction of the negative carboxylate part of the molecule for water and the hydrocarbon chain of the fatty acid for grease, oil and dirt. This end dissolves in the grease, encapsulates it and is then removed by rinsing it with water. However, as already discussed, soaps react with calcium and magnesium ions in water to form insoluble salts which are commonly referred to as ‘scum’. It is worth noting that no scum is formed with modern synthetic detergents.

Soaps and detergents have considerably different structures as shown in Fig. 2.1.

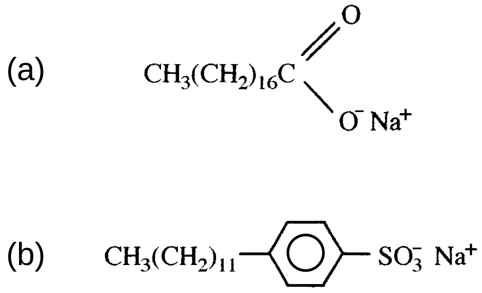


Fig. 2.1 *(a) a typical soap (the sodium salt of a fatty acid), (b) a typical synthetic detergent*

Originally the word detergent simply meant a cleaning agent but in modern times it signifies a soapless, or synthetic detergent, which does not produce a scum in hard water. Common examples of detergents are the alkylbenzenesulphonates, Fig. 2.2.

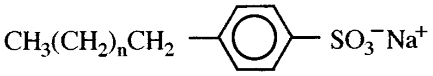


Fig. 2.2 *Alkylbenzenesulphonate salt*

The first synthetic detergents were developed as far back as the 1930s but it was not until about 1946 that they began to compete with the cleaning power of soap. Since that time, synthetic detergents have largely replaced soap for washing clothes and dishes. Soap is made from vegetable oils or animal fats whereas detergents are made from by-products of oil refining. Detergent molecules are often described as having a long hydrocarbon 'tail' and an ionic or polar ‘head’. The hydrocarbon end of the molecule mixes well with oil and grease but not with water - hydrophobic - and the polar head dissolves well in water - hydrophilic; ‘like dissolves like’.

A typical detergent molecule works in two ways. Firstly, the molecules congregate at the surface of the water with the polar ends in the water and the hydrocarbon ends out of it, Fig. 2.3. This destroys some of the hydrogen bonding at the surface of the water. The result is that the surface tension is reduced and this enables the water to wet the surface of the object being washed more effectively. This action of a detergent may easily be demonstrated by pouring a small amount of water on a non-stick frying pan. The water simply collects in droplets. If a little detergent is then added to the water, the water immediately spreads out over the entire surface of the pan. For this reason detergents are often referred to as ‘wetting agents’. Secondly, the detergent molecule allows grease to mix with water. The non-polar hydrocarbon end of the molecule dissolves in the grease. The polar end of the molecule then allows the grease into solution.

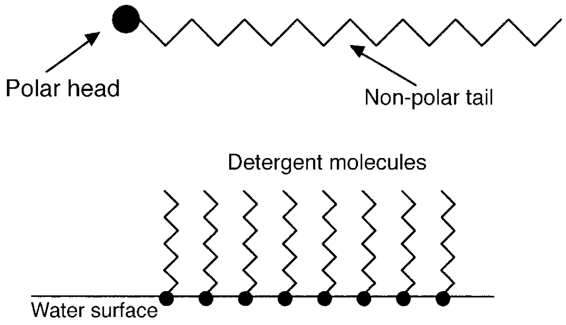


Fig. 2.3 *Action of detergent molecules*

It has been found that straight chain alkylbenzenesulphonates are biodegradable. However, as the number of branches in the alkyl group increases, bacteria become less able to break down the detergent molecule. The earliest synthetic detergents were not biodegradable. The cheapest and easiest detergents to make had a branched hydrocarbon chain rather than a linear one. In the 1960s the branched chain compounds tended to cause foaming in rivers, streams, sewage treatment plants, septic tanks, etc. For this reason, highly branched alkylbenzenesulphonates are no longer used in the manufacture of detergents.

It is a surprising fact that a typical packet of detergent contains only about 20% of actual detergent. About 30% of the contents consists of inorganic phosphates which help to soften the water by removing soluble calcium salts and thus increase the cleaning action of the detergents. The pollution problems caused by these phosphates are discussed in Chapter 3. The other ingredients found in a packet of detergent include bleaches, brighteners, enzymes, etc.

2.5 Total Hardness in Water

Estimation of Total Hardness in Water

As ethylenediaminetetraacetic acid, edta, and its disodium salt are used in schools to determine the hardness of water, it is appropriate to include some background information on the use of this reagent. It is important to realise that edta is a complexometric reagent and all such reagents have some common essential properties for use in titrations.

(a) The titrant must react stoichiometrically, preferably in a one-step reaction, or at most a two-step reaction.

(b) The reaction of the titrant with the ion being analysed must be at least rapid, if not instantaneous.

(c) The reaction must go to completion.

(d) The end-point of the titration must be capable of being detected - either instrumentally or by visual indication.

In complex formation there is a central metal cation, which is an electron pair acceptor reacting with ligand groups which are electron pair donors. In general, compounds containing atoms which have lone pairs of electrons make very good ligands, as these lone pairs are readily donated to a metal cation to form dative covalent bonds. For example, it is well known that ethanoate ions form complexes with many metal ions through the donation of a lone pair of electrons on the carbonyl oxygen atom. Compounds containing nitrogen atoms are also good complexing agents for a similar reason.

A great many compounds containing ethanoate or amino groups, or both, were tested by Schwarzenbach and co-workers in this field during the 1930s and 1940s in an effort to find a suitable complexing reagent which could be used in metal ion analysis. The main problem was to find reagents that would complex completely and in one step.

Carboxylic acid groups, taken in conjunction with amino groups as aminopolycarboxylic acids, were found to act as very good chelating agents. Schwarzenbach (1945) found the most outstanding of these to be ethylenediaminetetraacetic acid (edta). This is more correctly called bis[di(carboxymethyl)amino]ethane, but it is simply known as edta and is likely to remain so. Its structure is shown in Fig. 2.4.

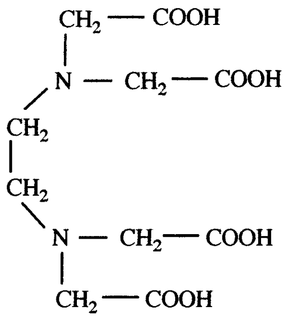


***Fig. 2.4** Bis[di(carboxymethyl)amino]ethane or ethylenediaminetetraacetic (edta) acid*

The complexing power of edta lies in the ability of two nitrogen atoms and an oxygen atom from each ethanoic acid group to act as an electron pair donor or ligand. In edta these ligands are built into a flexible molecule in such a way as to be easily accessible to metal cations. They are also correctly spaced along the molecule to allow the formation of stable planar five-membered rings with the metal cations. These chelate rings can be formed both across the aminoethanoic acid groups and the ethylenediamine bridge, Fig. 2.5.

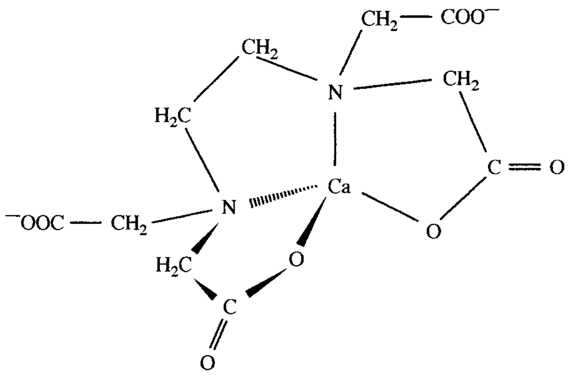


Fig. 2.5

It is found that edta forms very stable complexes with almost every metal in the periodic table.

M + edta → M-edta

The only exceptions are the alkali metals.

Ethylenediaminetetraacetic acid, edta, is said to be hexadentate, i.e. it has a total of six ligand groups - four carboxyl oxygens and two amino nitrogens - available for co-ordination to a metal cation. It can also operate as a tetradentate or pentadentate ligand. In the case of Ca^{2+} and Mg^{2+} complexes it is tetradentate, with only four ligands, the two carboxyl oxygens and the two amino nitrogens complexed to the cation. In this case, the complex formed contains three five-membered rings, Fig 2.5. The structure of such complexes is difficult to portray in two dimensions, and is best shown using molecular models.

In titrations where disodium edta is used to estimate water hardness the detection of the end-point involves the use of metallochromic indicators. Metallochromic indicators are substances which form stable, brightly coloured complexes with metal cations.

$$\underset{\text{Colour A, 'Free' indicator}}{\text{In}} + \text{M} \rightleftharpoons \underset{\text{Colour B, Metal-indicator complex}}{\text{M-In}} \qquad (1)$$

The free, uncomplexed indicator has a definite colour (colour A), and the metal-indicator complex has a different colour (colour B). During the titration, up to the end-point, the reaction in the titration flask may be represented by the equation

$$\text{M-In} + \text{M} + \text{edta} \rightarrow \text{M-edta} + \text{M-In} \qquad (2)$$

At the end-point, once all the free metal ions have been complexed by the edta, when further edta is added it breaks up the M-In complex to give the 'free' indicator and the colour changes to colour A. The reaction which occurs is

$$\underset{\text{Colour B}}{\text{M-In}} + \text{edta} \rightarrow \underset{\text{Colour A}}{\text{M-edta} + \text{In}}$$

These reactions impose very severe limitations on the indicator. It can be seen from reaction (1) that the M-In complex must be fairly stable in order to maintain colour B up to the end-point. If it is not stable enough, the edta will break it up before the end-point, the colour will change to A and a premature end-point will be obtained. On the other hand, it is essential that the stability of the metal-indicator complex is less than the stability of the metal-edta complex, so that at the end-point metal ions are stripped from the metal-indicator complex, releasing the free indicator and changing the colour of the solution from B to A. If the M-In complex is more stable than the M-edta complex, then at the end-point added edta will not break up the M-In complex, colour B will persist and a late or retarded end-point will be obtained. The development of edta titrations was held up for many years due to the lack of suitable indicators. Indeed, the search for new indicators is ongoing.

Titration with standard edta is widely used to determine the amount of hardness in water. Usually, it is the sum of the temporary and the permanent hardness (the total hardness) which is determined. As already discussed, the colour change of a visual indicator is used to mark the end-point of the titration. An 'inhibitor' is sometimes added to complex iron or other metal salts that might interfere with the action of the indicator. Although both calcium and magnesium are titrated with the standard edta, total hardness is calculated as if it were all calcium carbonate, $CaCO_3$. The hardness is expressed as p.p.m. of $CaCO_3$.

The total hardness is usually determined by titration with standard 0.01 M edta solution. The solution must be buffered to maintain a pH of 10 throughout the titration. In an acidic or neutral solution, the extent of complex formation between edta and calcium and magnesium will not be complete and thus, erroneous results are obtained. A suitable buffer for this purpose is the ammonium chloride-ammonia buffer (see Chapter 1).

The two most commonly used indicators are calmagite and a closely related compound, Eriochrome Black T (also called Solochrome Black T). Indicator solutions of calmagite are more stable than solutions of Eriochrome Black T which decomposes slowly on standing. Calmagite and Eriochrome Black T may be used interchangeably. The solvent used for the indicator solutions is usually alcohol. Indicator solution of suitable strength can conveniently be prepared by dissolving 1 g of Eriochrome Black T in 100 cm^3 of ethanol. Care must always be taken to ensure that a sufficient number of drops of indicator solution are added to the water sample under test. It is common to use Eriochrome Black T indicator as solid, in which case only minute quantities of the solid are required. Alternatively, the solid Eriochrome Black T may be dispersed in sodium chloride thus allowing larger quantities of solid mixture to be added to the water sample before titration.

As edta is not very soluble in water in its acid form, its disodium salt is used. The calcium (or magnesium) ions can react with either the acid or disodium salt and form a complex.

$$\underset{\text{}}{Ca^{2+}} + \underset{\text{edta ion}}{H_2X^{2-}} \rightarrow \underset{\text{calcium complex of edta}}{CaX^{2-}} + 2H^+_{(aq)}$$

It should be emphasised that Ca^{2+} ions or Mg^{2+} ions react with edta in a 1:1 ratio. The free indicator is blue but the magnesium complex formed with it in water is wine-red. When the free metal ions are all titrated, a drop or two of edta causes the end-point reaction to occur. This reaction involves breaking down the indicator-magnesium complex which is wine-red, generating the free indicator which is blue (see below).

If calcium and magnesium are present in the same sample, the free calcium and magnesium ions are titrated together. The end-point reaction is between edta and the magnesium/indicator complex (the indicator reacts with magnesium in preference to calcium) and the end-point is sharp. As the end-point is approached, the edta must be added very slowly and the flask swirled continuously, because the reaction between the edta and the metal ions is fairly slow.

If the water sample does not contain any Mg^{2+} ions some should be added, otherwise the initial wine-red colour of the magnesium/indicator complex will not be present. When the indicator is added to hard water, the indicator forms a complex with the Mg^{2+} ions rather than with the Ca^{2+} ions in the hard water. The amount of edta equivalent to the magnesium is subtracted from the total edta used in the titration. Alternatively, magnesium-edta may be added before the titration, in which case no subtraction is necessary (see below).

In the analysis of ‘real’ water samples, as opposed to ‘artificial’ water samples prepared in the laboratory for various purposes, some modifications in the titration procedure may be necessary to avoid interference from impurities that may be present in the water. Water frequently contains small amounts of iron ions and other dissolved metals which react irreversibly with the indicator and prevent an accurate end-point in the titration of magnesium and calcium ions. If the iron concentration is quite low, the ammonia buffer will keep the pH of the mixture sufficiently high to give rise to the formation of hydroxy complexes of the iron and so prevent interference with the performance of the indicator. Sodium cyanide will sometimes prevent interference from slightly larger amounts of iron and from copper(II) ions by forming cyanide complexes of the metal ions. Triethanolamine is effective with dissolved aluminium but somewhat less effective than cyanide with iron. Sodium cyanide and triethanolamine can both be described as acting as ‘masking agents’ in this sense, as they prevent any interference with achieving the correct analysis of calcium and magnesium ions in the water.

Difficulties Associated with the Indicator Eriochrome Black T

There are a number of difficulties associated with the use of Eriochrome Black T. The end-point can be blocked by the presence of traces of Fe(III) and Al(III) in the sample. The level of Fe(III) should be less than 20 p.p.m. and that of Al(III) less than 50 p.p.m. Both of these ions form very stable complexes with the indicator and these complexes do not break down at the end-point. The colour change from wine-red to blue does not occur at the true end-point, and indeed it may take several cm^3 of edta in excess beyond the true end-point before the colour changes. Eriochrome Black T is an azo dye and, like many such compounds, contains ionisable or labile protons. Loss or gain of these protons affects the frequency of vibration of the azo bond, thus changing the colour of the dye. Such loss or gain of protons is a function of the pH of the solution and the exact form of the Eriochrome Black T in solution and consequently its colour depends on pH. In simple terms Eriochrome Black T is not only a metallochromic indicator but also an acid-base indicator, and the colour changes depend not only on the presence or absence of metal ions but also on the pH. If the pH of the sample is not correct (pH = 10) then serious problems leading to loss of metallic indication arise.

Eriochrome Black T is a tribasic acid and we can represent the free indicator as H_3In. Depending on pH, the uncomplexed free indicator can exist as H_2In^-, HIn^{2-} or In^{3-}, each of which has a different colour - red, blue and orange-red, respectively. When complexed to a metal ion, the M-Eriochrome Black T complex is always wine-red irrespective of pH. If Eriochrome Black T is used for metallic indication at too low a pH ($pH < 5.5$) then the colour change at the end-point is from wine-red to red and no clear indication is observed. Similarly, if the pH is too high ($pH > 11.5$) the colour change is from wine-red to an orange-red and it is impossible to judge the end-point. At pH = 10, which is the normal pH used for water hardness determination, the colour of the free indicator is blue, and thus the colour change for metallic indication is wine-red to blue, Fig. 2.6.

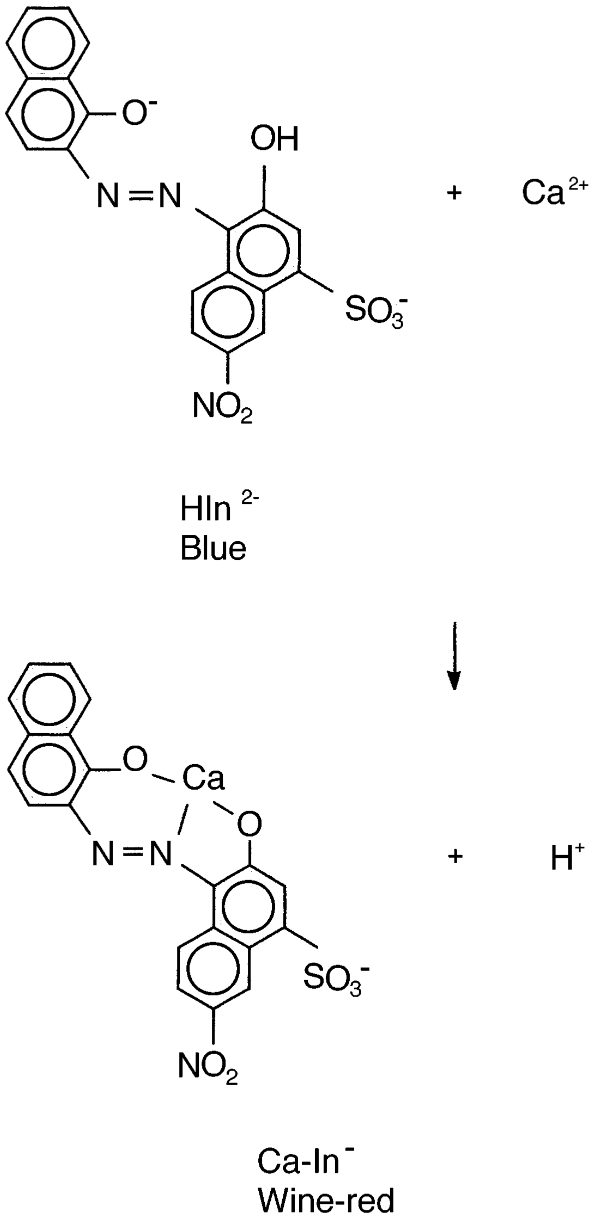


Fig. 2.6

Therefore, Eriochrome Black T can only be used for metallic indication between pH = 7.5 and pH = 10.5. For reasons connected with the instability of the Ca-edta complexes at lower pH values, water hardness determinations are usually carried out towards the higher end of this pH range, i.e. at pH = 10.

It must be remembered that the metal-Eriochrome Black T complex must be fairly stable, otherwise it will dissociate before the end-point is reached, giving a premature drifting end-point. In addition, the metal-Eriochrome Black T complex must be less stable than the metal-edta complex, or it will not break down to give the free indicator and a colour change until perhaps a large excess of edta is added, well beyond the end-point. Unfortunately, the Ca-edta complex is not very stable. The Ca-Eriochrome Black T complex, while being less stable than the Ca-edta complex as required, is not as stable as might be desired to give good end-points. That is, the end-point tends to be premature, and this is particularly true for samples of low hardness, where the relative error may be quite high.

If the sample contains some magnesium the problem is circumvented because the Mg^{2+} will form the more stable Mg-Eriochrome Black T complex whose breakdown at the end-point gives the colour change. In samples in which the hardness is low and which contain no Mg^{2+} some analysts add a few cm^3 of a Mg-edta solution to the sample to improve the end-point. This is accomplished by titrating a solution containing Mg^{2+} just to the end-point, and then adding a few cm^3 of this solution to the water sample whose hardness is to be determined. A further problem which may be encountered is the fact that some natural water samples contain buffering agents, such as phosphates, and have a buffered pH around a pH of 5. The natural buffering of these samples may need more than the usual 2-3 cm^3 of buffer pH10 normally added to bring the sample to pH10.

Making Up Your Own Hard Water Solutions

To avoid any problems arising from the presence of Fe(III) or Al(III) and natural buffering systems, it may be convenient for school laboratory work to make up an artificial water sample. Such a sample can be made to contain both permanent and temporary hardness. Since it is made from laboratory-grade chemicals and deionised water there is no possibility of outside interference. A sample, containing about 250 p.p.m. $CaCO_3$ total hardness (150 p.p.m. $CaCO_3$ permanent hardness and 100 p.p.m. $CaCO_3$ temporary hardness), can be made up. Weigh out about 0.5 g of calcium chloride hexahydrate, $CaCl_2.6H_2O$, and about 0.1 g of magnesium chloride hexahydrate, $MgCl_2.6H_2O$ (remember that these salts are deliquescent - weigh quickly and re-seal the bottle at once) and dissolve in about 600 cm^3 of deionised water in a one litre volumetric flask. When this has dissolved add about 0.17 - 0.20 g of sodium hydrogencarbonate, $NaHCO_3$, allow it to dissolve and make up to the mark with deionised water. (**Note**: the $CaCl_2.6H_2O$ and the $MgCl_2.6H_2O$ must be well dissolved before attempting to dissolve the $NaHCO_3$.) A 50 cm^3 sample of this solution will require 12 - 13 cm^3 of 0.01 M edta to titrate the total hardness and about 7 - 8 cm^3 to titrate the permanent hardness.

Hard Water Regions and Industrial Implications

The hardness or softness of water varies from place to place and reflects the nature of the geology of the area from which the water has come. In general, surface waters are softer than ground waters, although not always. Hard waters are associated with chalk and limestone catchment areas, whereas soft waters are associated with impermeable rocks such as granite. Some areas of Ireland have geological formations which are largely limestone, e.g. the Burren. The water in this area would be expected to have high temporary hardness levels.

The hardness of a water supply causes a nuisance in industry whenever water is to be heated. When heated, temporary hardness will result in carbonate precipitates forming on the insides of pipes and boilers. This reduces their efficiency considerably. Hence industry, particularly chemical industries, often locate where soft water is available, e.g. Cork Harbour. The infrastructural nature of this area is among the many other important parameters which dictate the location of an industry.

2.6 Student Experiment

Estimation of the Total Hardness in Water

This titration involves titrating a sample of water (usually but not always 100 cm^3) with a solution of disodium ethylenediaminetetraacetic acid (Na_2edta) in the presence of a buffer which holds the pH at about 10.

$$Na_2edta + Ca^{2+} \rightarrow Caedta + 2Na^+$$

The indicator is Eriochrome Black T and it changes colour at the end-point from wine-red to blue. An unusual feature is that the indicator is added as a tiny pinch of solid.

Notes

1. When the disodium edta solution is being made up a small quantity of magnesium sulphate is always added. This is done because the end-points observed for titrations involving water samples containing only calcium hardness are difficult to detect. This problem does not arise in the presence of magnesium ions. The amount of magnesium ions added in making up the solution is not a significant factor in the accuracy of the experiment. It can be allowed for in making up the disodium edta solution for high accuracy work.
2. Buffer solutions are solutions which resist change in pH when small amounts of either acids or bases are added to them. In this case the buffer is a mixture of ammonium chloride and aqueous ammonia and maintains a pH of just above 10 for the titration.
3. The pH is maintained at 10 because at this pH the indicator works well (its complexes with the magnesium ions present break down rapidly and allow a clearly detectable end-point).
4. The structure of disodium ethylenediaminetetraacetic acid is shown in Fig. 2.7.

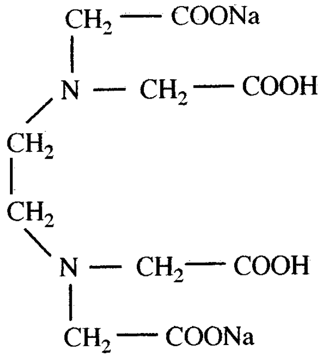


Fig. 2.7

5. The calculation involves application of the formula

$$\left(\frac{VM}{n}\right)_{Na_2edta} = \left(\frac{VM}{n}\right)_{Ca^{2+}}$$

where V = volume, M = molarity, n = number of moles in the balanced equation.

Having got the molarity of the Ca^{2+} ions, express this as moles $CaCO_3$ per litre and then as mg per litre, i.e. parts per million (p.p.m.).

CHAPTER 3

WATER AND WATER TREATMENT

3.1 Requirements of a Safe Supply of Water for Domestic Use

Water is a necessity of life. However, because of the ability of water to act as a solvent for a wide range of organic and inorganic materials and its ability to act as a habitat for micro-organisms, few, if any, natural waters are suitable for domestic use in an untreated form.

All water is essentially derived from the water cycle, ending up on land as a result of rain, hail or snow. Some of the rain falling on the ground flows into rivers, streams, natural ponds, lakes and man-made reservoirs. These are the main sources of surface water. Underground sources include boreholes and springs. There are considerable reserves of water in the polar ice caps, and permanent snow and ice at high altitudes and in the atmosphere.

Water is liable to pollution from a variety of sources. It is the responsibility of the water chemists and sanitary engineers to convert raw water into a safe, potable (drinkable) water supply that is free from colour, odour, suspended solids, toxic compounds, bacteria and other micro-organisms.

A list of the problems associated with water sources/supplies are summarised here.

Colour contamination of natural water can originate from dissolved organic matter from peaty land. Salts of iron or manganese can also be dissolved from rocks and impart a colour to the water.

Suspended solids consist of vegetable and mineral debris which is unable to settle. This inability of material to settle is a function of prevailing conditions, e.g. a river in flood will carry more suspended material than would be the case in calmer conditions.

Turbidity refers to the lack of clarity of a water sample. Turbidity originates from material which does not settle even when the water is left undisturbed. The size of the particles causing turbidity is small and such that small electrostatic repulsions between them prevent them from settling. The nature of the particles ranges from microscopic bubbles of air to fine particles of clay or high concentrations of bacteria.

Pathogenic material originating from sewage and animal waste products can take the form of viruses, bacteria or protozoa.

Hardness due to dissolved salts of calcium and magnesium is a major problem in some areas where dissolution of minerals from the calcium- and magnesium-containing rock formations occurs. Ions other than calcium and magnesium also cause water hardness though they are rarely significant contributors to the total hardness of a supply (see Chapter 2).

Taste and odour of a water sample can be affected by contaminants such as sewage, chemical pollution, decayed vegetation or stagnation due to a lack of oxygen in the water.

Toxic chemicals of inorganic and organic origin can contaminate a water supply. These can be either absorbed from the soil or originate from seepage of sewage or industrial waste.

Treatment is necessary to deal with one or more of these problems, any or all of which can be encountered with raw water. In most cases the water treatment process uses simple physical separation techniques. Treated water should be reasonably soft and free from the problems listed above.

3.2 Water Treatment

Most water treatment processes consist of several stages. These normally include storage, screening, settling or clarification, chlorination, pH adjustment, fluoridation and filtration. The sequence of the stages may vary from one water treatment plant to another and some stages may involve more than one step. However, the basic principles always remain the same.

Stages of Water Treatment

The various stages of water treatment are summarised in Fig. 3.1.

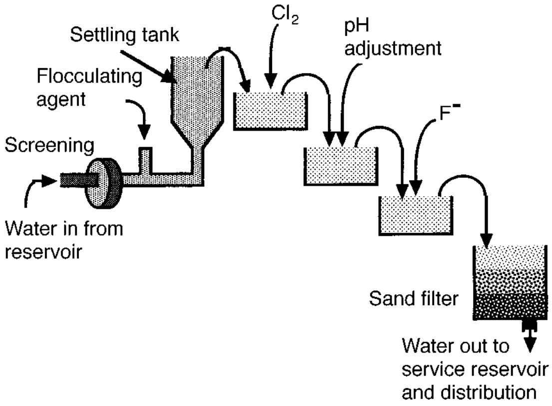


Fig. 3.1 *Stages of water treatment*

Storage

To ensure a continuous supply of large quantities of raw water of consistent quality water is often stored in large reservoirs before it is taken into a water treatment works. This is essential to overcome seasonal variations in the availability of raw water and to enable supplies to be uninterrupted during periods of low rainfall.

Following treatment it is necessary also to store large quantities of product water in service reservoirs or water towers, so that a supply of water to the customer at a steady pressure is guaranteed, and to overcome daily fluctuations in demand.

In general, the longer water is stored in the open before treatment the better. As water is stored, several natural processes serve to give the water an excellent pre-treatment. Larger suspended solids can settle or, in some cases, be biologically degraded by micro-organisms present. Sunlight can have a bleaching effect, removing or reducing colour contamination. The ultraviolet radiation present in sunlight can destroy some bacteria present, including some pathogenic micro-organisms. The main disadvantages of storing water for long periods prior to treatment are pollution from the atmosphere, pollution from birds and algal growth. Algal growth becomes a significant problem when water is stored for periods of more than about ten days.

Screening

The raw water is passed through coarse screens and then fine screens or microstrainers. The former remove large debris while the latter, which usually take the form of rotating stainless steel drums with about 25 000 openings per square centimetre, remove fine particles. These processes also remove much of the algal content of the water and even some pathogens.

Settling or clarification

Even after screening through very fine screens the water still contains small suspended particles (turbidity) which may not settle even if the water is allowed to stand for prolonged periods. These particles, which generally have a diameter less than 10 µm, may be clay, metal oxides, large proteins or micro-organisms. Very small particles often have a negative charge and repulsion between the particles does not allow them to settle and keeps them suspended. Hence coagulation of these particles does not tend to occur. Larger particles usually coagulate and sink.

The precipitation of the particles causing turbidity is achieved using coagulating agents. The most common coagulating agents are aluminium sulphate, $Al_2(SO_4)_3$, iron(III) sulphate, $Fe_2(SO_4)_3$ and iron(II) sulphate, $FeSO_4$. The latter is normally used in conjunction with chlorine, making the active coagulating agent iron(III) sulphate iron(III) chloride, $Fe_2(SO_4)_3.FeCl_3$. Aluminium sulphate reacts with hydrogencarbonates in the water to form flocs which settle rapidly. In addition, the positive ions attract the tiny negative particles towards them, also assisting the formation of flocs, i.e. larger particles formed by agglomeration of fine suspended particles.

Polyelectrolytes are often added to speed up flocculation or coagulation. There is a wide range of these materials available. They are sold mostly under trade names with little detail as to their exact composition but they are often salts with organic cations or anions of large formula mass. They are used to ‘condition’ the precipitating flocs so that they form larger aggregates which sink more quickly and are less likely to clog the filters encountered later in the treatment works. Usually, laboratory trials are carried out to select the most suitable polyelectrolyte for a given purpose. Polyelectrolytes are also used widely in detergents as anti-foaming agents, in wastewater treatment plants for the same purpose and for the 'conditioning' of sludge prior to settling (see p. 46).

In water treatment the coagulant or flocculating agent is normally added in a concentration of the order 30 - 100 p.p.m. and is usually ‘flash mixed’ with the screened water. This high speed mixing is followed by slower stirring. The colliding particles form aggregates or flocs. Too low a dose of flocculating agent can be ineffective, as flocculation can take a very long time or flocculation may not occur at all. Too large a dose of flocculating agent can lead to unacceptably high residues of the flocculating agent carrying through with the treated water. There is much discussion about this problem in areas where water treatment plants are stretched to meet public demand. Aluminium contamination is probably the most controversial of these agents; there has been ongoing speculation linking it with neurodegenerative diseases such as Alzheimer’s disease.

The flocs produced are separated from the clarified water either by flotation or sedimentation. Flotation involves the use of a ‘dissolved air flotation’ system where air is dissolved in the water-floc mixture under high pressure and this air-water-floc mixture is then released into a tank. The dissolved air comes out of solution and forms microscopic bubbles on the surface of the flocs. This makes the flocs buoyant and carries them to the surface where they are skimmed off. Sedimentation is more common. In sedimentation, as the water rises from the bottom of hopper-shaped tanks, a ‘sludge blanket’ forms and tends to settle, while clarified water decants over the edges into collection trays.

The sludge, which can be removed from the settling or sedimentation tank by either intermittent or continuous ‘bleeding’, has to be handled with care and disposed of under the specifications of environmental legislation.

Chlorination

Elemental chlorine and compounds of chlorine are regularly added to water during the treatment of the water for public supplies. Chlorination is one of a number of possible treatments whose purpose is to disinfect the water to keep the pathogen content down to a safe level. The quantity of chlorine or other chemicals required to sterilise water fully would render the water unfit for human consumption. Ozone treatment and treatment with ultraviolet radiation are two other methods used for disinfecting water, though these are far less popular than chlorination.

The introduction of chlorination in 1908 was accompanied by a dramatic fall in deaths and illnesses associated with water-borne pathogens.

The solubility of elemental chlorine in water (7 g l^{-1}) and its low cost both contribute to its widespread use in water treatment. It is, however, an unpleasant, dangerous treatment process. Large quantities of liquid chlorine have to be transported and handled, with the accompanying risk of release of toxic chlorine gas. The on-site generation of chlorine gas avoids the risks associated with transport and handling the chemical in its liquid state.

The addition of sodium hypochlorite, [sodium chlorate(I)], NaClO, to water is another common method of chlorination. Again, there is a risk associated with the transport of concentrated sodium hypochlorite solutions, including the risk of release of toxic chlorine gas. The on-site production of sodium hypochlorite by the electrolysis of aqueous sodium chloride has to date proved unsatisfactory.

Chlorine reacts with water to give hydrochloric acid, HCl, and hypochlorous acid [chloric(I) acid], HOCl.

$$Cl_2 + H_2O \rightleftharpoons HOCl + HCl$$

The hypochlorous acid, HOCl, is eighty times more effective as a disinfectant than the hypochlorite [chlorate(I)] ion, OCl^-. This effectiveness is measured by the contact time required to kill specified control bacteria. The pH at which the water is treated with chlorine is very significant as it greatly affects the position of the equilibrium involving the dissociation of hypochlorous acid, which is a weak acid.

$$HOCl + H_2O \rightleftharpoons OCl^- + H_3O^+$$

At pH > 9 the dissociated ion, OCl^- is almost exclusively present in solution. At pH = 7.5 the acid is about 50% dissociated, while at pH < 5 the associated acid is almost exclusively present. Thus, at pH < 5 the most effective disinfecting agent is present. The low pH requirement is convenient as alum, the most widely used flocculating or coagulating agent, is the salt of a strong acid and a weak base and tends to render the water acidic as it passes through the settling, clarification and sedimentation stage. The pH is adjusted later in the treatment process (see p. 35).

Chlorine is very reactive and combines with most substances present in water. Metal ions are oxidised and often form colloidal solids. The reaction of chlorine with organic molecules is of particular concern as many halogenated organic compounds are carcinogenic. The formation of compounds such as chloroform, $CHCl_3$, seems to rise in parallel to increases in the dosage of chlorine as disinfectant, particularly if chlorination is carried out at high pH. Other mutagenic organic compounds have also been isolated from chlorinated water. It is therefore desirable to keep the quantities of organic compounds present in water as low as possible to avoid risk from these hazards. Chlorine is often not chosen as the disinfecting agent in water supplies from peaty areas as there is likely to be a significant humus or organic content in the raw water.

Ammonium ion, NH_4^+, is converted to mono-chloroamine, NH_2Cl, dichloroamine, $NHCl_2$, or trichloroamine, NCl_3, by contact with chlorine during the disinfecting process. This uses up chlorine and the dosage has to be increased so that there is still 'free' chlorine to disinfect the water. One advantage of the formation of chloroamines is that they also have disinfecting properties, even though their effectiveness is much lower than that of chlorine. They do however tend to persist in the water supply longer than ‘free’ chlorine. This is a major benefit as it gives protection into the distribution network. Chlorine present in the form of compounds such as chloroamines and chlorinated organic compounds is termed combined chlorine, while chlorine in the form of hypochlorous acid or hypochlorite ion is termed ‘free’ chlorine.

In disinfecting water, the addition of chlorine has to be in sufficient quantity to combine with any reactive species in the water, kill pathogens and provide enough excess chlorine to give protection into the distribution network. Care has to be taken not to add so little chlorine that those a distance down the distribution network have water which may be unsafe. At the same time care must be taken not to add so much chlorine that those consumers closer to the treatment plant do not get too large a dose of chlorine. In general water discharged from a treatment plant has a ‘free’ chlorine level in the region of 0.5 to 1.0 p.p.m.

Where there are problems of odour and taste in a water supply a process called superchlorination can be carried out. Here a large excess of chlorine is added to oxidise any organic compounds present. The excess chlorine is subsequently removed by adding sulphur dioxide.

In the United States the levels of chlorine in treated water are much higher than in Europe. American studies have shown some correlations between cancer of the bladder and chlorine levels.

Ozone is a powerful disinfectant. At a concentration of 1 p.p.m. it will kill all bacteria and reduce taste, odour and colour in a contact time of 10 minutes. It has to be produced on-site. It is more expensive than chlorine, but it is suitable for treating water from peaty areas where a high humus or organic content in the water is observed. It does present one major disadvantage in that it does not have any residual disinfecting effect and does not persist into the distribution network. To counter this problem ozone treatment is often followed by a low chlorine dose to give residual disinfection into the distribution network.

pH adjustment

Before the water leaves the treatment plant its pH is adjusted if necessary. The pH may be adjusted at any point in a treatment plant. It is, however, generally adjusted before fluoridation and the final filtration. If the pH is too low lime, sodium carbonate or caustic soda may be added to raise the pH, while if the pH is too high sulphuric acid is added. Generally it is lime that is needed as the common flocculating agent, aluminium sulphate, is a salt of a strong acid and a weak base and renders the water acidic. The use of lime as a neutralising agent adds hardness to the water (see Chapter 2). Water supply boards rarely worry about this unless the hardness levels rise to the point where problems of sedimentation in the distribution network may occur. Tap water usually has a pH range of 6-8. Water of pH < 6 must be avoided because of the danger of corrosion of pipes. This would be particularly undesirable where old lead pipes were part of the supply system as it would introduce lead salts into the drinking water supply. Lead salts have a cumulative effect in the body tissues and may result in lead poisoning.

Fluoridation

Over the past forty years a number of studies have shown some correlation between fluoride concentration in water and the incidence of tooth decay. It would appear that at fluoride concentrations of around 1.0 p.p.m. maximum benefit is obtained. At concentration levels above 1.5 p.p.m. a dental condition called fluorosis is in evidence. This involves the teeth becoming mottled and brittle. At the higher concentration no benefits vis-à-vis prevention of tooth decay were observed. As fluoride concentrations decreased below 1.0 p.p.m. the occurrence of tooth decay increased again, with little benefit from fluoridation being evident at concentrations lower than 0.1 p.p.m.

Based on these early results a programme of fluoridation was started in Ireland in 1963. Ireland is not alone in this policy. The fluoridation of drinking water is widespread in the USA, Canada, New Zealand, Brazil and much of Eastern Europe. It is not practised in Northern Ireland and is not common in the UK where only about 10% of supplies are fluoridated. Spain has been introducing fluoridation of domestic water supplies gradually since 1985. Fluoridation has been banned in Sweden and phased out in the Netherlands. Evidence that similar reductions in tooth decay amongst children were also observed in population samples where fluoridation was not practised has cast doubt over the cause-and-effect connection which had been made between fluoridation and reduction in tooth decay in the initial studies. Nonetheless, there seem to be some physiological processes which take place at the surface of teeth which suggest that fluoridated water and tooth paste can fight tooth decay. The EU sets directives as to the maximum concentration of fluoride ion present in drinking water as 1.5 p.p.m. at 8 - 12 °C and 0.7 p.p.m. at 25 - 30 °C.

The chemicals added to water to supply fluoride ion include simple salts such as sodium fluoride, NaF, and calcium fluoride, CaF_2. Hexafluorosilicic acid, H_2SiF_6, and its salts, sodium fluorosilicate, Na_2SiF_6 and ammonium fluorosilicate, $(NH_4)_2SiF_6$, are commonly used as fluoridating agents for water supplies. The fluorosilicate ion in all these decomposes in water, generating fluoride ion.

$$SiF_6^{2-} + 3H_2O \rightarrow 6F^- + 6H^+ + SiO_3^{2-}$$

Sodium fluorosilicate is the most commonly used fluoridation agent for reasons of cost and because hexafluorosilicic acid is highly corrosive. It is added as a solid from a hopper, usually at the end of the treatment, and after pH adjustment, to avoid losses.

Filtration

The purpose of filtration is to remove particles from the water, whether these exist in the raw water naturally or whether they have been produced by the coagulation process. Filtration is usually achieved by the downward passage of water through about a metre of finely divided inert material (sand or anthracite) which is on a support bed of coarser material (usually gravel). Drains at the bottom of the filter collect the water as it filters through. As particles are removed, the filter becomes clogged, making the passage of water through it more difficult and ultimately the filter has to be cleaned. The cleaning process with the various types of filter will be described below. The efficiency of the filter depends upon several factors, the nature of the particles to be removed, the size and shape of the media (the sand and the gravel) and the rate of flow through the filter.

Rapid sand filtration is usually used for the final ‘clearing’ of water which has been previously treated by flocculation and sedimentation. Rapid sand filters consist of a layer of coarse grade sand about one metre thick supported on gravel which in turn is on a bed of larger stones. The water is passed down through the filter. Filtration speeds of up to 10 m h^{-1}, i.e. 10 m^3 of water per m^2 of surface per hour, can be achieved with these types of filter (about fifty times the rate of a slow sand filter). However, the filtration speed drops as the surface becomes clogged by the filtered particles. Rapid sand filters are cleaned by ‘air scouring’, i.e. blowing air up through the sand followed by rapid back-washing with clean water. The filter washing takes several minutes and the filter is restored to normal running at full capacity after about twenty minutes. Depending on the quality of the water being filtered and the condition of the sand filter, the washing process may be repeated at intervals ranging from once every few days to several times a day. The wash water is not recycled in the water treatment plant because of the risk of its containing a high concentration of pathogens. The risk of pathogens passing through the sand filter is greatest immediately after back-washing. There are two main types of rapid sand filter, open top systems which allow the water through under gravity and closed systems where the filter is enclosed within a metal shell and the water is forced through under pressure. The latter are more efficient in terms of the quantities of water that can be filtered relative to the space they take up. Rapid sand filtration only provides a coarse filtration of the water and no other treatment. It has to be used in conjunction with other treatment processes if a safe product is to be produced. This contrasts with slow sand filtration (see below).

Slow sand filters, as the name implies, filter water through sand at a comparatively slow speed - about 0.3 m h^{-1}, i.e. 0.3 m^3 of water per m^2 of surface per hour. They consist of a layer of fine sand (c. 0.5 - 2 m deep) over a layer of coarse sand (c. 1 - 2 m deep) which is in turn on a bed of gravel. This treatment process not only provides a very fine filtration but also provides a high degree of biological treatment. The top few millimetres contain denitrifying bacteria which remove compounds of nitrogen and phosphorus from the water. The next 30 cm of fine sand is colonised by bacteria and other micro-organisms which remove organic material from the water. These filters cannot be ‘back-washed’. Cleaning involves scraping off the upper layers of sand every few months. This makes slow sand filters labour intensive and expensive to run.

The quality of the water produced by slow sand filtration is excellent, as the treatment combines physical and biological processes. Pathogenic bacteria, taste and odour are largely removed in the process. Because of the slow filtration rate, they take up much more space than rapid sand filters.

Distribution of water

When water has been treated by a combination of the methods outlined above, it is ready to be distributed to the consumer. In general, the pipes or mains leaving the treatment works, which are often some distance from the area of demand, are of comparatively large diameter (trunk mains). In some cases these will feed by gravity and in other cases it is necessary for the water to be pumped. Generally, these mains feed into covered service reservoirs or towers, the purpose of which is to enable local storage of water to help meet varying demands without directly reflecting that variation on the treatment works. From these reservoirs, outlet mains which branch into progressively smaller pipe work, carry the water to the consumer. In urban areas each individual street has a service main from which individual consumer connections are taken.

Dublin’s Water Supply

To supply the water requirements in the Dublin area, the major treatment plants operated by Dublin Corporation and the County Councils produce over 400 million litres of potable water every day. A population of 1.1 million people is served by these plants. The areas serviced include the City and County of Dublin and parts of Kildare and Wicklow. The demand for water in the Dublin area has increased fourfold since 1930 and to keep pace with this demand major capital schemes have had to be undertaken.

The water for the Dublin area is obtained mainly from rivers, with a smaller proportion from ground water sources. The main sources of water supply are from the man-made reservoirs at Roundwood (River Vartry), Bohernabreena (River Dodder), Poulaphouca (River Liffey) and Leixlip (River Liffey). Water quality can vary a lot depending on where it is obtained, as can its physical and chemical character. For example, water from Roundwood is soft, and that from Leixlip is hard.

Cork’s Water Supply

Cork city's oldest water treatment works is a small waterworks on the western side of the city. It draws water from the River Lee. This waterworks no longer produces enough water to meet the needs of the city. There are two other large water works, one at Inniscarra, taking water from behind the hydroelectric dam on the river Lee at Inniscarra, and one at Glashaboy, which takes water from the Glashaboy River. Together, the three produce water for the growing population of the city, its suburbs and indeed the industries of the lower harbour region.

3.3 Production of High Purity Water

Water of high purity is required for use in hospitals and many industries. For these purposes it is necessary to further purify tap water using advanced purification techniques. This is often called water softening which has been covered in section 2.3. Ion exchange can be used to remove all dissolved ions both cations and anions. Reverse osmosis, involving semi-permeable membranes, can be used to remove all dissolved materials, both ions and organic molecules. Activated charcoal can be used to remove organic compounds from solution by absorption. These processes are expensive but ultra pure water is vital for many industries. The electronics industry requires water 25 000 times purer than the water we drink. Kidney patients on dialysis machines also require pure water supplies, as otherwise harmful ions could build up in the body. In particular, the transfer of aluminium ions from the very large quantities of water used in dialysis into the patient’s bloodstream is a concern here.

3.4 Bottled Water

Bottled water is a general term. It is used to describe all water sold in containers. Bottled water is relatively expensive because of the high transportation costs, costs of packaging and marketing. Water in this form is purchased where tap water suitable for drinking is not available.

Even where potable tap water is available, bottled water is purchased for its superior taste and, more and more, as an alternative refreshment to soft drinks or alcohol or because it is perceived to be 'purer' than tap water. The terms spring, natural, table or mineral are further sub-classifications. The specifications for each of these are defined by legislation.

Mineral Waters

Mineral waters are waters from recognised and licensed sources. Perrier, Evian, Vittal, Volvic and Ballygowan are some of the better-known mineral waters. Of these, Perrier is the only naturally carbonated mineral water. While Perrier water is naturally carbonated the company separates the water and carbon dioxide while processing the water and re-carbonates it before bottling. This is done to ensure a consistent product. Perrier have been challenged under trade description legislation as to the validity of using the term 'naturally carbonated' since their process involves removal of the CO_2, though they do use the same CO_2 to re-carbonate. The other bottled water brands are available in still or carbonated forms, depending on whether or not carbon dioxide is added before bottling. They are not, and do not purport to be, 'naturally sparkling'. Producers of mineral waters have their own EU legislation, that of the Natural Mineral Waters Directive. They are not subject to the Drinking Water Directive laid down by the EU. Thus, they have no restrictions on mineral content. Consequently, certain mineral concentrations in these waters can exceed the maximum admissible concentrations specified in the EU Drinking Water Directive. Water traded under other terms, e.g. spring, table, etc., must comply with all aspects of the EU Drinking Water Directive and so these often have a lower mineral content than mineral waters. It is often convenient to classify waters as natural mineral waters and other types of bottled water, since mineral waters are the exception to the requirement to satisfy the strict parameters set down for drinking water. The argument for this exemption from the Drinking Water Directive was made to allow for difference in personal taste.

In 1980, what was the EC at that time introduced the Natural Mineral Waters Directive. It applies to mineral waters which are sold within its jurisdiction. The directive lists stringent conditions which must be met for a source to be classed as a source of natural mineral water. National authorities oversee the adherence to these specifications. Some countries have since introduced even more stringent regulations than those specified by the EU. Only the purest of ground waters may be bottled and marketed as natural mineral waters. They must be free from contamination by organic material. There are, however, no restrictions on the maximum admissible concentration, for individual ions or for total dissolved solids. It is therefore possible for the concentrations of, for example, sulphate or nitrate to exceed the maximum admissible concentrations specified for drinking water. It is essential for the consumer to be aware of this fact, particularly if any form of bottled water is given to small children or in preparing bottled food for babies.

There are three categories of natural mineral water on the market. These are: natural mineral water which is still; carbonated mineral water which is still water with added carbon dioxide and is sometimes called 'sparkling'; and naturally carbonated mineral water, which as the name suggests is carbonated in its natural form.

A number of interesting restrictions are imposed by the Natural Mineral Water Directive. The water must be bottled at source; it cannot be transported off-site for bottling. Bottles must have tamper-proof seals. Labels must include the name and location of the source. There are restrictions on the health benefits which can be claimed by the product. Strict regulations are imposed regarding the microbiological assay of the water.

Bottled Waters Other Than Mineral Waters

Bottled waters other than mineral waters described above have to comply with the EU Drinking Water Directive. This includes limits on certain anions and cations, total dissolved solids, organic matter and microbiological contamination. With such strict parameters set down one would expect bottled water to be of a very high quality. It must be remembered that drinking water from the tap also has to meet these same high standards (higher standards than natural mineral waters in fact) and there is little to suggest that most tap water in this country is not as good as bottled water. Any water supply is always liable to contamination by organic compounds. Over-pumping of ground water supplies to satisfy the market needs has altered the quality of the water from some sources over the years. There are also records of breaches of bacteriological quality standards at some bottled water plants and also at public and private water treatment works.

Composition of bottled waters

There is some divergence on the amount of information given on the label of a bottle of water. While some details of the chemical content of the water are nearly always given, vital information such as nitrate and sulphate content or bacteriological analysis may be absent. Interestingly, the same product in another European country may have this information.

In light of the fact that the exact composition of mineral and other natural waters depends on many factors, including the rock type with which the water makes contact, the acidity of rainfall, how long the water is in the ground, etc., it is easy to understand that the concentrations of the typical constituents of mineral water and other natural waters vary considerably from one source to another.

Calcium ion concentrations for example can vary from as little as 2 - 3 p.p.m. in the case of water such as Cerist to about 10 p.p.m. in the case of Volvic and to over 500 p.p.m. in water such as Vittel. Many bottled waters have concentrations of 100 - 150 p.p.m. of calcium ion, equivalent to a calcium hardness of 250 - 375 p.p.m. Calcium is essential for building bones and there is no health risk associated with consuming water with these calcium ion concentrations. High levels of calcium ion give the water a pleasant taste. However, calcium ions cause water hardness and this can be a problem (see Chapter 2).

While magnesium is also a major contributor to water hardness, it too is a major dietary requirement in humans. The magnesium ion concentration is usually low but waters such as Vittel have high magnesium ion concentrations - c. 110 p.p.m. This corresponds to a hardness of about 460 p.p.m. expressed as $CaCO_3$. Though magnesium is beneficial it must be stressed that magnesium sulphate, $MgSO_4$, Epsom salt, is a laxative.

Potassium is also an essential element for humans. Potassium is not classed as toxic, but high intake of potassium ion causes stress to the kidneys and can lead to kidney failure. For drinking it is best to consume a low-potassium water. Many bottled waters have potassium levels below 1 p.p.m. However, some bottled waters have very high potassium levels (up to 90 p.p.m.).

Sodium is an important element in bottled water and is again essential for health. A healthy adult excretes any excess sodium. However, those with hypertension and heart weakness, infants with immature kidneys and the elderly often have problems in this regard and so a low-sodium diet is often advised. The EU maximum admissible concentration for sodium is 150 p.p.m. for drinking water but some mineral waters can have higher sodium ion concentrations. Values of less than 20 p.p.m. are very common but there are mineral waters with as much as 1200 p.p.m. on the market. This is eight times the EU maximum admissible concentration of sodium ion allowed in drinking water. Sodium sulphate, Na_2SO_4, Glauber salt, can also act as a laxative.

The sulphate ion concentration of mineral water also often exceeds the EU maximum admissible concentration which is 250 p.p.m. The laxative properties of magnesium and sodium sulphates is the major problem with sulphate. Some bottled waters contain over 1400 p.p.m. of sulphate ion. Again, drinking a low-sulphate-concentration bottled water is advised.

Nitrate concentration is a source of concern. Many bottled waters do not give analytical data for nitrate. There is no safe limit, so drinking a water with as low a nitrate ion concentration as possible is advisable. A portion of ingested nitrate is reduced to nitrite ion, NO_2^-, which is a precursor in reactions leading to the formation of nitroso compounds, many of which are carcinogens, and compounds giving rise to methaemoglobinaemia, a blue-baby condition, in infants. The EU has set a maximum admissible concentration for nitrate ion of 50 p.p.m.

Chloride is not present at dangerous concentrations in bottled waters. Typical concentrations are less than 50 p.p.m. and it cannot be tasted at these levels.

Fluoride concentrations are not always given on bottles. To avoid fluorosis the use of water with a fluoride concentration above about 1 p.p.m. for drinking and cooking should be avoided (see p. 35).

The pH of still mineral water ranges from 6.0 to 8.0. Carbonated waters may have a pH as low as 4.5. While this keeps the water free from bacteria, it can lead to the leaching of minerals from the teeth, particularly if the water is consumed in large quantities and regularly. It is, however, no more destructive in this regard than most soft drinks.

Sugar is now regularly added to mineral and other bottled waters to produce ‘sweetened, flavoured natural waters’. In effect they are simply mineral or spring waters with sugar and flavours (possibly artificial flavours) added to create a further appeal to consumers. Details of the sugar content and flavours are given on the bottle.

The total dissolved solids consist largely of mineral salts which were dissolved in the water and which make the water taste salty. The EU has set a maximum admissible concentration for total dissolved solids of 1500 p.p.m. for bottled water other than mineral water. Generally water with more than about 500 p.p.m. total dissolved solids has a distinctive mineral taste, and above 1000 p.p.m. it has a strong mineral taste. Above 1500 p.p.m. it will taste salty, although this will vary according to personal tastes. Determination of total dissolved solids is given in section 3.8, p. 51.

In general it is better to avoid, where possible, giving bottled waters to children under seven years old. Babies have died from drinking formula feeds made up with high-sodium mineral waters, so only bottled water with the lowest sodium content should be used, if at all. Similarly, fatalities have resulted from high sulphate dosages. High doses of potassium are also undesirable. Particular care must be taken not to give infants water with high nitrate concentrations. The utmost care must be taken when using bottled water for making up formula milk for babies. Only still water should be used and all water should be boiled, as bottled water has not been sterilised; if only carbonated water is available boiling will also remove the carbon dioxide.

There is a strong tradition of drinking and bathing in natural waters for health reasons in Western Europe. Towns such as Bath in England, Aix-les-Bains in France, Trier, Wiesbaden and Baden-Baden in Germany, Mallow and Lisdoonvarna in Ireland, are all famous for this reason. In many cases the tradition of drinking and bathing in these waters can be traced to Roman times. Beneficial effects, including the curing of respiratory and urinary disorders, the breaking up of kidney stones and the soothing of skin diseases and indigestion, have all been attributed to water from one or more of these sources.

3.5 Disinfection of Swimming Pool Water

Elemental chlorine and chlorine compounds are the most popular disinfectants used in swimming pools. Among the compounds commonly added are hypochlorous acid (chloric(I) acid, HOCl), calcium hypochlorite (calcium chlorate(I), $Ca(OCl)_2$), and sodium hypochlorite (sodium chlorate(I), NaOCl). Other less popular disinfectants include ozone, hydrogen peroxide and bromine.

The need for a disinfectant stems from the ability of water to harbour a wide range of microbiological contaminants such as algae, bacteria and viruses. All of these can multiply rapidly in water, particularly in swimming pool water which is warm. Each user adds of the order of half a million bacteria to a swimming pool.

Living organisms multiply rapidly in water, especially if warm, causing it to go green, cloudy and partly opaque, soon making it unsafe for swimming. Bacteria and viruses are added by bathers from nose, throat, sores and wounds. Chlorination has proved to be the most economical and effective disinfectant to keep swimming pool water safe for bathers. Free chlorine will kill all bacteria almost immediately and render the water safe for swimming.

It is an interesting point that the top 150 mm or so of a pool can contain up to 75% of the pool's bacterial population. It is also interesting to note that chlorine is often blamed for irritation which may really have been caused by bacteria. Bacteria which can be present in poorly treated pools can result in eye and ear infection of the bathers. Other infections contracted frequently at swimming pools include the skin infection athlete's foot (a fungus) and verruca (a virus).

Since swimming pools are subject to physical, chemical and biological pollution, filtration and chlorination are required at all times to maintain water quality. In addition to acting against biological pollution, 'free' chlorine and its compounds can also react with a wide range of nitrogenous pollutants which have been added by swimmers. Chlorine and its compounds can react with these compounds to form chloroamines, which can then continue to break down until they form harmless substances. The formation of chloroamines and their residual disinfecting properties have already been referred to (p. 34).

The testing of swimming pool water for chlorine is discussed in section 3.8, p. 53.

The term 'balanced water' is applied to water to show when it is neither corrosive nor scale forming. The American **W. L. Langelier** developed a formula for calculating whether water is in balance based on five variables: pH, temperature, total alkalinity, calcium hardness and total dissolved solids. This is not discussed further here but the typical range within which each parameter is expected to fall for swimming pool or jacuzzi water is given in Table 3.1.

Parameter	**Min.**	**Max.**
pH	7.2	7.8
Total alkalinity	100 p.p.m.	200 p.p.m.
Calcium hardness	100 p.p.m.	500 p.p.m.
Total dissolved solids	300 p.p.m.	500 p.p.m.
Temperature of pool	20 °C	28 °C
Temperature of jacuzzi	25 °C	30 °C

Table 3.1 *Recommended pool water control parameters*

3.6 Waste Water Treatment

The large-scale use of water for domestic needs by an urban community or an industry renders it unfit for direct return to nature. The raw effluent would constitute a pollutant as it contains matter which would disrupt the fine ecological balance that exists in our rivers, lakes, estuaries, etc. This inability of a waterway to cope with a pollutant is regularly a problem of capacity rather than an inability to break down a specific contaminant. In other words, small quantities of a particular contaminant may be degraded quickly and pose no threat to the environment while larger quantities cannot be broken down in a reasonable period of time, place too high a demand on dissolved oxygen, serve to accelerate growth of weeds, drastically affect the clarity of the water, change its temperature, etc., and so constitute serious pollution. However, treatment techniques have been developed to restore wastewater to a state of purity which poses no threat to the environment so that it can be returned to nature without any measurable environmental impact.

There is often little difference in the methods used in treating effluent from domestic sources in a modern sewage works, aqueous waste from the food processing industry and aqueous waste from a modern pharmaceutical plant. They are all subject to the same environmental regulations regarding the quality of their outflow. Industries which produce aqueous wastes containing heavy metals, non-biodegradable material or radioactive material have to treat their waste using special techniques to meet the current legislative requirements. The treatment of such waste material is not dealt with here.

Two measuring parameters are regularly used in analysis of wastewater effluent. These are biochemical oxygen demand (BOD) and chemical oxygen demand (COD).

Biochemical oxygen demand is taken as a measure of the degree of pollution of a water sample based on the quantity of oxygen consumed by the micro-organisms present in a one litre sample stored in the dark at 20 °C for five days. It can be expressed in milligrams of oxygen per litre of sample, i.e. mg l^{-1} or p.p.m. The measurement of BOD is described in section 3.8, p. 57.

Chemical oxygen demand is defined as the oxygen equivalent of the organic matter content of the sample that is susceptible to oxidation by a strong oxidising agent. It can be expressed in milligrams of oxygen per litre of sample, i.e. mg l^{-1} or p.p.m. The measurement of COD is discussed in section 3.8, p. 58.

General Principles Involved in Aqueous Effluent Treatment

Aqueous effluent from domestic sewage, the food industry and most pharmaceutical plants contains nutrient material, mostly in the form of organic matter (with smaller quantities of inorganic matter). Domestic waste water contains a variety of organic material of biological origin and a population of living micro-organisms, as does the effluent from the food processing industry. The effluent from a pharmaceutical plant may consist of organic compounds rather than living micro-organisms. In cases where microbiological processes are used to produce a pharmaceutical some microbiological effluent may also arise. The outflow from treatment plants in this country has historically been under the remit of County Councils or Corporations who apply emission levels which are in accordance with the Royal Commission Standards. Of late, the Environmental Protection Agency (EPA) has taken control of the setting of standards and the monitoring of emissions from larger industries and in time they will solely implement and enforce the standards laid down by the EU.

In general, variations on the same technology are employed to reduce the BOD and COD of effluents from industrial and domestic sources to below a specified level. These principally involve biologically digesting or degrading the nutrient in the effluent. The digestion of nutrients can be aerobic, or anaerobic. If the digestion is aerobic, it generates carbon dioxide and water as its products. If the digestion is anaerobic, methane may be produced and this can be used to generate heat or electricity. Anaerobic digestion is not as efficient at removing nutrients and it also produces unpleasant gases such as hydrogen sulphide, H_2S. These gases have to be absorbed in gas filtration systems and not vented to the atmosphere. Aerobic digestion is by far the most common method of effluent nutrient digestion used. The micro-organisms which grow and multiply as they digest the effluent are removed as humus or sludge in settling processes and are disposed of by different methods. The final settled filtrate is discharged from the treatment plant under continuous monitoring and in accordance with legislative regulations. It should present no measurable environmental hazard. In many cases it is very important that treatment facilities operate to high standards as they often discharge their treated waste and final effluent into rivers. (Other towns may have waterworks downstream from a sewage plant.)

As a rough guide, domestic sewage effluent has a BOD of the order of 300 - 350 p.p.m. which corresponds to a COD of about 450 - 525 p.p.m. Effluent from a food processing or pharmaceutical plant could contain several hundred times this COD/BOD. The micro-organisms which digest the effluent are largely the same in all three cases. They do however become acclimatised to their diet and changes in effluent streams have to be made gradually to have best results. It is also common to stream industrial waste into 'strong' (very high nutrient content) and 'weak' (low nutrient content) streams. These are usually blended before treatment to give a consistent intermediate strength feed to the biological digestion system. It is also common to add nutrients such as phosphate if the effluent is low in phosphorus so that the microbes can feed and grow on the waste. The pH is also usually adjusted to the optimum value for the respiration of the microbes. The requirements of additional nutrients and pH adjustment are worked out from trials on laboratory-scale treatment systems.

Stages Involved in Waste Water Treatment

Pre-treatment

The incoming sewage is pushed through mechanically raked screens to macerate the sewage and remove large debris. The debris caught in the screens is removed either manually in older sewage plants or mechanically in more modern sewage works.

The effluent is then passed through concrete grit channels. Here the effluent flows slowly (0.2 m s^{-1}) in shallow streams along long channels. This allows dense material to settle. The flow can be diverted from one channel to another while settled material is removed.

Primary treatment

The pre-treated sewage flows into primary settling tanks. The sewage enters at the centre of the tank, (c. 12 m in diameter and c. 2 m deep), and rises, allowing sludge to settle, Fig. 3.2. The decanting liquid is transferred to the secondary treatment system. The settling tanks have a skimmer mechanism at the top to remove floating particles and a scraper on the settling tank floor (the base of the tank is hopper-shaped, i.e. sloping to the centre) to gather the settling sludge. Sludge treatment will be dealt with separately (p. 46).

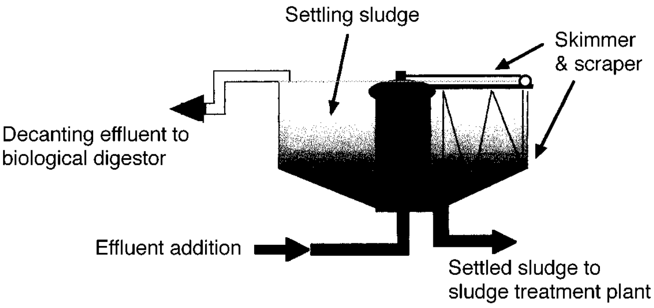


Fig. 3.2 *Primary settling tank*

Secondary treatment

This involves the biological degradation of the nutrient content of the effluent. This is usually done aerobically using percolating filters, activated sludge digestion units, aeration basins or bio-towers. Percolating filters and activated sludge digestion units are commonly used in sewage works but all four methods can be found in use separately or in pairs industrially.

Percolating filters

Following primary settling, effluent is biologically digested by micro-organisms in aerobic processes as it trickles down through a percolating filter. The percolating filter (diameter c. 25 m and depth c. 2 m) consists of a container loosely packed with fist-sized stones, Fig. 3.3. The stones act as a support for micro-organisms. The loose packing of the stones allows a good circulation of air. In the presence of the air, micro-organisms grow and digest the nutrients in the effluent aerobically. The liquid is applied by rotating arms and re-circulated over the stones for a time. The liquid exiting at the bottom contains water and micro-organisms washed down from the stones. Finally, the liquid goes to final settling tanks (humus tanks or clarifiers) (see p. 45).

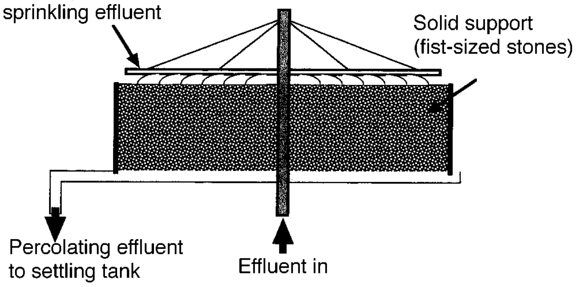


Fig. 3.3 *Primary settling*

Activated sludge digestion unit

It is not uncommon for effluent to be passed directly from the grit channels to an activated sludge digestion unit without primary settling. Here the effluent is digested aerobically by suspended micro-organisms in what is termed 'activated sludge', Fig. 3.4. The micro-organisms are kept suspended and the system aerated by large mechanical agitators. The sludge may have a retention time of 5 to 6 days in this unit. The oxygen level has to be kept above 2 p.p.m. in order to avoid anaerobic processes. The liquid from here is passed to the final-stage clarifiers (final settling tanks) where the sludge or humus settles. Some of the sludge is used for 're-seeding' the activated sludge digestion unit and most of it goes for disposal after further treatment (see below).

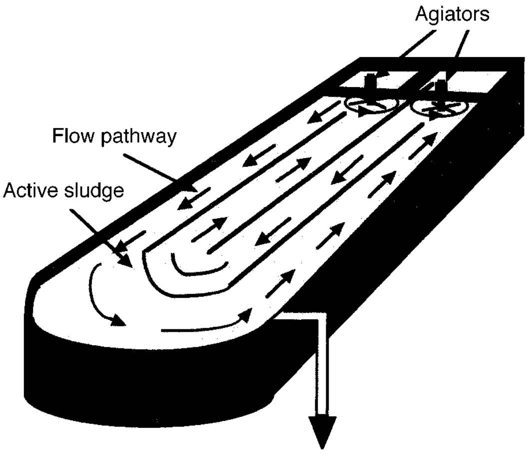


Fig. 3.4 *Activated sludge digestion unit*

Bio-towers

Bio-towers act somewhat like percolating filters. They consist of a large tower (10 - 15 m high) which is closed at the sides and is packed with an open solid support somewhat like a framework of milk crates, Fig. 3.5. The solid supports micro-organisms which aerobically digest the effluent. There is an algal growth at the top where there is light. The effluent trickles down through the large tower, undergoing biological digestion as it comes in contact with the micro-organisms. The liquid exiting at the bottom of the bio-tower is passed to settling tanks or clarifiers where sludge or humus settles. It is not unusual to recycle some of the liquid which has had one run through the bio-tower as a dilutant for raw effluent. Sludge treatment is dealt with separately (p. 46).

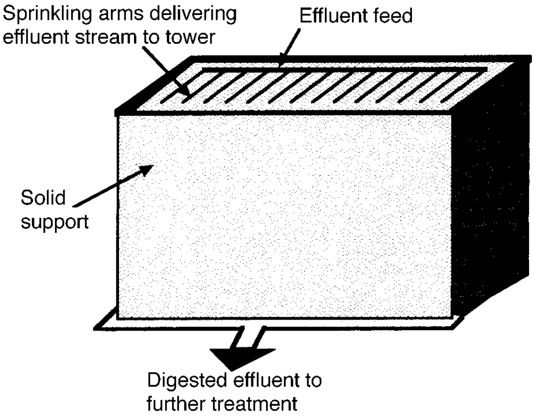


Fig. 3.5 *Bio-tower*

Aeration basins

Aeration basins are usually rectangular to minimise space requirements. Typically these have a depth of about 6 m. They are aerated by a jet aeration system. Effluent is pumped upwards together with compressed air released through jets at the base of the basins, Fig. 3.6. The air which is dissolved in the effluent at high pressure comes out of solution, rises and brings the activated sludge with it. This operation keeps the system well aerated and also serves to agitate the mixture. The retention time of the effluent in an aeration basin can vary from 2 - 3 days to about 7 - 8 days, depending on the amount of BOD/COD to be removed. The retention time is important as it ensures that an adequate time is allowed for biological degradation of the effluent, yet maintains a reasonable food/micro-organisms ratio for the survival of the microbe population. Sometimes more than one aeration basin may be employed, with the effluent passing through settling tanks between the aeration basins. The aeration basins are usually covered over to prevent the escape of volatile compounds. The exhaust gases are usually passed through peat/heather biological air filters. These absorb any volatile compounds which would otherwise be vented to the atmosphere. The peat/heather mixture has to be kept moist and loosened at intervals. A 'fill' of peat has an estimated lifetime of over five years.

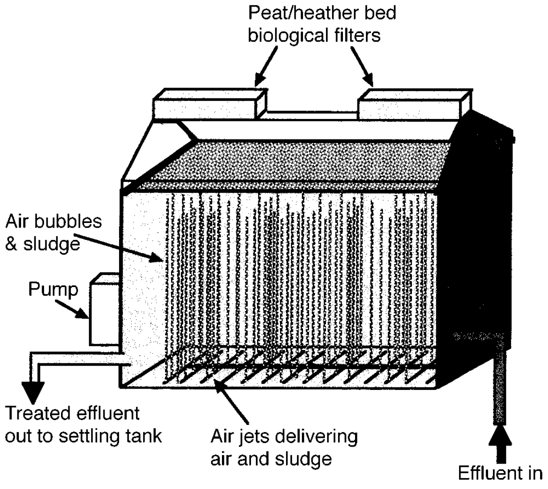


Fig. 3.6 *Aeration basin*

Final settling or clarification

Following biological digestion, sludge or humus is removed in settling or clarification tanks. The liquid portion should have sufficiently low BOD/COD to meet the standards set and it is safe to discharge it to the river or sea where it is diluted. It has no environmental impact. Currently, the output of sewage treatment works is continuously monitored by County Councils who have the responsibility for ensuring that the effluent is of satisfactory standard. In time, the Environmental Protection Agency will take over all this monitoring role.

Tertiary treatment

While primary and secondary treatment of effluent largely concentrate on the reduction of COD/BOD levels they have a lesser impact on phosphate and nitrate concentrations under the conditions normally applied. High levels of nitrogen and phosphorus are environmentally harmful as they act as nutrients which give rise to algal bloom, leading to eutrophication. Ammonium salts and nitrates are the common sources of nitrogen and usually originate from animal waste or fertilisers.

Industrially, the problem of high nitrogen content in effluent can be addressed by having a second aeration basin containing denitrifying bacteria and operating the system at carefully controlled oxygen levels in the biological treatment stage. Thus, in industrial sites nitrogen content is often controlled as part of what is normally considered secondary treatment.

Nitrogen is usually present in sewage effluent either as ammonium ions or as nitrate ions. Nitrogen in the form of ammonium ions can be removed by bringing the pH of the effluent up to 10 using lime, then blowing air through the effluent which liberates the ammonia from the water. The ammonia can then be trapped in filters. Biological filters such as peat/heather beds (which are usually dosed with small amounts of well-chosen microbes) act as biological air filters, absorbing gases such as ammonia. Nitrate content is often removed biologically, using denitrifying bacteria which, in anaerobic processes, reduce the nitrate ions to form nitrogen gas. Ion exchange, though expensive, is the best method of removing all nitrate ions from effluent.

Phosphates are precipitated by treatment with lime, $Ca(OH)_2$, aluminium sulphate, $Al_2(SO_4)_3$, or iron(III) sulphate, $Fe_2(SO_4)_3$. In each case an insoluble salt is produced which can be filtered off. The reaction of aluminium or iron ions with phosphate ions can be represented as

$$M^{3+} + PO_4^{3-} \rightarrow MPO_4$$

Removal of phosphates using aluminium sulphate, $Al_2(SO_4)_3$, or iron(III) sulphate, $Fe_2(SO_4)_3$, tends to lower the pH of the treated water. If sodium aluminate, $NaAlO_2$, is used as a source of aluminium ions instead of aluminium sulphate the pH of the water is raised. It is believed that organophosphates and polyphosphates are trapped or absorbed in the precipitating flocs. Separate precipitation of phosphates in tertiary treatment as described here also requires the addition of polyelectrolytes as flocculating aids (see sedimentation in section 3.2, p. 33). The phosphate content of effluent can be reduced to 0.2 p.p.m., or below, using this method. Less effective (80 - 90% effective), though more convenient, is the simultaneous precipitation of phosphates during clarification in secondary treatment. Tertiary treatment is not common in Ireland to date. Three of the more notable tertiary treatment plants are at Killarney, Mullingar and Castleblaney.

Over two-thirds of the population of Ireland live in towns and are connected to sewers. The remainder live in rural areas and are served by septic tanks (see below). Dublin has a population of about one million people. Approximately two thirds of the sewage produced gets primary treatment. The remaining third goes directly to the sea in two sea outfalls. There are over forty other coastal towns which discharge untreated sewage to estuaries or directly to the sea. Less than twenty coastal towns have primary or secondary sewage treatment at present. Nearly seventy inland towns discharge sewage to inland waters. The Department of the Environment is committed to the elimination of discharges of untreated sewage from major coastal towns and from major inland towns by the year 2000. This commitment carries an estimated cost of over £500 million.

Sludge treatment

A picket fence thickener is used to thicken sludge. This is a deep tank (c. 6 m deep, 8 m diameter) where sludge enters at the bottom and the liquid it contains decants over a number of weirs within the tank. Sludge can be thickened from a solid content of about 1% solids to 3 to 5% solids in a picket fence thickener, particularly if the sludge is conditioned by dosing it with small quantities of polyelectrolyte to encourage the formation of flocs. The thickened sludge is passed to a belt press for de-watering. This brings the dry matter content to about 14 - 20%. The water removed is returned to the treatment system for further treatment.

It is common practice to dispose of the solid sludge by removal off-site for land fill at licensed land fill sites which are lined to prevent seepage to ground water. Any liquid draining from the lined site is removed for treatment. Solid sludge of this type can be heat treated and sold as fertiliser. Alternatively, sludge, particularly from the processing of waste water from the food industry, can be applied to land as a fertiliser. This can only be done where the soil has been previously tested to ensure that no seepage contamination of nutrients to ground water is likely. Disposal of sludge at sea is practised in some areas. Sludge can be fermented to produce methane or it can be incinerated.

Landfill remains the most common method of disposal of sludge. As EU regulations continue to discourage landfill as a means of disposal of waste it is likely that the more environmentally friendly methods of disposal will be explored in the future.

Septic tanks

Septic tanks are designed for the digestion of sewage by anaerobic bacteria. Larger septic tanks are usually preceded by primary treatment. Aerobic sewage treatment is preferred, as anaerobic systems are not as efficient in BOD reduction as are the aerobic systems. Consequently, anaerobic systems (large septic tanks) are not common in the large-scale treatment of sewage. Smaller units (e.g. for households) normally consist of a concrete tank buried in the ground. These are common as they are self contained and require little maintenance. The sewage enters from one side, anaerobic bacteria digest the effluent, and a sludge settles to the bottom. The treated effluent flows out at the other end of the tank and is discharged to a river or is allowed to percolate into the ground via a percolation area made by filling a very large hole with stones. Anaerobic bacteria produce gases, one of which is hydrogen sulphide, hence they may have a foul smell. As the sludge builds up in the tank, it may have to be removed periodically. Users of septic tanks are advised not to add too much domestic bleach to their effluent because of the risk of destroying the entire microbe population of their septic tank and rendering it ineffective.

3.7 Water Pollution and its Causes

One definition of water pollution is the loss of any of the actual or potential beneficial uses of water caused by any change in its composition due to human activity. Apart from drinking and domestic use the beneficial uses of water include its use for watering livestock, irrigation of crops, fisheries, industries and food production, bathing, recreational and amenity use. If water is rendered unsuitable for any of these purposes then it is polluted to a greater or lesser degree depending on the extent of the damage caused. The natural biochemical processes of the water may eventually be able to break down or dilute the substances added.

Major Sources of Pollution

One cannot assume that natural waters will be immediately suitable for the whole range of beneficial uses. Nor should one expect to be able to drink the water in any river without its being treated first. In its natural state, depending on local usage, the weather and other factors, the water may be turbid or very highly coloured and hence unattractive to the user. More importantly, the river water is unlikely to be free from microbes, i.e. free from micro-organisms, some of which can cause disease in humans.

Natural water contains dissolved gases and salts. These substances are often the very factors which make the water suitable for particular beneficial uses. Water must have an adequate level of dissolved oxygen if fish are to thrive - if the concentration of dissolved oxygen falls below certain levels they cannot survive. In most cases pollution of rivers in Ireland is due to the depletion of the dissolved oxygen. Drinking water without dissolved oxygen, and with only a very low level of dissolved salts, is not very palatable. It is the presence of salts in solution, such as natural hardness, which gives many waters their refreshing taste.

In many cases, water pollution means that some human activity has led to the water being no longer suitable for some potential use such as drinking, even after treatment. Treatment works are usually designed to remove the natural contaminants such as colouring matter, particles causing turbidity, micro-organisms, etc. Consequently, they may be unable to cope with a heavy load of completely foreign matter such as chemical waste. Thus, if a river from which water is taken for treatment for drinking receives a discharge of chemical, or possibly toxic, waste, the water will be made completely unsuitable for eventual distribution.

The main causes of pollution include sewage and other oxygen-demanding wastes, largely organic material whose decomposition leads to oxygen depletion. Infectious agents, petroleum (especially from oil spills), inorganic minerals and chemical compounds also cause pollution. Plant nutrients cause problems in that they stimulate the growth of aquatic plants which can then interfere with water uses and, when decaying, deplete the dissolved oxygen and produce unpleasant odours. Pesticides and detergents have an adverse effect on the flora and fauna of waterways apart from the hazards they present to humans. Heat from the cooling waters of factories and power plants affect the solubility of oxygen in water (see below). Radioactive substances from uranium and thorium mining and refining, from nuclear power stations, reprocessing plants and from the industrial, medical and scientific use of radioactive materials present a major hazard if they are released into waterways.

The Role Played by Fish in Pollution Monitoring

In Ireland, fish and fishing are very important for the food industry and for sport and tourism. The health of fish stocks provides a method of monitoring pollution in waterways. Fish, especially salmon and trout, are very sensitive to water pollutants. Game fish in general are very sensitive to the lowering of the dissolved oxygen content. In addition, they are far more sensitive to heavy metals than humans. Consequently, the water quality standards required for salmon to live in river waters are very high. It follows that if water is suitable for fish such as salmon it is virtually certain to be suitable for all the other actual or potential beneficial uses. The presence of game fish in water is a positive sign in terms of overall water quality. In fact, use is often made of game fish in water treatment plants to detect the presence of pollution in the intake water.

Significance of Dissolved Oxygen

The importance of an adequate supply of dissolved oxygen for fish has already been mentioned. However, the actual concentration of dissolved oxygen present in even the cleanest water is extremely small. The solubility of oxygen in water at a temperature of 20 °C is 9 p.p.m. (see Table 3.2) This is a water temperature one might find in a river during a typical Irish summer. If the temperature of the water in a river drops to 6 °C in winter, the solubility of oxygen in the water is raised to 12.5 p.p.m. We see therefore that more oxygen dissolves in the water during winter. However, it is essential to base pollution control measures on the lowest natural (i.e. summer) levels which occur.

As stated above, around 9 p.p.m. is the maximum solubility of oxygen in water in summer. This level is more usually referred to as the 100% saturation value at the actual temperature (which must be specified if saturation values are used). Saturation levels above 80% are desirable if game fish are to thrive; for coarse fish the corresponding value is 55% saturation (at summer temperature). Expressed in terms of p.p.m., the respective values are 7 p.p.m. and 5 p.p.m. Thus, quite small amounts of pollutants will reduce the natural oxygen levels to the minimum desirable figures, and small increases in pollution will seriously disrupt fish life.

An important consideration where dissolved oxygen content is concerned is the possibility of variations during the day. These are likely to be most marked in summer in stretches of rivers where there is excessive algal growth. In the early morning minimum values of oxygen concentration, which may be considerably less than the maximum daytime reading, are observed. This is because the rate of photosynthesis, which produces oxygen, is a maximum at midday at high light intensity and is zero in the dark. Therefore minimal oxygen concentrations are expected at dawn. Variations of 50 to 150% saturation over 24 hours are not uncommon in very weedy, though unpolluted, rivers in summer. Where there is significant pollution, the early-morning minimum may be reduced to lethal levels below 30% saturation. Therefore dissolved oxygen measurements must be made at the period of day when levels are likely to be lowest. Table 3.2 shows the 100% saturation concentrations of oxygen in water at temperatures from 0 °C to 25 °C.

Temperature/°C	**Solubility of oxygen in water/p.p.m.**
0	14.6
1	14.2
2	13.9
3	13.5
4	13.2
5	12.8
6	12.5
7	12.2
8	11.9
9	11.6
10	11.3
11	11.1
12	10.8
13	10.6
14	10.4
15	10.2
16	10.0
17	9.7
18	9.5
19	9.4
20	9.2
21	9.0
22	8.8
23	8.7
24	8.5
25	8.4

Table 3.2 *Concentration of oxygen in water saturated with oxygen (for fresh water at sea level)*

The majority of pollution instances in Ireland are caused by the discharge into water of non-toxic organic matter, e.g. waste from creameries, sewage (treated or untreated), manure slurry, food production waste and silage effluent. While the pollutants may not be considered toxic, they disrupt the balance of nature in a waterway by acting as a readily available food or nutrient source for aerobic bacteria whose numbers then increase extremely rapidly. This creates an increased demand for the oxygen dissolved in the water. The sudden growth of bacteria due to the extra available nutrients tends, therefore, to reduce the amount of dissolved oxygen in the water. The extent of the oxygen depletion depends on the speed with which the water takes up oxygen from the atmosphere. This ability to become re-aerated is greatest in fast-flowing, turbulent streams and least in deep, slow-flowing rivers. In addition, the loss of oxygen may be counteracted by the photosynthesis of green plants which produce oxygen during daylight. However, these plants respire by day and by night and so, at night, they too constitute a net demand on oxygen. If pollution is severe, the oxygen-replacing factors may be insufficient to prevent the oxygen content of the water decreasing to critically low levels. In extreme cases anaerobic processes can begin if there is a complete absence of free oxygen. In such conditions, foul smelling and toxic compounds such as hydrogen sulphide may be formed. Before this, fish are killed and the flora and fauna of the water receiving the pollution may be wiped out. Deoxygenation is the single most important potential effect of organic waste discharges.

Compounds such as ammonia may be present in organic wastes, particularly where they have been stored for some time.

The dumping of toxic wastes, such as waste metal solutions, is particularly reprehensible as its consequences can be devastating to a water habitat and the resultant damage is not readily reversed.

Eutrophication

The over-enrichment of waters by nutrients, such as nitrate and phosphate, gives rise to a problem known as eutrophication. Added nutrients act as fertilisers and result in increased growth of algae and other plant matter in waterways. This increased growth is often very apparent from algal blooms and scums on stretches of waterways. When this type of algal bloom is followed by death and decay of animal and plant life in a competition for depleting oxygen supplies, the term eutrophication is used. Eutrophication is a problem of increasing concern in Ireland. It is of greatest concern in lake waters, though its effects are becoming more evident in rivers. Eutrophication gives rise to greatly increased weed growth, which can lead to blockage of channels, deposition of silt, and, in extreme cases, total deoxygenation.

Both nitrates and phosphates are present in significant quantities in sewage, even when it is treated. The control of the volumes of nutrient-bearing wastes reaching waterways may be seen as one means of controlling nutrient enrichment. The provision of tertiary treatment of wastes to remove the nutrients is effective, as described on p. 45. However, agricultural practices are a major problem. Leaching of the nutrients from animal slurry disposal by land-spreading and from the use of artificial fertilisers provides rich sources of nitrate and phosphate contamination. This type of pollution is known as ‘non-point source’ pollution, whereas direct addition of a nutrient from an outflow constitutes ‘point source’ pollution. The only way to control this problem is to regulate the way in which these materials are applied to the land. In the disposal of waste from the milk processing industry, sludge was formerly spread on land as fertiliser. This is now only done under strict control to avoid run-off and seepage into waterways. The land is tested in advance and the slurry applied by an injection type process during suitable weather conditions.

Lakes are more susceptible to this problem than rivers and streams because water in a lake has a significant retention time, i.e. the ratio of the total volume of lake water to the volume of water entering and leaving the lake each day is very large. This contrasts with rivers and streams where the retention time is usually low except in very dry periods in very hot summers.

At present (1998), Teagasc, the farm advisory board, is examining whether existing controls are sufficient to prevent chemical pollution due to excess phosphorus discharges from farm sources. The Environmental Protection Agency and the Fishery Protection Board have expressed concern that important fishing lakes such as Lough Conn and Lough Mask are at serious risks from phosphate wastes. Run-off, containing fertilisers and slurry, from agricultural land has been identified as the main source of this problem. While fertiliser and slurry applications on farms are the biggest contributors to the nitrate and phosphate discharges, phosphates in domestic detergents are also contributors. Awareness and a sense of responsibility on behalf of the public at large, together with the introduction of wide-scale tertiary treatment, is the only solution to this problem.

Marine Pollution

In the past the sea has been seen as a place where huge quantities of waste can be dumped because of its enormous diluting potential. The vast bulk of material dumped at sea originates from dredging, with sewage and industrial waste being the two other major components. In the UK the dumping of sewage at sea was scheduled to cease in 1998. The addition of toxic substances to the sea is a serious problem as marine organisms are often quite sensitive to them. Toxic substances and their residues may also accumulate in fish and these can be transmitted to humans as food.

The large-scale accidental discharges of crude oil along shore lines are a major cause of pollution in many parts of the world. The most obvious and spectacular cases of oil pollution involve supertankers used for transport of oil but many other ships also spill oil, often deliberately to empty their ballast tanks. Forensic science has an important role here as oil can be analysed by gas chromatography and mass spectrometry and a match can be made to identify if a suspect ship is responsible. Off-shore drilling operations also contribute to oil pollution. It is estimated that for every million tonnes of oil transported, 1 tonne is spilled.

The past twenty five years have seen some very large spills of oil. These include the tanker Amoco Cadiz off the French coast in 1978 (1.6 million barrels of crude oil) and the oil spill in the Gulf of Mexico in 1979 (3.3 million barrels). The spill of 240 000 barrels by the tanker Exxon Valdez in the Gulf of Alaska in 1989 caused a 67 000 km^2 slick. The Sea Empress lost about 350 000 barrels of oil off Milford Haven in February 1996, causing widespread environmental damage. The spill of an estimated 75 000 barrels from the Japanese-operated supertanker Diamond Grace in Tokyo Bay in July 1997 followed a smaller spill earlier that year. It is interesting to note that the spill of 680 000 barrels from the Braer on the coast of the Shetland Islands in January 1993 was broken up by the wave action of exceptionally severe storms and had largely dispersed in a few days. Further spills have occurred in the Middle East during times of conflict. In the Persian Gulf in 1993, during the Iran-Iraq war and in 1991 during the Gulf War, when up to 8 million barrels were released, enormous ecological damage was done.

Assessment of Water Quality

The assessment of river water quality is best achieved using a combination of physico-chemical and biological techniques. These methods complement each other. The physico-chemical techniques include the measurement of conductivity, pH, colour, alkalinity, hardness, dissolved oxygen, BOD, ammonia, chloride, orthophosphate, oxidised nitrogen and temperature. For lakes, chlorophyll, transparency and total phosphorus are also measured.

The biological monitoring of rivers is based on the relative abundance of aquatic life forms. The presence or absence of certain aquatic life forms, whether they be plant, animal, microscopic or large, is a good indicator of the state of health of a waterway. Different flora and fauna have different tolerances for pollutants and their presence or absence serves as an indicator of the presence or absence of different pollutants. Consequently, a river or lake may be classified as good, fair to good, fair, slightly polluted, moderately polluted or seriously polluted on the basis of biological analysis.

In general, unpolluted rivers contain, at most, very small quantities of biodegradable organic waste and there is little or no interference with the beneficial uses of the river. Slightly polluted rivers are likely to have more significant levels of enrichment periodically. However, they remain usable. Rivers which are moderately polluted are likely to suffer from eutrophication. The water may be able to support some beneficial uses. While fluctuations of dissolved oxygen may cause fish kills, coarse fish are more tolerant of pollution and this type of fishing may survive the lowering of water quality. Seriously polluted rivers are likely to be excessively eutrophic and the water uses are seriously curtailed. There are usually no fish present.

A 1991 survey of Irish rivers listed 76.5% as unpolluted, 12% slightly polluted, 10.5% moderately polluted and 1% seriously polluted.

Only the strict enforcement of national and EU standards, the licensing and policing of discharges, the implementation of approved procedures in agriculture, together with good environmental awareness on the part of the public, will ensure the preservation of rivers and lakes.

3.8 Aspects of Water Analysis

Because water is such a good solvent and because it can support the existence of a wide variety of plant and animal life a large number of parameters have to be analysed to get a full picture of the status of a water sample. The parameters analysed include conductivity, colour, clarity, suspended solids, dissolved solids, total and temporary hardness, BOD, COD and about thirty specific elements and complex ions.

Suspended and Dissolved Solids

Suspended solids can be particles of plant and animal remains or silt. These neither sink nor float; they are held in suspension in the liquid but are not dissolved. The amount of suspended solids in a sample of water can be determined by weighing a dried sheet of fine-grade filter paper and filtering through it a known volume of water (a reasonably large volume of water will usually be needed, e.g. one litre). The filter paper is then washed with distilled water, dried carefully and reweighed. The increase in mass is the mass of solids suspended in the sample. Suspended solids are usually expressed in p.p.m. The washing with distilled water is essential to remove any dissolved solids from the water on the filter paper. A fine-grade sintered glass funnel would be superior to a filter paper for this experiment.

It should be noted that if the water is very clean (clear), a large volume (e.g. one litre) will be necessary to obtain a significant amount of solid matter. If the water is obviously dirty, a smaller volume (e.g. 500 cm^3 or 200 cm^3) will suffice. In addition, an accurate balance measuring to one milligram will be necessary to obtain meaningful results.

The suspended materials may include small particles of iron oxide which may come from rusty machinery and pipes or from the oxidation and precipitation of dissolved iron in water. Far more common are suspensions of silt and fine sand, particularly in water from wells which are pumped at high discharge rates. Suspensions of clay are often encountered in some wells drawing water from limestone regions. Turbidity often occurs following rains when rapidly flowing water carries clay from surface soil, fissures and caves into wells, rivers and streams.

Concentrations of suspended inorganic sediment rarely exceed 500 p.p.m. and most commonly do not exceed 5 p.p.m. Even concentrations of 5 p.p.m. may cause trouble, as the sediment will, in time, accumulate to significant levels in a distribution system. This greatly increases maintenance costs. Organic suspended material may arise from bacteria and algae which can gain entry to water in a variety of ways. Most organically contaminated wells are in limestone regions where caverns and smaller openings allow direct connection between the surface and the ground water.

Total dissolved solids in a water sample includes all solid material in solution, whether ionised or not. It does not include suspended material, colloids, or dissolved gases.

It must be understood that the solid material left after evaporation does not coincide completely with material originally in solution. Hydrogencarbonate is converted to carbonate, sulphate may be deposited as gypsum which traps some of the water and small amounts of material may be volatilised. Nevertheless, the residue after evaporation affords a rough check on the total dissolved solids.

Natural waters range from less than 10 p.p.m. of dissolved solids for rain and snow to more than 300 000 p.p.m. for some brines. Water for most domestic and industrial use should be less than 1000 p.p.m. and water for most agricultural uses should be below 3000 p.p.m.

The final classification of water in relation to potential use, however, should be based on concentrations of individual ions rather than on total dissolved solids.

The dissolved solids can be determined by taking a known volume of filtered water (to ensure that all suspended solids have been removed) in a previously weighed dry beaker, and then boiling the contents gently to dryness. The dissolved solids will remain in the beaker and their mass can be accurately found by reweighing the beaker when it has cooled. The concentration of dissolved solids should also be expressed in p.p.m.

The Atomic Absorption Spectrometer

Both atomic emission spectra and atomic absorption spectra are used widely in chemical analysis. Atomic emission spectra are discussed in the module titled ‘Atomic Structure and Trends in the Periodic Table’.

Atomic absorption can be used to detect and measure the concentration of certain heavy metals which may be present in water. The atomic absorption technique is based on the fact that atoms in their ground state can absorb photons of light of specific energy (i.e. frequency, since $E = hf$). In atomic absorption spectrometry the absorption of ultraviolet radiation or light by gaseous atoms is determined. The sample to be analysed is converted into atomic vapour by spraying the solution into a flame or graphite tube cuvette (sample holder). The gaseous atoms are irradiated by light from a hollow cathode discharge lamp containing the element to be determined. Every element has its own characteristic emission frequencies which correspond to the absorption frequencies in the ground state. The light emitted from the discharge tube provides the exact frequencies of light which can be absorbed by the gaseous atoms of the sample. The frequency spread for both an emission line of the light source and an absorption line of the same element is extremely narrow. For this reason, interference from the spectral lines of other elements is almost nil. This contrasts with absorption and emission spectra of molecules where broad bands are observed.

Atomic absorption spectrometry has an important advantage over atomic emission spectrometry. Atomic emission spectra consist of several sets of lines corresponding to electrons from all excited states falling back to all lower energy levels. Atomic absorption spectra consist of just one set of lines corresponding to excitations from the ground state. The single biggest disadvantage in the technique is the necessity to acquire and maintain an expensive light source for each element to be determined.

About seventy different elements have been determined by atomic absorption. All are metals with the exception of boron, arsenic, selenium and tellurium. It is a sensitive technique, used to measure concentrations of the order of parts per million or less. In general accuracies of about ± 2% are achieved.

The actual operation of the atomic absorption spectrometer involves light from the source being directed at the flame into which the sample solution is sprayed. Some of the light from the discharge lamp is absorbed in the flame by atoms of the element being determined. The unabsorbed light passes through. The transmitted beam is passed to a monochromator where a single line of the spectrum is selected for analysis. The line picked is usually the most intense of the spectrum, provided it is in a region of the electromagnetic spectrum where there is likely to be no overlap with the absorption of any other species present. The intensity of that line is measured using a photocell or photomultiplier. The ratio between the intensity of the incident beam and that of the transmitted beam is determined. Provided the flame is hot enough to convert a chemical compound to free atoms, the amount of light absorbed depends on the number of atoms in the light path and is almost independent of the flame temperature. In some instances, an excessively hot flame may promote so many free atoms to the excited state that the number of unexcited atoms, and hence the light absorption, is significantly reduced. If flame conditions and the rate of aspiration of the sample into the flame are kept approximately constant, the absorbance (log I_0/I, where I_0 is the intensity of the incident beam and I is the intensity of the transmitted beam) will be proportional to the concentration of the given metal in the sample. A series of standard samples (i.e. solutions of known concentration) are run and then the unknown is analysed. The concentration of the unknown is determined from the graph of the absorbance versus concentration for the standards. Most of this data processing is now done by having the atomic absorption spectrometer linked to a data logger and processor. An outline of the main components of an atomic absorption spectrometer is given in Fig. 3.7.

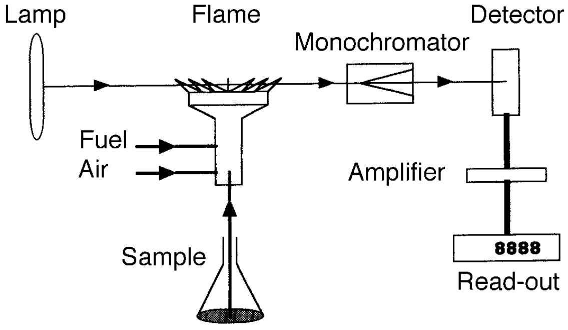


Fig. 3.7 *Atomic absorption spectrometer*

Testing Swimming Pool Water for Chlorine

Because bathers continually add bacteria and nitrogenous matter to the water in a swimming pool, chlorine must be added in proportionate amounts to destroy these pollutants. In addition, sunlight, other strong light or agitation will accelerate the reduction of chlorine. It is therefore necessary to have a reliable yet simple method of monitoring chlorine in swimming pools. It is also essential to know the differing concentrations of 'free' and 'combined' chlorine, as they produce differing degrees of disinfection. The pH is also an important factor, as the disinfecting powers of hypochlorous acid and hypochlorite ion differ dramatically. This was discussed earlier (p. 34) in the context of chlorination of mains water. A number of portable analysis kits such as the Lovibond-Tintometer or the Hach Meter allow a realistic reading for chlorine to be obtained by staff who have little chemical background or training. There are of course laboratory-based techniques, such as iodometric titrations using standard sodium thiosulphate, but these are not discussed here.

Chlorine in the form of dissolved elementary chlorine, Cl_2, hypochlorous acid, [chloric(I) acid], HOCl, or hypochlorite ions, [chlorate(I) ions], OCl^-, is referred to as 'free chlorine'. Chlorine in compounds formed by reaction of hypochlorite ions with ammonium or organic compounds containing amine groups is known as 'combined chlorine'. These compounds are usually chloroamines, e.g. NH_2Cl.

One of the methods most commonly used for the determination of chlorine concentrations in water is the *N,N*-diethyl-1,4-phenylenediamine (DPD) method. The *N,N*-diethyl-1,4-phenylenediamine test differentiates between, and measures, both 'free' and 'combined' chlorine residuals in samples of clear water. In the absence of iodide ion, 'free' chlorine reacts instantaneously with DPD indicator to produce a red colour. Subsequent addition of a small amount of iodide ion acts catalytically with monochloroamine to produce colour. Addition of excess iodide causes a rapid response for dichloroamine. The intensity of the colour development, which is proportional to the amount of chlorine, can be measured using a photoelectric colorimeter with a filter having maximum transmission wavelength in the range of 490 - 530 nm. A colorimeter is a device used to measure the concentration of a constituent of a solution by comparison with colours or colour intensities of solutions of known concentration of that constituent. The colour or intensity comparison can be done with a calibrated colour chart or with a more sophisticated and expensive pre-programmable electronic device which provides a digital read-out of chlorine concentration.

While the instructions with the kit should be read carefully and followed precisely, it is possible to give a general procedure to outline the reactions and observations at each stage. Particular attention is drawn to the Material Safety Data Sheets which accompany these kits. The chemicals used in these kits must be handled with care.

Most kits have a test range of 0 - 4 p.p.m. so if the chlorine concentration exceeds this value an appropriate dilution with distilled water is required before testing to bring the chlorine concentration of the sample within the test range of the kit.

When testing for ‘free’ chlorine a buffer solution and DPD indicator solution or more commonly a DPD1 tablet, which incorporates the buffer, is used. The water sample is mixed with the buffer and DPD tablet or with the DPD1 tablet and the colour development is read immediately from the colorimeter. The comparison of colour with the chart accompanying the kit gives the ‘free’ chlorine concentration. To determine the monochloroamine (NH_2Cl) concentration, one small crystal of potassium iodide, KI, is added to the same test sample used above and mixed. The intensity of the colour is read again. The chlorine derived from monochloroamine can then be estimated by finding the difference between this reading (‘free’ + monochloroamine-derived chlorine) and the first reading (‘free’ chlorine only).

The dichloroamine, $NHCl_2$, is estimated by addition of a few more crystals of KI to the sample. After about two minutes, the final colour intensity is measured. This gives a third reading which corresponds to ‘free’ chlorine, chlorine derived from monochloroamine and dichloroamine.

Hach Test kits would not have sufficient accuracy for measuring chlorine in drinking water. However, they are commonly employed to monitor chlorine levels in swimming pool waters. They come complete with DPD1 (for ‘free’ chlorine analysis) and DPD3 (for 'total' chlorine) in tablet form or as powder sachets. The water samples are placed in the sample tubes or cuvettes provided. The tubes of water are placed in a holder or ‘Black-Box Comparator’. One is treated with DPD1 and the ‘free’ chlorine concentration read by placing the colour disc behind the untreated sample to see which colour matches the colour developed in the treated sample. The match must be made within one minute of the addition of the DPD1 tablet. The tablet does not need to dissolve fully. Addition of the DPD3 tablet or powder sachet to the same sample, i.e. the one already containing the DPD1 tablet, further develops the red colour. The ‘total’ chlorine is estimated after two minutes by colour comparison with the colour disc held behind the untreated water sample. The difference in the two results is the value of the ‘combined’ chlorine.

Test samples should always be taken from the same place in the pool. The choice of location depends on the flow pattern of the pool. A few tests in various places should be taken initially and then the location of the lowest reading used as the regular test site. Samples should be taken at a depth of about 30 cm below the surface. Sufficient water to do the test should be taken and a plastic bottle should be used rather than glass. If high concentrations of monochloroamines are present they may interfere with the ‘free’ chlorine determination.

More sophisticated and expensive colorimeters are available which are pre-programmable and will give a digital read-out of chlorine concentration.

The chemistry behind the DPD test for chlorine is relatively straightforward. The main ingredient of the chlorine-test tablet DPD is *N,N*-diethyl-1,4-phenylenediamine in the form of its sulphate as shown in Fig 3.8.

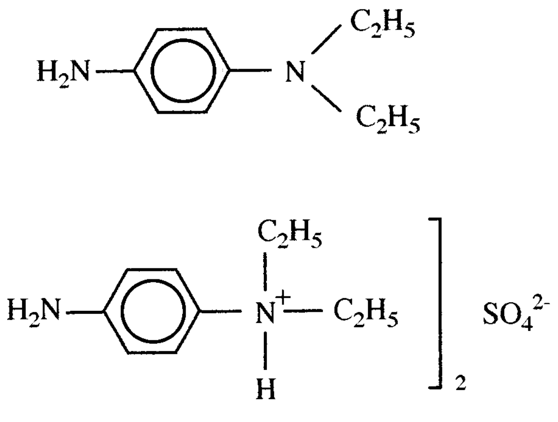


Fig. 3.8 *The structure of DPD and its sulphate salt*

Hypochlorous acid, [chloric(I) acid] and the hypochlorite ion, [chlorate(I) ion] oxidise *N,N*-diethyl-1,4-phenylenediamine sulphate to a soluble red product. The red product is a free radical. The formation of this free radical is shown in

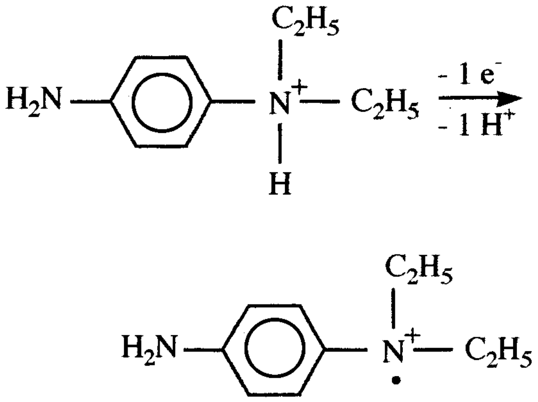


Fig. 3.9

The test must be carried out within a few minutes of mixing the reagents to make sure that it only measures the ‘free’ chlorine and not the combined chlorine. The depth of the red colour is a measure of the concentration of the oxidising substances present in the water. A rough guide to these colours is given in Table 3.3.

Chlorine/p.p.m.	**Colour**
No chlorine	colourless
0.2 - 1	faint pink to pink
1 - 5	pink to red
5 - 10	red to purple

Table 3.3 *Reading chlorine concentrations in swimming pool water using DPD*

When the tester compares the colour of the mixture with the standard colour chart, the value for the ‘free’ chlorine should be in the range 1 - 5 p.p.m.

The DPD1 tablets also contain a buffer to keep the pH at a level which favours reaction with free chlorine while inhibiting reaction with combined chlorine. The buffer is made up with phosphates which would normally form precipitates with calcium ions in hard water. For this reason the tablets also contain edta, to prevent insoluble calcium salts forming.

The DPD3 tablet used to determine the ‘total’ chlorine contains DPD and potassium iodide. The chloroamines oxidise the potassium iodide to iodine. The iodine formed will then oxidise more DPD, so darkening the colour of the dye. Thus, the second reading with the colour chart gives a value for the ‘total’ chlorine (i.e. ‘free’ + ‘combined’).

Teachers and students can best understand and appreciate this area of analysis if it is done in conjunction with a visit to a pool. With the permission of pool management, samples may be analysed on site or taken back to school for analysis.

In general, in a busy swimming pool, tests are carried out at regular intervals. Twice daily checks are made on ‘free’ chlorine and pH. ‘Combined’ chlorine is checked after heavy use. Weekly checks are carried out on ‘total alkalinity’ and calcium hardness.

The significance of pH control is due to the importance of ensuring that the concentration of hypochlorous acid [chloric(I) acid], is as high as possible. There may be enough ‘free’ chlorine in the pool water but it will not be effective if the pH is too high. This means that accurate pH control is very necessary and must be measured regularly. Pool test kits are available which are based on phenol red indicator. The tester adds a tablet containing a measured amount of the indicator to a 10 cm^3 sample of pool water. Phenol red changes colour from red to yellow over a narrow range of pH values. The tester finds the pH of pool water by comparing the shade of red or yellow with a colour chart supplied with the indicator. Chlorine interferes with this test, so the tablet also contains sodium thiosulphate which acts as a ‘dechlorinating’ agent.

Pool supervisors also have to look after the fabric of the pool. If the circulating water becomes too acidic it may corrode steel pipes and tanks as well as etching concrete surfaces. The recommended pH range of 7.2 - 7.8 is a compromise which retains a sufficiently high proportion of chlorine as HOCl while being comfortable to bathers and limiting corrosion of the plant and equipment.

A buffer system in the pool water prevents wide fluctuations in the pH. The buffering system is based on the carbonate ion/hydrogencarbonate ion system which is present in most Irish tap waters. Only in soft water areas is it necessary to add sodium hydrogencarbonate. Pool supervisors can lower the pH by adding sodium hydrogencarbonate or raise the pH by adding sodium carbonate. In this way they can keep the value within the range 7.2 - 7.8. This is an example of a one-component buffer, i.e. a buffer consisting of a single species capable of increasing the pH by accepting H^+ ions and lowering the pH by donating H^+ ions. In this case the HCO_3^- ion is the one-component buffer.

$$H_2O + HCO_3^- \rightleftharpoons H_3O^+ + CO_3^{2-}$$

Addition of sodium hydrogencarbonate drives the equilibrium to the right, forming more hydronium ion and lowering the pH; addition of sodium carbonate drives the equilibrium to the left, consuming hydronium ion and increasing the pH. Problems can arise if the concentration of hydrogencarbonate ions is too high. The pH of the water drifts outside the accepted range and the large hydrogencarbonate concentration has a buffering effect which makes it difficult to pull the pH back into the recommended range.

The ‘total alkalinity’ is a measure of the buffering capacity of the water. This buffering capacity is measured by recording the amount of acid needed to change the pH of a sample of pool water from 7.2 - 7.8 to 4.5. The acid reacts with hydrogencarbonate ions. The tester carries out a ‘titration’ but, instead of using a solution in a burette, tablets are added one at a time to a 50 cm^3 sample of pool water. The tablets contain an acid and methyl orange indicator. The tester counts the number of tablets needed to turn the solution from yellow to bright red. A simple calculation is used to convert the number of tablets to a value equivalent to p.p.m. of $CaCO_3$ to allow comparison with tests carried out on other waters. This does not mean that the alkalinity is present in this form - in fact it is present mainly as hydrogencarbonates. The ‘total alkalinity’, given as p.p.m. of $CaCO_3$ is kept within the range 100 - 150 p.p.m.

Another ‘tablet titration’ is used to measure the hardness due to calcium ions. This time the titration is not based on an acid-base reaction; instead it uses the complex-forming reaction involving edta and calcium ions in solution (which was covered in section 2.5). The tester takes a 50 cm^3 sample of water and adds tablets one by one, shaking after each one to make sure that the tablet breaks up and dissolves. The tester adds tablets until the colour changes from pink to violet.

The tablets for this titration contain a fixed amount of edta, together with a small amount of an indicator called murexide. At first, the indicator forms an unstable pink complex with calcium ions. As more tablets are added the edta forms a much more stable, colourless complex, with calcium ions replacing the indicator molecules. Once enough tablets have been added to provide sufficient edta to react with all the calcium ions the solution takes on the colour of the free indicator which is blue. The tablets also contain a base so that the solution is alkaline during the titration. This stops magnesium ions interfering with the test. Again a simple calculation converts the number of tablets needed for the titration to a value equivalent to p.p.m. $CaCO_3$. The value should be in the range 100 - 150 p.p.m. $CaCO_3$.

Estimation of Dissolved Oxygen in Water

Estimation of the concentration of dissolved oxygen in water is used in the determination of the quality of surface waters and also in waste waters, particularly from biological treatment plants.

The most common titrimetric procedure to measure dissolved oxygen is called the Winkler method. It relies on reactions involving manganese ions, iodide ions and oxygen. Under alkaline conditions the oxygen dissolved in the water oxidises the Mn^{2+} ions to Mn^{3+} ions. When the mixture is acidified, the Mn^{3+} ions are reduced back to Mn^{2+} ions by the iodide ions. This reaction liberates iodine whose concentration can be estimated by titration against standard sodium thiosulphate solution. The concentration of the iodine in the final solution is twice the oxygen concentration of the original solution (see below).

The water is initially treated with manganese(II) sulphate and alkaline potassium iodide solutions. The manganese ions and the hydroxide ions react together to form a white precipitate of manganese(II) hydroxide.

$$Mn^{2+} + 2OH^- \rightarrow Mn(OH)_2$$

The oxygen present in the water will now oxidise the Mn^{2+} and the colour of the precipitate changes to brown. The identity of the brown precipitate seems to be the source of some doubt. Some advanced analytical texts list it as manganese(III) hydroxide while others as manganese(IV) oxide or manganese oxide hydroxide, $MnO(OH)_2$. The fact is that the exact formula or oxidation state of this precipitate is unimportant, as this oxidised species is not to be analysed and is reduced again to manganese(II). If manganese(III) hydroxide is formed the reaction occurring may be represented as

$$4Mn(OH)_2 + O_2 + 2H_2O \rightarrow 4Mn(OH)_3$$

If manganese(IV) is formed the reaction can be represented as

$$2Mn^{2+} + O_2 + 4OH^- \rightarrow 2MnO(OH)_2$$

or

$$2Mn^{2+} + O_2 + 4OH^- \rightarrow 2MnO_2 + 2H_2O$$

When concentrated sulphuric acid (or phosphoric acid) is added, the oxidised manganese ions are reduced to Mn^{2+} by the iodide ions (from potassium iodide) and iodine is liberated.

$$6H^+ + 2I^- + 2Mn(OH)_3 \rightarrow I_2 + 6H_2O + 2Mn^{2+}$$

If manganese(IV) were present in the intermediate species the reaction could be represented by

$$Mn^{4+} + 2I^- \rightarrow Mn^{2+} + I_2$$

The same number of moles of oxygen are used and iodine liberated whichever way the reactions are written. The free iodine can now be determined in the usual way by titrating it with standard sodium thiosulphate solution. The amount of oxygen used up is exactly half the amount of iodine obtained. Overall, every molecule of oxygen liberates two molecules of iodine which in turn require four thiosulphate ions in the titration.

$$O_2 \rightarrow 2I_2 \rightarrow 4S_2O_3^{2-}$$

The amount of dissolved oxygen is determined in moles per litre and then converted to grams per litre and finally to p.p.m. The experimental details are given at the end of this section.

The value for the dissolved oxygen obtained can be used to find the percentage saturation value of the water sample at a given temperature by Table 3.2 (p. 48).

Since the solubility of oxygen in water decreases significantly with increasing temperature, it is often useful to relate the concentration of dissolved oxygen to the saturation concentration at the temperature of the water and express it as a percentage saturation. To do this, the concentration of the dissolved oxygen at the temperature at which the sample was taken is divided by the corresponding value for the 100% saturation and then multiplied by 100.

For example, if the measured value of dissolved oxygen is 8.5 p.p.m. at 18 °C (the saturation value at this temperature is 9.5 p.p.m.), then the percentage saturation is 8.5/9.5 x 100 = 89%.

The Winkler method for dissolved oxygen was first published in 1888 and, although it has been improved over the years, more modern analytical methods, e.g. electronic oxygen probes, are now available and are becoming very widely used in preference to the titration technique.

Biochemical Oxygen Demand (BOD)

The BOD test was first devised by the Royal Commission on Sewage in the early 1900s. The biochemical oxygen demand is the amount of dissolved oxygen consumed by biochemical action when a sample of water is kept in the dark at 20 °C for five days.

Fresh water approaching a sewage outlet usually has a normal dissolved oxygen level. After the addition of the sewage, the dissolved oxygen content will not change much initially, but now the water is polluted and has an oxygen 'demand'. The oxygen content of the water will start to fall as it is used by bacteria decomposing the pollutants. Chemists call this demand the biochemical oxygen demand, or BOD. The BOD is a good measure of the extent of water pollution, and is the most widely performed test in water-control laboratories. Controlling authorities often base their standards on a measurement called the five-day BOD. For this test to be valid, dissolved oxygen must be present in the water sample throughout the five-day period - with at least 2 p.p.m. remaining at the end of it. For normal waters, carrying out the test on an undiluted sample is satisfactory, since the likely result should be between 1 and 7 p.p.m. and water saturated with oxygen at 20 °C contains about 9 p.p.m.

However, when testing water samples in which the demand for oxygen is greater than the concentration present (such as sewage, sludge, etc.) the water must be diluted quantitatively in order to obtain a correct result. The dilution is based on the expected result and suggested dilutions, for various BOD ranges, are given in Table 3.4.

BOD range	Dilution factor
3 - 21	3
6 - 42	6
10 - 70	10
20 - 140	20
50 - 350	50
200 - 1400	200

Table 3.4 *Dilution factors for various BOD ranges*

The dilution factor is the volume to which one part of the sample water should be diluted, e.g. for the 3 - 21 BOD range, take 100 cm^3 of the sample water and dilute to 300 cm^3. When diluting the sample, fresh distilled water should be used and the resulting mixture should be thoroughly shaken for 5 - 10 minutes in order to fully oxygenate the water. Dissolved oxygen is then determined in the usual way by the Winkler method. The BOD value is the difference between the initial dissolved oxygen value and the value measured after the five-day period. If the sample has been diluted, the value obtained is multiplied by the dilution factor in order to obtain the BOD. However, it must be mentioned here that this method of measuring and calculating BOD is somewhat simplified from that used by water authorities, but is quite adequate for school purposes.

Limitations of BOD test

The precision of a five-day BOD test is not very high (20% approximately). However, it has the advantage of providing information about the microbial activity of a sample even if some pollutants are undetected. The oxygen consumed during algal respiration is included and, in some cases, this may account for up to 50% of the total BOD. In waters that are not heavily polluted the bacterial degradation of the organic matter is slow and often continues for ten, twenty, or more days. The standard BOD method is not usable under these conditions. To avoid the minimum of five days required for the determination of BOD, to include those wastes which are only slowly oxidised by oxygen and to avoid problems of poisoning of micro-organisms by toxic substances in the wastes, the chemical oxidation demand (COD) test has been devised. In this case the water sample is treated with a known quantity of a strong oxidising agent, usually potassium dichromate ($K_2Cr_2O_7$), which rapidly oxidises most of the organic matter. The remaining $Cr_2O_7^{2-}$ is then determined by back titration with a suitable reducing agent. Although COD can be determined in 2 - 5 hours and is reproducible it may not give a complete picture of the amount of pollution either. For instance, dichromate oxidises Cl^- to Cl_2 and thus an uncorrected COD includes the chloride content of a sample even though Cl^- would not be oxidised in natural waters and would not be considered as a pollutant. Interferences by chlorides can be eliminated by adding mercury(II) sulphate prior to oxidation. Potassium manganate(VII) (potassium permanganate, $KMnO_4$) can also be used and the excess $KMnO_4$ back titrated using ammonium iron(II) sulphate solution. However, $KMnO_4$ is not as stable as $K_2Cr_2O_7$, hence $K_2Cr_2O_7$ gives more reproducible results and is the preferred reagent.

The COD and BOD tests only provide certain information about the water sample tested. Many compounds, e.g. aromatics, including benzene and pyridine, and a number of hydrocarbons are not determined by either COD or BOD. Thus, a wide variety of potential pollutants may be missed if only BOD and COD tests are considered. Nevertheless, oxygen demand is a good general indicator of pollution. However, the BOD test cannot be used with confidence to measure accurately the strength of industrial waste waters. Industrial wastes can have an almost infinite variety of ingredients, many of which are not biodegradable but have a high COD. For example, the BOD test will not reveal the presence of toxic heavy metals, or organic and inorganic complexes in industrial effluent, hence the COD test is preferred. Neither BOD nor COD tests are indicators of the number of pathogenic bacteria or viruses in sewage or polluted water. Bacterial contamination is measured by the coliform bacteria count, a bacteriological test indicating the amount of human faecal matter recently entering the water at a nearby point. Coliform bacteria themselves are not pathogenic, but they serve as an important indicator organism because their origin in the human intestinal tract is the same as that of the pathogenic organisms of typhoid, cholera, dysentery, and a whole host of other micro-organisms. Furthermore, because coliform bacteria do not survive long in natural waters, their presence indicates recent pollution.

3.9. Student Experiment

Estimation of the Dissolved Oxygen in a Water Sample by the Winkler Method

This experiment involves using the oxygen dissolved in a water sample to oxidise manganese(II) ions. The manganese(III) or manganese(IV) ions produced are in turn used to oxidise iodide to iodine. This iodine, which has been produced as a direct consequence of the oxygen present at the start, is estimated in a titration with standard sodium thiosulphate solution.

Collection of the water sample

The bottle should be of the reagent bottle variety, i.e. one with a pop-on stopper, Fig. 3.10(a). The bottle should be rinsed with the water from the river (or whatever source) first to avoid trapping of air bubbles.

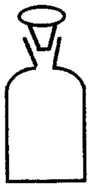


Fig. 3.10(a)

The bottle should be filled under the level of the water and agitation or any aeration must be avoided. The bottle should be filled to the top. The bottle should be stoppered under the level of the water so as to avoid trapping of air bubbles. Usually a number of water samples are taken.

Laboratory analysis

1. The stopper is removed from the bottle and a few cm^3 of the water removed using a dropper.

2. A few cm^3 of manganese(II) sulphate solution, $MnSO_4$, and a few cm^3 of alkaline potassium iodide, KOH/KI, are added under the level of the water using a dropper, Fig. 3.10(b). Care is to be exercised so as not to bubble any air into the water.

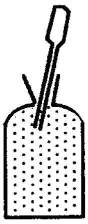


Fig. 3.10(b)

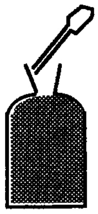


Fig. 3.10(c)

3. The bottle is stoppered, again avoiding the trapping of air bubbles, and then shaken vigorously. A muddy brown precipitate results as the air oxidises the manganese(II) ions.

4. The stopper is removed again and a few cm^3 of the contents removed. A few cm^3 of concentrated sulphuric acid are added using a dropper. This time the addition is made down the side of the neck of the bottle, Fig. 3.10(c). The mixture begins to clear immediately as the oxidised

manganese ions are reduced to manganese(II) again and the iodide ions oxidised to iodine under the acidic conditions. The bottle is stoppered once more and shaken. Since conditions are now acidic and the oxidation of the Mn^{2+} ions requires alkaline conditions, it is no longer necessary to avoid contact with air. A golden brown solution of iodine results.

5. This iodine solution is titrated with standard sodium thiosulphate solution. Freshly prepared starch solution is used as indicator.

The following reactions take place.

1. Treatment of manganese(II) sulphate with alkaline potassium iodide

$$4Mn(OH)_2 + O_2 + 2H_2O \rightarrow 4Mn(OH)_3$$

or

$$2Mn^{2+} + O_2 + 4OH^- \rightarrow 2MnO(OH)_2$$

or

$$2Mn^{2+} + O_2 + 4OH^- \rightarrow 2MnO_2 + 2H_2O$$

2. Treatment with sulphuric acid

$$6H^+ + 2I^- + 2Mn(OH)_3 \rightarrow I_2 + 6H_2O + 2Mn^{2+}$$

3. Titration with sodium thiosulphate

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

Overall every O_2 present leads to the production of two I_2 molecules and the consumption of four $S_2O_3^{2-}$ ions in the titration.

Notes

1. When the water sample is being treated with the Winkler reagents only small volumes of water are removed and concentrated solutions added. This is done so as to minimise the interference with the test sample.

2. When titrating sodium thiosulphate against the iodine solution freshly prepared starch solution is added close to the end-point (when the solution becomes straw yellow) and the end-point is detected by the change of colour from blue-black to colourless. Any return of the blue-black colour upon standing is disregarded. The titration should be repeated a number of times to get results which agree within 0.1 cm^3.

3 The calculation to get the concentration of oxygen directly involves application of the formula

$$\left(\frac{VM}{n}\right)_{O_2} = \left(\frac{VM}{n}\right)_{S_2O_3^{2-}}$$

where V = volume, M = molarity,

$$n_{O_2} = 1 \text{ and } n_{S_2O_3^{2-}} = 4$$

4. The calculation of the iodine concentration involves application of the formula

$$\left(\frac{VM}{n}\right)_{I_2} = \left(\frac{VM}{n}\right)_{S_2O_3^{2-}}$$

where V = volume, M = molarity,

$$n_{I_2} = 1 \text{ and } n_{S_2O_3^{2-}} = 2$$

Having got the molarity of the I_2, the molarity of the O_2 is simply half this value. The concentration of O_2 is then converted to grams per litre and finally expressed as mg per litre, i.e. parts per million.

5. To prepare a suitably concentrated solution of manganese sulphate (2 M) dissolve either 120 g of $MnSO_4.4H_2O$ or 100 g of $MnSO_4.2H_2O$ in water and make up to 250 cm^3 of solution. The former is the recommended salt.

To prepare the alkaline potassium iodide solution (12.5 M NaOH and 0.9 M KI) dissolve 125 g of NaOH (stirring continuously) and 37.5 g of KI in 250 cm^3 of deionised water. Cool to room temperature before use. This solution is caustic so care is required.

To prepare the starch indicator, make a paste of about 2 g of starch in cold water. Pour it into 200 cm^3 of boiling water and stir. When it is cool, add a few drops of trichloromethane (chloroform).

To make the 0.025 M sodium thiosulphate, $Na_2S_2O_2.5H_2O$, crystals should be used. Dissolve 1.55 g of the crystals and make up to 250 cm^3 of solution. If the crystals have turned white, because of loss of water of crystallisation, they should not be used.

6. If the Biochemical Oxygen Demand is being estimated, a second water sample, collected under the same conditions, should be stored in the dark for five days at 20 °C. The reduction in its dissolved oxygen concentration after five days, expressed in p.p.m., is the BOD. The time of analysis of the first sample is taken as $t = 0$.

   For samples of particularly high contamination the sample may be diluted and aerated initially and suitable scaling up of the result done at the end to take into account the dilution. This is necessary since the pollutants in the water would have consumed all the oxygen present long before the end of the five-day period.

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MODULE 5

Stoichiometry I

CONTENTS

Chapter 1 **Chemical Composition**

Chapter 2 **Skills**

Chapter 3 **The Mole**

Chapter 4 **Chemical Calculations**

CHAPTER 1 CHEMICAL COMPOSITION

1.1 Introduction to Chemical Composition

It is essential to have information about the nature of chemicals at the atomic, molecular and bonding scales for chemical formulae and equations to be completely meaningful and before calculations are attempted. Many chemical calculations involve decisions about adjusting figures for diatomicity, triatomicity, etc., and for dissociation into ions or for dilution by various factors, etc. An understanding of the composition of chemicals helps in the decision-making process. The importance of studying chemical composition in a purposeful way to help solve chemical problems is not often emphasised and as a result a knowledge of chemical composition is often acquired in an accidental way and remote from calculations. As this module concentrates on an introduction to calculations in chemistry, it begins with a systematic study of chemical composition.

1.2 Elements

Monatomic Gases

Just a few elements exist in their standard states as isolated free atoms. These are the noble (or inert/rare) gases and they can be denoted monatomic gases. These elements are represented by their atomic symbols, e.g. He, Ne, etc. Of all substances these gases come closest in behaviour to the ideal gas concept because of the small size of the particles and their very weak attraction for one another (see intermolecular forces, p.11).

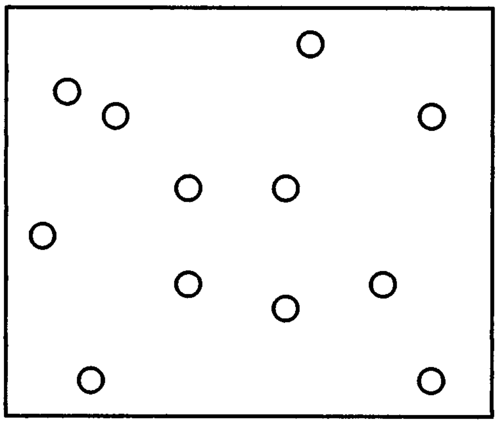

***Fig. 1.1** Monatomic gas*

Diatomic Gases

Most other elemental gases are diatomic, e.g. hydrogen, oxygen, nitrogen and chlorine consist of pairs of atoms. These gases are represented by the formulae H_2, O_2, N_2 and Cl_2. However, the pair of atoms may be linked by a single covalent bond or multiple covalent bonds. This information about the bonding is not conveyed by the formulae.

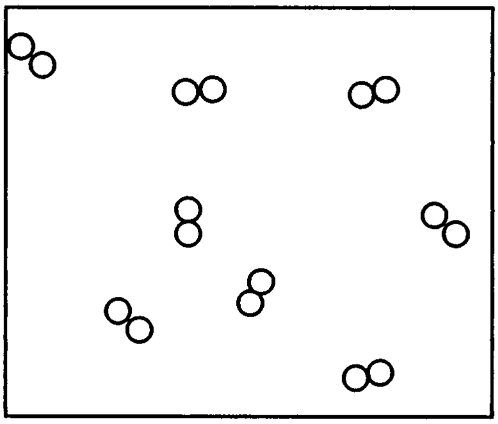

***Fig. 1.2** Diatomic gas*

Note that when calculations involve the mass of 'oxygen' or 'hydrogen', consideration must be given to whether the question refers to elemental hydrogen or oxygen or to combined hydrogen or oxygen. In the first case the substances in question are hydrogen gas, H_2, and oxygen gas, O_2, and have relative molecular masses of 2 and 32 respectively. However, if referring to combined hydrogen in methane, say, or oxygen in titanium oxide, then individual atoms of hydrogen and oxygen with relative atomic masses of 1 and 16, respectively, must be considered. The same point clearly applies to chlorine, nitrogen, etc.

Ozone[1,2]

Allotropes are different physical forms of the same element. Oxygen has two allotropes, the diatomic gas mentioned above, oxygen (dioxygen), O_2, and the triatomic gas, ozone (trioxygen), O_3. Oxygen gas, O_2, is colourless and stable and makes up a little more than 20% of the lower atmosphere. It is the main respiratory gas. Ozone, O_3, is blue and is very toxic. It occurs in traces in the upper atmosphere where it plays a very important role in controlling the intensity of ultraviolet radiation reaching the earth's surface by absorbing a certain quantity of this radiation. Oxygen and ozone exist in a dynamic equilibrium, with certain photolytic processes in the upper atmosphere converting oxygen to ozone and the ozone back to oxygen again. This natural cycle maintains a layer of ozone in the stratosphere at a height of about 25 km above the earth's surface.

Atmospheric ozone has become a cause for concern in the last decade as breakdown of ozone, creating a hole in the ozone layer above Antarctica, threatens to allow greater quantities of ultraviolet radiation to reach the earth's surface and cause an increase in skin melanomas and crop damage. International agreements to reduce the use of ozone-damaging gases will arrest the damage and in time, it is hoped, reverse it. Oxygen in its most common form, O_2, is the gas referred to when the substance oxygen is mentioned unless either the name ozone or the formula O_3 is specifically denoted. Several other elements exhibit allotropy, e.g. sulphur, carbon, phosphorus, tin, iron, etc. (See p. 3.)

Liquid Non-metallic Elements

The non-metallic element bromine exists as diatomic molecules, Br_2, but is a liquid at room temperature. The only other element which is liquid at room temperature is mercury which is a metal. Mercury, in both liquid and vapour form, is monatomic. (Gallium, m.p. 30 °C, is a liquid in hotter climates.)

Solid Non-metallic Elements

There are two types of solid non-metallic element. The first type consists of single atoms occupying the lattice points of a repeating crystalline structure. The atoms are held together by covalent bonds. Such arrangements are called covalent macromolecular crystals. Examples include the diamond structures of carbon and silicon and the planar structure of graphite. The planes of graphite however are bonded together by van der Waals forces. (See section 1.3.) These structures are generally stable and difficult to melt or vaporise since separating or disturbing the atoms involves breaking strong covalent bonds. The formulae used for these elements, which exist as giant molecules, are simply C, Si, etc.

The second type of solid non-metallic element consists of molecular crystals. Here the atoms are joined together by covalent bonds to form small molecules which then occupy the lattice points of a regular crystalline structure. The molecules are bound into the crystalline structure by van der Waals forces. Since van der Waals forces are relatively weak, these molecular crystals have rather low melting points and often sublime. The covalent bonds of the molecules which occupy the lattice positions are not broken in the melting or subliming processes.

Examples of molecular crystals include iodine and sulphur. In an iodine crystal, the lattice points are occupied by diatomic I_2 molecules which contain a single covalent bond. Weak van der Waals forces hold these non-polar molecules together in a dark coloured, almost black, body-centred orthorhombic lattice which sublimes easily upon heating to give a purple vapour which has an unpleasant smell and is harmful.

The melting point of iodine, 113.60 °C, is very close to the temperature at which it will sublime at atmospheric pressure. Since the individual molecules of the crystalline structure are non-polar, the solubility of iodine in polar solvents is limited.

A number of allotropes of sulphur exist. The most common of these is orthorhombic cyclooctasulphur. In a crystal of this species, the lattice points are occupied by puckered rings of S_8 molecules where the atoms are joined by single covalent bonds. Weak van der Waals forces hold these non-polar molecules together in a yellow-coloured orthorhombic crystal system which melts easily at 113 °C to give a yellow liquid which ignites easily and is an irritant. Like iodine molecules, sulphur molecules, S_8, are also non-polar and therefore insoluble in polar solvents but dissolve in the non-polar solvent carbon disulphide, which is also an irritant, highly flammable and may cause harm to an unborn child. In equations the formula S is nearly always used for elemental sulphur rather than S_8, but iodine, like the other halogens, is always represented by the formula I_2.

Allotropy

Allotropy is the existence of elements in different physical forms. Many of the solid non-metallic elements exhibit allotropy. Allotropes can have distinctly different physical properties or may merely show subtle differences in physical properties, for example, in densities or melting points. Diamond and graphite, allotropes of the element carbon, illustrate how dramatically different the physical properties of allotropes can be. While diamond is colourless when pure, very hard (10 on Mohs' scale of hardness of minerals which ranges from 1-10) and a non-conductor of electricity, graphite is described as soft (a degree of hardness of only 1-2 on Mohs' scale), is black and is a good conductor of electricity. These contrasting properties can be explained by examining the structure of the macromolecular crystals of the two allotropes. Models are essential to show the three-dimensional nature of the structures but Figs. 1.3(a) and 1.3(b) give a two-dimensional view of the structures.

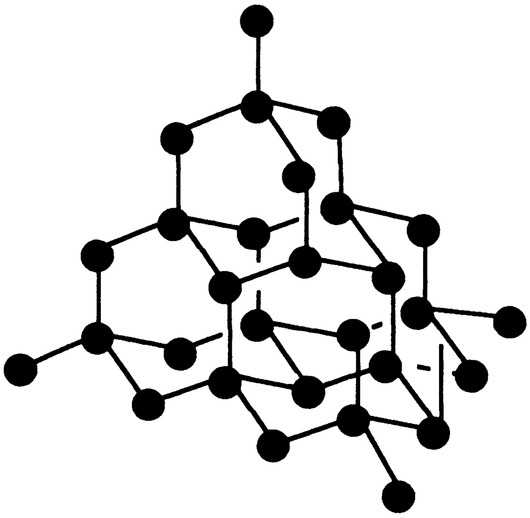

Fig. 1.3(a) *Diamond*

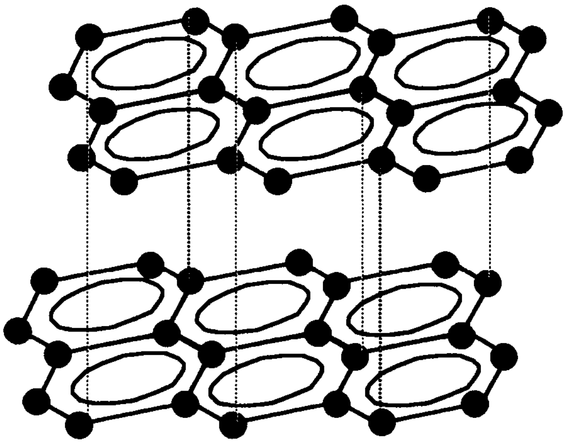

Fig. 1.3(b) *Graphite*

Diamond consists of a giant molecular crystal composed of carbon atoms joined by single covalent bonds, the symmetry about each carbon atom being tetrahedral. (See section 1.3.) The valence electrons of each carbon atom are located in these carbon-carbon bonds and thus are not free to move through the structure, hence diamond does not conduct electricity. The hardness of diamond derives from the C-C bonds which are equally strong at any point in the crystal and, as the model shows, many bonds must be broken to divide a sample of diamond in two. Some of the main uses of natural and synthetic diamonds take advantage of the hardness of diamond for drilling and cutting. Heating will transform diamond to graphite. Note also, in the model, that diamond has large hexagonal spaces in its structure and a very regular geometric internal arrangement of atoms. The crystal system is face-centred cubic (see p. 6).

If diamond is cut along a cleavage plane, i.e. a plane passing through a set of bonds all orientated in the same or equivalent directions, a very regular reflecting surface is obtained. Diamond has a high refractive index (2.4). Therefore, light undergoes total internal reflection for a large set of angles. It also has a high dispersive power so light readily forms a spectrum on passing through diamond. The internal and external reflections and dispersion of light make diamond a very valuable jewel, well known for its sparkling powers. It does not absorb the visible light which passes through it, hence is colourless. The mass of diamonds and other gemstones is often measured in carats; one carat is equal to 0.200 g.

Graphite is also a giant molecular crystal. It consists of planes of carbon atoms arranged in hexagonal rings joined by single carbon-carbon bonds with additional delocalised bonding, somewhat similar to that in benzene, as indicated in Fig. 1.3(b). Layers of planes are arranged on top of one another and are held in place by van der Waals forces, (see section 1.3). There is a slight displacement of atoms from one layer to the next, i.e. the carbon atoms in one layer are not exactly above the carbon atoms in the lower layer. The crystal system is hexagonal. Graphite sublimes at a temperature of 3652 °C.

Graphite is a good conductor of electricity because the electrons of the delocalised bonds are free to move along a layer. These particular electrons can also absorb light in the visible region of the spectrum and so graphite is dark grey, almost black. The ability of the layers to slip over each other is responsible for the softness and lubricating properties of graphite. The layers can be easily sheared away from one another because the van der Waals forces between the layers are weak and easily broken. As graphite is moved across paper, the layers separate from one another, leaving a dark mark on the paper, hence graphite is used as the lead in pencils, where it is mixed with various proportions of clay to give different hardnesses. The name graphite comes from the Greek word for writing.

Graphite is thermodynamically more stable than diamond and is less dense. Hence high pressures and high temperatures favour the industrial production of synthetic diamonds. Other forms of carbon are sometimes incorrectly described as allotropes. These include charcoal, soot and lampblack but it has been shown that their structures are composed of graphite microcrystals.

However, there are further, quite recently synthesised, allotropes of carbon called fullerenes. These substances have very regular cage-type structures. Carbon clusters of formulae C_{60} and C_{70} have been made by shining a laser beam onto graphite. The smaller of these spherical cages consists of 12 pentagons and 20 hexagons of carbon atoms in a perfectly symmetrical soccer ball-shaped hollow molecule which forms a mustard-coloured crystalline solid. The second structure, C_{70}, has the shape of a slightly squashed sphere and again consists of pentagons and hexagons of carbon atoms. There are four different carbon environments in C_{70}. It is a red brown solid. Other clusters are under investigation, including C_{240} and tubular arrangements.

Those who in 1985 discovered and have since characterised this new allotrope, were awarded the 1996 Nobel Prize in Chemistry. The recipients were **Robert F. Curl, Jr.** (1933-), **Sir Harold W. Kroto,** (1939-) and **Richard E. Smalley** (1943-).[3,4,5,6]

Phosphorus has three common allotropes, white, red and black phosphorus. White phosphorus is extremely toxic, ignites spontaneously in air and must be stored under water. Red phosphorus is much less toxic and more stable in air, although highly flammable. Black phosphorus is relatively inert. Thus, allotropes differ in chemical reactivity. However, when they do react with the same reagent the same products are formed from all the allotropes of the same element. Other elements which have allotropes include selenium, sulphur and arsenic.

Crystals

Crystals are symmetrical solids bounded by flat faces. The regular crystal shape results from the regular internal arrangement of the ions, atoms or molecules of which the crystal is composed. Corresponding flat faces of crystals of the same material always meet each other at the same angle although the sizes of individual crystals of the same substance may differ. There are seven crystal systems[7] according to the number of planes and/or axes of symmetry possessed by a crystal. The simplest crystal system is the cubic crystal system. Crystals of this system have three axes at mutual right angles and all of equal length. The next simplest is the tetragonal system which has three axes, mutually at right angles, two of which have the same length. The other five crystal systems are defined by other elements of symmetry. Three-dimensional space can be filled only by repeating these seven crystal systems. Space cannot be completely filled by repeating any other geometric shape.

SYSTEMS	AXES	ANGLES
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°$ $\beta \neq 90°$
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°$ $\gamma = 120°$
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$

Table 1.1 *Crystal systems*

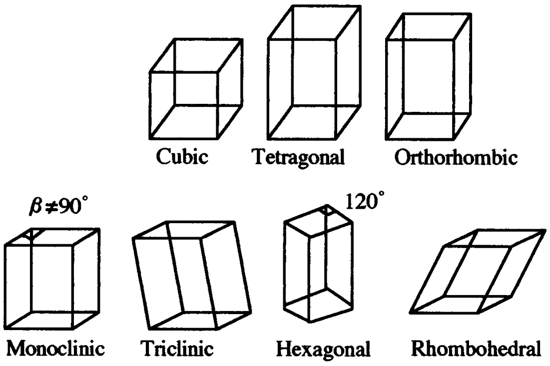

Fig. 1.4 *Seven crystal systems*

Within a crystal system there may be more than one crystal structure[8]. For example, within cubic crystals layers can be positioned in three different ways: simple cubic, body-centred cubic and face-centred cubic packing. In simple cubic crystal structures, Fig. 1.5, horizontal layers are arranged vertically so that one atom is always in line with another. Each atom or ion is surrounded by six others. In simple cubic structures 52% of the total volume is occupied by atoms or ions.

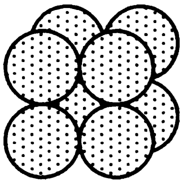

Fig. 1.5 *Simple cubic packing, e.g. Po*

In body-centred cubic structures, Fig. 1.6, each atom or ion touches eight other atoms or ions - single out the sphere at the centre of the cube in the diagram and the eight spheres touching it are at the corners of a cube. In body-centred cubic structures 68% of the total volume is occupied by atoms or ions.

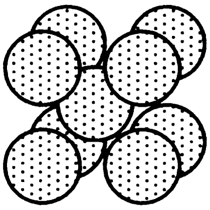

Fig. 1.6 *Body-centred cubic packing, e.g. sodium or iron*

In face-centred cubic crystals, Fig. 1.7, each atom or ion touches twelve others. In this case 14 spheres occupy a cube, eight in the corners and one in the centre of each of the six faces of the cube.

The sphere in the centre of the front face can be seen to touch the four spheres in the same face as itself and the four spheres forming a diamond or rhombus behind it which lie at the centres of four other faces of the cube; clearly it will likewise touch four more spheres in another diamond to the front in the crystal structure. The packing of atoms is more dense in this arrangement than it is in body-centred cubic crystals, with 74% of the space occupied by atoms or ions in face-centred cubic crystals.

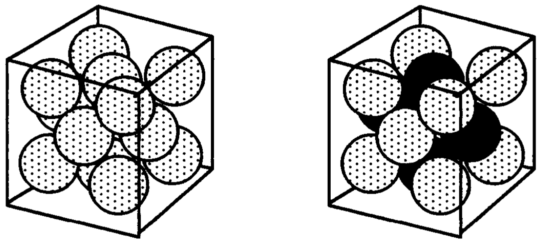

Fig. 1.7 *Face-centred packing, e.g. gold or diamond*

The tetragonal crystal system has two crystal structures associated with it, namely simple tetragonal and body-centred tetragonal. In all, the seven crystal systems named above give rise to a total of the fourteen crystal structures shown in Fig. 1.8.

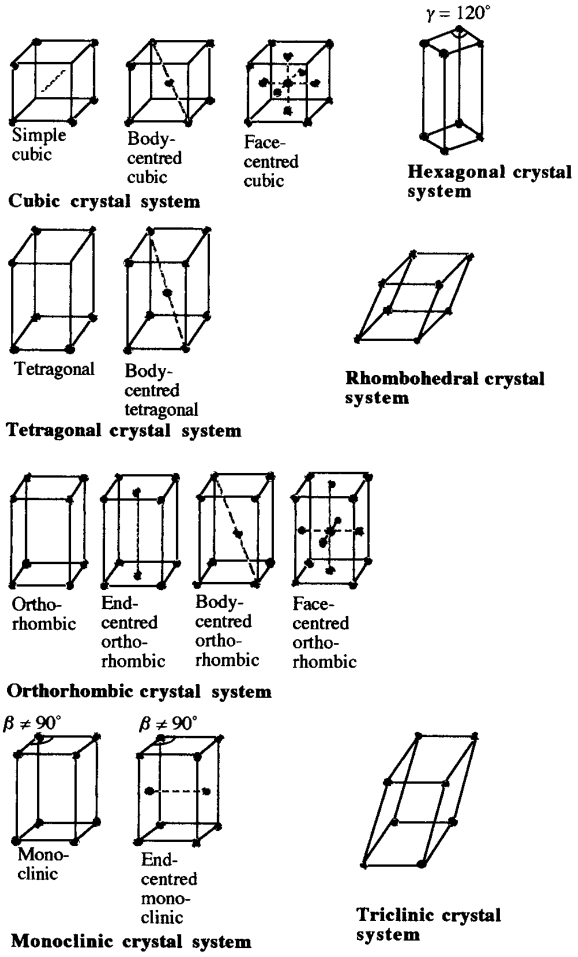

Fig. 1.8 *Fourteen crystal structures*

Crystal Structure - X-ray Diffraction

Resolution in optics is the separation of the images of two objects at close proximity to each other such that these images can be distinguished from one another by the observer. Resolution becomes limited when the wavelength of the incident radiation is of the same order as the dimensions of the object being examined. Therefore light waves can be used to examine the main features of a biological cell but waves of very short wavelength, of the order associated with high-speed electrons, are required to examine cell ultrastructure. Crystal structure determination uses waves of even shorter wavelength than those associated with high-speed electrons.

However, crystal structures can be deduced using X-rays although they have wavelengths actually longer than, or of the same order as, the interatomic spacings in a crystal. This is because the regular array of atoms, ions or molecules within the crystal will scatter the incident X-rays in a meaningful pattern. This technique, known as X-ray crystallography, does not give a picture of the crystal structure in the same way that an electron microscope produces photographs of the cell fine structure. Instead it produces data which must be interpreted to build up a picture of interatomic spacings within and between layers in the crystal.

X-ray crystallography techniques were first developed by **Max von Laue** (1879-1960) and by father and son **William Henry Bragg** (1862-1942) and **William Lawrence Bragg** (1890-1971). In 1912 von Laue discovered that X-rays were diffracted by crystals. The Braggs took up the study, interpreting the von Laue results and applying them to the determination of X-ray wavelengths and crystal structure. In 1802, **Thomas Young** (1773-1829) had measured the wavelength of light by diffraction at the larger gaps created by scratches on a glass slide. The Braggs used inter-ionic spacings, calculated from the density and relative molecular mass and assumed arrangements of the ions in rock salt (NaCl) to calculate the wavelengths of X-rays (see the Bragg equation below). The X-ray technique was then applied in reverse, i.e. they

Wave type	**Approximate wavelenght range/m**
Visible light	**4.3×10^{-7} to 6.9×10^{-7}**
Fast electrons	**2×10^{-12}**
X- rays	**1×10^{-8} to 1×10^{-12}**
Spacing	**Distance/m**
Resolving abilty of eye	**1×10^{-4}**
Interionic distance in NaCl	**2.8×10^{-10}**
Ionic diameter of Cl^-	**3.62×10^{-10}**
Typical animal cell diameter	**1×10^{-5}**
Cell ultrastructure membrane width	**7×10^{-9}**

Table 1.2 *Wavelengths and spacings associated with optic resolution*

used X-rays of known wavelengths to determine the spacings of atoms and ions in other crystals.

Crystal structure determination can be carried out using a single crystal of a high degree of purity or using a powdered sample. In either case a collimated beam of monochromatic X-rays of known wavelength is directed at the sample which is surrounded by an almost completely cylindrical strip of photographic film. The sample is rotated so that scattering takes place in all possible planes.

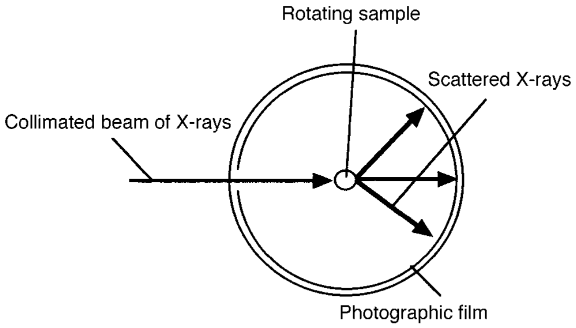

Fig. 1.9 *X-ray scattering to determine crystal structure*

Parallel X-rays strike regularly arrayed layers of particles in a crystal and are scattered at the electron clouds of the atoms.

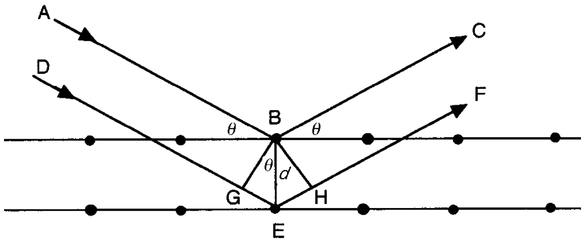

Fig. 1.10 *X-ray scattering at adjacent layers in a crystal*

Consider the two adjacent X-rays, AB and DG, striking two adjacent layers of atoms in the crystal in Fig. 1.10. If these are scattered by the crystal particles at B and E such that they emerge from the crystal still in phase, they reinforce one another, i.e. they interfere constructively, and a dark image is produced where they strike the photographic film. These rays will be in phase provided that the difference in their paths within the crystal is equal to a whole number of wavelengths. Note that the angle of deviation of the X-ray beam is 2θ, where θ is the angle between the incident ray and the surface of the crystal. Their path difference is equal to $|GE| + |EH|$. Therefore, for constructive interference

$$
\begin{aligned}
n\lambda &= |GE| + |EH| \\
&= 2|GE| \\
&= 2d\sin\theta \\
\Rightarrow d &= \frac{n\lambda}{2\sin\theta}
\end{aligned}
$$

This condition is known as the Bragg equation and the spacing, *d*, between layers within the crystal can be obtained if it is solved. The angle θ may be obtained from the deviation of the X-ray by 2θ from its original pathway. Sufficient information about the spacings between various layers enables the crystal structure to be fully deduced. Fig. 1.11 shows that a single atomic crystal has several sets of planes with different separations, *d*, at which scattering of X-rays could occur.

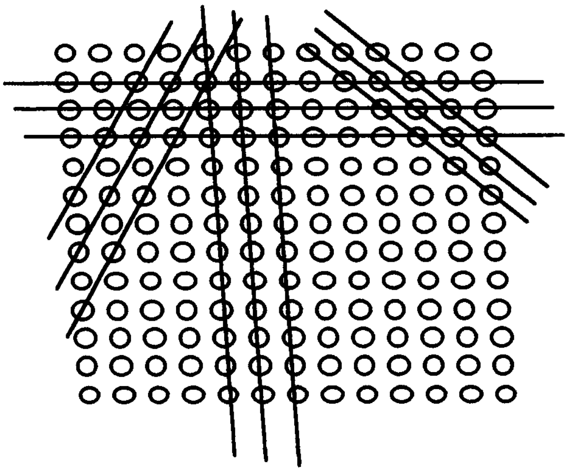

Fig. 1.11 *Several sets of planes for X-ray scattering within a crystal*

Information obtained about all of these *d* values eventually allows a crystal structure to be assigned.

Dororthy Mary Crowfoot Hodgkin (1910-1994) was an English biochemist who was awarded the 1964 Nobel prize for chemistry for her work on the determination of complex organic structures through X-ray diffraction techniques. She established the structures of the digestive enzyme pepsin, penicillin and Vitamin B_{12} using X-ray crystallography data and other chemical evidence. She was the first person to use a computer to help solve a biochemical problem - she used it to analyse the data obtained from the X-ray scattering experiments. Up until this time the only way of establishing structure was to succeed in making a synthetic copy of the original molecule. In 1969 Hodgkin was able to determine the structure of insulin, a huge molecule, containing more than 800 atoms, by these techniques.

Metallic Elements

The metallic elements are, with the exception of mercury, all found in the solid state at room temperature. Metals consist of an orderly array of positively charged ions in a sea of valence electrons (or more technically, a delocalised electron cloud). The attraction of the positive ions for the electrons overcomes the repulsion of the positive ions for one another. Electrons are free to move through the arrangement and are not associated with any particular atoms. The electrons move in a random way ensuring overall neutrality in the solid. If an electrical potential difference is applied between the two ends of a piece of metal the electrons will move from low to high potential, constituting an electric current. Thus, metals conduct electricity. The electrons lost by the metal atoms and which become the delocalised electron cloud of the metallic bond are usually the valence electrons - inner electrons are not involved in the metallic bond. The orderly arrangement of the metal ions differs from metal to metal, e.g. gold and silver have a face-centred cubic crystal structure, while chromium and iron both have body-centred cubic crystal structures. In mercury, which is a liquid at room temperature, the metallic bond exists but there is no orderly arrangement of positive ions. They are in continuous movement. Any other metal in the molten state has a similar totally mobile set of ions and electrons as mercury.

Iron

Two European capitals have important landmarks which have great scientific and technological interest. Both emphasise the important role of iron metal in our lives. The Eiffel Tower in Paris is a monument to the large-scale grandiose constructions of immense strength, complexity and beauty which can be achieved with iron while the Atomium in Brussels looks at iron on the atomic scale and also reminds us of iron's constructional value.

The Eiffel Tower was built as the centre point of the 1889 Universal Exposition in Paris. The tower was designed by two engineers and an architect, **Alexandre Gustave Eiffel** (1832-1923), after whom it is named. The building costs of $1 000 000 were paid for by admission fees in the first year. It was the tallest structure in the world for many years after its construction. It is 317.96

metres in height with a view of 135 kilometres from the top, has a mass of 10 100 tonnes and consists of 18 000 pieces of wrought iron connected together with 2 500 000 rivets. At the top of the tower there is a glass dome which houses physical, meteorological and biological laboratories. There are three lifts which transport visitors to three viewing levels where there are souvenir shops, restaurants and technical, tourist and photographic exhibitions.

The Atomium was built in Brussels for the Universal and International Exhibition of 1958. The Atomium was the concept of engineer Andr Waterkeyn and his intention was to give Belgian industry an opportunity to display its metalworking, engineering and electrotechnical skills. The Atomium represents part of an iron crystal magnified 160 billion times. It shows the body-centred cubic crystal structure of iron metal using nine hollow spheres interconnected by tubes containing escalators and lifts. The weight-bearing structures are composed mainly of steel and the exterior covering of the spheres is a special aluminium alloy chosen for its low density and light-reflecting properties. It originally housed an exhibition of peaceful uses of atomic energy with a restaurant in the uppermost sphere. It is still used as an exhibition centre with pedagogical displays of BIOGENIUM on evolution, genetics, immunology, etc., in the various spheres.

Alloys[9]

Alloys have a metallic bonding system similar to pure metals. Alloys are intimate mixtures of elements, usually metals. The metals are normally mixed in definite proportions so that the properties of the resultant alloy have a certain combination of the desired properties of the constituent metals, e.g. 18-carat gold contains 18 parts gold and 6 parts copper and/or silver. The rich gold lustre is thus conserved for jewellery and other precious objects, while the copper and silver improve the hardness of the metal, pure gold being quite soft. The proportion of copper to silver determines the colour of the alloy. If there is no silver the copper imparts a red colour to the alloy; if there is no copper the silver makes the alloy very pale in colour; silver and copper together produce the shades of golden yellow most popular for jewellery.

The carat is a measure of the purity of the gold. Pure gold is described as 24-carat gold. 22-carat, 18-carat, 14-carat and 9-carat gold have 22, 18, 14 and 9 parts gold, respectively, and 2, 6, 10 and 15 parts copper and/or silver, respectively, the hardness increasing as the proportion of the gold decreases. Gold must be hallmarked to indicate its composition.

Brass consists of copper and zinc and is widely used for cartridge cases for bullets, plumbing joints and fittings, door handles, etc. It was formerly used, partly for decoration since it has a bright gold appearance when polished, on the harness of horses, on ships and on scientific instruments.

Bronze, one of the earliest alloys, is composed of copper and tin and nowadays is often used for sculpture. Several well-known Irish sculptures are bronzes, as is the statue of Robert Bunsen in Bismarkplatz in Heidelberg, Germany. Bronze was used for brown coins but modern pennies and tuppences are copper-coated steel, as tests with a magnet on old and new coins will indicate.

Another example shows that alloys can have quite complex compositions. Pewter is an alloy of tin and lead, usually 63% tin and less than 35% lead if the pewter is to hold food or drink; a trace of copper is added to improve ductility and antimony is added if a hard alloy is required.

Alloys most usually consist of mixtures of metals but occasionally consist of a metal and a non-metal, e.g. steel consists of iron with a small percentage of carbon. An alloy of a certain name, e.g. steel, can actually represent a very wide range of materials with variable proportions of the constituent elements. So steel is predominantly iron, with any small percentage (up to about 1.7%) of carbon and small amounts of various other metals added. Stainless steel alloys constitute a further subdivision of steels. Stainless steel is a corrosion-resistant steel containing a fairly high percentage - between 11 and 26% - of chromium and sometimes other elements including manganese, vanadium, molybdenum, nickel, tungsten, etc., in addition to iron and carbon. In fact there are a few hundred different stainless steel compositions, the exact composition depending on the end use. Stainless steel is used for cutlery, draining boards and other domestic uses, car exhausts, car, aircraft and oil rig structural components, chemical industry vessels and pipes, etc. These alloys are highly resistant to corrosion under various severe conditions, because of a protective microfilm of a chromium oxide which forms on the surface of the steel. If scratched, chromium oxide will form on the exposed steel in the scratch. Stainless steel is dull silver-grey in colour but can be polished to a high degree. De Lorean cars, built in Belfast in the 1980s, and one of which was used for time travel in the Back to the Future movies, had very attractive stainless steel panels instead of the usual painted steel panels used for bodywork in most cars.

Alloys often have properties associated with their constituent elements; but they can have new properties not derived from any of the original elements. The strength of steel is an example since neither pure iron nor carbon have the strength of steel. (See Experiments 1.1 and 1.2.)

1.3 Compounds

Ionic Compounds

Ionic compounds do not exist as discrete molecules. When an electropositive and an electronegative element react, electrons are transferred from atoms of the former to atoms of the latter. Where the transfer is over 50% the compound formed is referred to as an ionic compound. The positive and negative ions formed as a result are mutually attracted to one another but the positive ion is simultaneously attracted to other neighbouring negative ions also, while the negative ion is attracted to a number of other positive ions. As a result ionic compounds exist as extended, electrically neutral, crystalline lattices of positive and negative ions held together in a regular array by electrostatic attraction. For example, in sodium chloride each positive sodium ion is attracted to six negative chloride ions which form a sphere of negative charge around the positive ion. Each of these negative chloride ions is in turn surrounded by six positive sodium ions in a cubic face-centred packing crystal structure. A model of a sodium chloride crystal shows this arrangement very clearly. In a crystal of sodium chloride the ratio of sodium to chloride ions is 1:1. In a crystal of sodium chloride, the vast majority of the ions are surrounded by six ions of the opposite charge except on the surface. The ions on the surface of the crystal have only five, four or three bonds to oppositely charged ions in the crystal. These ions on the surface may become weakly bonded to water or other polar molecules if they are present in the environment of the crystal. An ionic crystal dissolves in water and other polar solvents as a result of this type of bonding between the polar solvent molecules and the ions on the surface. The crystal is dismantled by the attraction of the negative ions of the crystal for the electropositive ends of the polar molecules while the positive ions are attracted towards the electronegative ends of the solvent molecules. The ions which are detached from the crystalline structure become surrounded with water molecules, i.e. hydrated. The positive ions are stabilised by the electronegative oxygen atoms of water while the negative ions are stabilised by the electropositive hydrogen atoms. (See ion-dipole interactions on p. 11.)

Note that a model of sodium chloride showing a small portion of the repeating pattern has a relatively small number of ions and there may not necessarily be equal numbers of sodium and chloride ions present, hence the ratio of sodium to chloride ions may not seem to be 1:1. Mathematically the ratio is still taken as 1:1 since the model represents only a tiny part of a real crystal. Also, in the small model, there is clearly relatively less bulk crystal and there are relatively more edge effects than in a real crystal.

Ionic compounds often have elements present in ratios other than 1:1. Depending on the valencies of the elements combining there may be double or even triple the number of atoms of one element required to electrically balance the atoms of the other element present. For example, in magnesium chloride there are twice as many chloride ions as magnesium ions since each magnesium atom loses two electrons, thus requiring two chlorine atoms, each of which accepts one of these electrons. The packing of these ions in the crystal lattice will arrange the ions so as to maximise the electrostatic interactions of oppositely charged ions.

The formula of an ionic compound represents the simplest whole number ratio of the number of atoms of the elements present, i.e. the empirical formula. The electropositive element is usually given first in the formula. The terms molecule and molecular mass are inappropriate with reference to ionic compounds. The term formula mass is used to indicate the mass of the ionic substance corresponding to its formula.

Intermolecular Forces

Intermolecular forces of the order of 2 - 40 kJ mol^{-1} are collectively known as van der Waals forces after **Johannes van der Waals** (1837-1923) who first described their effects in calculations involving gases in 1879. The typical, rather weak, intramolecular single covalent bond of F_2 has a value, by comparison, of 154 kJ mol^{-1}. Clearly therefore, these intermolecular forces are significantly weaker and more easily broken than covalent bonds. They include the following.

(i) Dipole-dipole interactions between polar molecules

The molecules of polar substances tend to associate together to form large clusters of several hundred molecules. This molecular association is due to dipole-dipole interaction or bonding and is responsible for the higher than might be expected melting points, boiling points and specific heat capacities of these substances. Dipole-dipole interactions arise in polar covalent substances when the electronegative end of one polar molecule is attracted to the electropositive end of a neighbouring dipole. Occasionally, the molecular association is at a very organised level and crystals result. Crystals composed of polar covalent molecules held in the lattice structure by dipole-dipole interactions belong to the molecular crystal category. An example is the substance ICl which has a melting point of 27.2 ^{o}C. Br_2, by contrast, a substance with similar intramolecular bonding and molecular mass but which is non-polar, is a liquid at room temperature; its melting point is -7.1 ^{o}C.

(ii) Hydrogen bonding between polar molecules which contain hydrogen

Hydrogen bonding is a specific type of dipole-dipole interaction involving polar covalent molecules which contain hydrogen and any small highly electronegative atom (in practice F, O or N) and is again responsible for the abnormally high melting points, boiling points and specific heat capacities of these substances, e.g. water or hydrogen fluoride. Hydrogen bonds are stronger than other dipole-dipole interactions because of the large difference in electronegativity between hydrogen and the other electronegative element. The small size of the hydrogen atom allows the two interacting molecules to approach close to one another, thus increasing the strength of the interaction.

(iii) Ion-dipole interactions between an ion and the oppositely charged end of a polar molecule

These often arise in water or other polar solvents when an ionic compound is dissolved, e.g. sodium chloride dissolved in water (see below). The electronegative oxygen atoms of the water molecules interact with positive ions of the ionic compound while the negative ions form ion-dipole interactions with the electropositive hydrogen atoms of water. Several water molecules help to solvate (interact with) each ion, as the ionic compound dissolves.

(iv) London dispersion forces in non-polar molecules

London dispersion forces are weak attractive intermolecular electrostatic forces which are caused by the movement of electrons within a non-polar molecule. They were first described by **Fritz London** (1900-1954) in 1928. Electrons located temporarily at one end of a molecule set up a weak temporary dipole in the molecule which can interact with similar dipoles in neighbouring molecules and induce similar dipoles in neighbouring molecules. This results in a tendency for gases composed of non-polar molecules to condense into liquids at high pressure. At low temperature, when the reduced speed of movement of the molecules makes it more difficult for them to overcome the attractive forces drawing them together, a tendency of these gases to condense into liquids is also observed. These London dispersion forces are more likely to arise in large molecules rather than in small and in molecules of certain complex geometry rather than in simpler molecules. Since London dispersion forces are electrostatic they increase as the intermolecular distance decreases. Of all gases, the noble gases come closest in behaviour to the ideal gas concept of molecules exerting no attractive or repulsive forces on one another except during collisions. In particular, the noble gases are the most ideal because they are single atoms and therefore have the simplest geometry and least degree of London dispersion interactions. Of the noble gases helium is the most ideal because of the small size of its atoms. In accurate work, corrections must be made for these forces when applying the gas laws to real gases, particularly at high pressures or low temperatures.

A practical illustration of the significance of intermolecular bonding was discussed by T. T. Earles in an article entitled *'Can London Dispersion Forces be Stronger than Dipole-Dipole Forces, including Hydrogen Bonds?'* - reprinted with permission from the Journal of Chemical Education (No. 72, August 1995, p. 727).

'Can London dispersion forces be stronger than dipole-dipole forces, including hydrogen bonds?" The answer is a resounding and mouth-watering, "Yes!". And here is an example that all high school and college chemistry students will identify with in a very personal way. That example is French Fries - the staff of life of the fast food set.

In cooking French Fries, the process is possible because the London dispersion forces in the cooking oil are stronger than the hydrogen bonds in the water of the potato. Cooking oil contains high molecular weight hydrocarbon chains typically in the C_{18} range. This allows the oil to stay below boiling at a temperature that is above the boiling point of water. Thus, the potato becomes dehydrated, and that, along with the partial caramelization of the starch, produces that wondrous crispy delight we call "French Fries".

... many students think "weak" when they think of dispersion forces and "stronger" when they think of hydrogen bonds. They do not take into account the additive effect of dispersion forces between large molecules. The point should be made that, while on an individual basis dispersion forces are considerably weaker than hydrogen bonds, it is the additive effect of many dispersion forces between large molecules that causes those molecules to have a greater intermolecular attraction and, hence, a greater boiling point than water.

A traditional example of this would be to refer to a table showing the increase in boiling points with molecular weight in the normal alkanes. Such a table will show that once you get to octane, the boiling point of water is exceeded.

...This traditional example is a good one and should be used by all means, but the French Fry example is one students can really sink their teeth into.'

Non-polar Covalent Compounds

Covalent compounds exist as individual molecules. Small non-polar covalent molecules are gases which have almost no tendency to associate with one another. They may, however, experience attractions towards one another due to (London dispersion) van der Waals forces. The cumulative effect of the latter causes higher molecular mass non-polar compounds to be liquid or even solid. Non-polar covalent compounds have simple formulae, representing the structure of the individual molecules of which they are composed, e.g. CO_2, CH_4, PH_3, etc. They are usually gaseous.

Polar Covalent Substances

Polar covalent substances are often found as liquids or low-melting-point solids. The molecules of these substances tend to associate together to form large clusters with several hundreds of molecules linked together. This molecular association is due to dipole-dipole interactions or hydrogen bonding and is responsible for the higher than might be expected melting points, boiling points and specific heat capacities of these substances, particularly if hydrogen bonding is involved. Crystals composed of polar covalent molecules held in the lattice structure by dipole-dipole interactions or hydrogen bonds are molecular crystals. An example is ice, where the water molecules associate into hexagonal rings using hydrogen bonds leaving large empty spaces in the bulk of the crystal. When the crystal is heated and the hydrogen bonds holding the water molecules in hexagonal rings begin to break, the water molecules collapse into the spaces in the crystal which were previously empty and so the volume contracts as ice at 0 ^oC melts to water at 0 ^oC. Hence ice is less dense than water at 0 ^oC. As water is heated from 0 to 4 ^oC further collapse of the hydrogen bonded structure occurs, and the volume continues to decrease, reaching a minimum at 4 ^oC, i.e. water has its maximum density at 4 ^oC. After 4 ^oC, as heating continues, normal thermal expansion occurs.

Hydrogen bonding between dissimilar polar molecules is involved in ammonia dissolving in water and other examples of polar solutes dissolving in polar solvents.

Polar covalent compounds have simple formulae representing the structure of the individual molecules of which they are composed, e.g. H_2O, PCl_3, NH_3, etc. The formula does not indicate the association of the molecules into clusters. See section 3.4 in the module on Atomic Structure and Trends in the Periodic Table of the Elements for means of distinguishing between polar covalent and pure covalent substances.

Shapes of Covalent Molecules

Might a student expect NH_3 and BF_3 to have the same shape? Yes, the student might reasonably expect both of these compounds to have the same shape since each consists of three atoms of one type joined to a central atom. Similarly, $BeCl_2$ and H_2O might be expected to have the same shape since in each case two atoms of the same element are bonded covalently to another atom. However, the student is expected to overcome his or her surprise to find that NH_3 is pyramidal and BF_3 is trigonal planar and that $BeCl_2$ is linear while water is v-shaped. Understanding the meaning of these new terms uses a skill which is rarely required in everyday life, i.e. thinking three-dimensionally in order to understand why these shapes arise. Not surprisingly, the shapes of covalent molecules can be a troublesome topic.

Three Dimensional Geometry

How would two drumsticks or pencils, or any such object which has two distinct ends, attached together at their handles be arranged in space so that the handles are as far apart as possible? Obviously, two drumsticks would be arranged in a line. Any other arrangement reduces the distance between the handles, Fig. 1.12.

Fig. 1.12 *Two linear objects repelling*

How would three pencils attached together at their heads be arranged so that the tips are as far apart as possible? If the three pencils become arranged in the same plane at angles of 120^o to each other, the tips are arranged at maximum distances from one another, Fig. 1.13. This is called a trigonal planar arrangement. Any alternative arrangement will reveal a smaller distance between at least two of the tips.

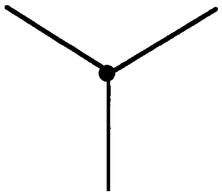

Fig. 1.13 *Three linear objects repelling*

How would four pencils attached together at their heads be arranged so that the tips are as far apart as possible? The solution here is not immediately obvious but to maximise the spacing between all the tips equally, the pencils are arranged so that the tips occupy the corners of a tetrahedron, Fig. 1.14. A tetrahedron is a three-dimensional four-sided figure. The heads of the pencils meet at the centre of the tetrahedron. The angle between any two pencils is exactly 109^{o} 28^{l} (or approximately 109.5^{o}).

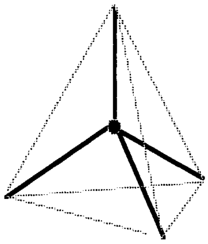

Fig. 1.14 *Four linear objects repelling*

Five pencils arranged in space form a trigonal bipyramidal arrangement, Fig. 1.15. A trigonal bipyramid is a three-dimensional object with six faces. The three pencils in the same plane are at angles of 120^{o} to one another and each of these is at an angle of 90^{o} to the pencils lying above and below this plane.

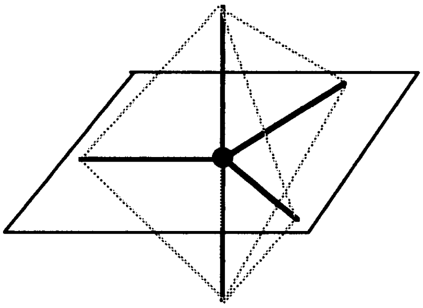

Fig. 1.15 *Five linear objects repelling*

Six pencils arranged in space make up an octahedron which is a three-dimensional object with eight faces, Fig. 1.16. The four pencils in the same plane are at angles of 90^{o} to one another and each of these is also at an angle of 90^{o} to the pencils lying above and below this plane.

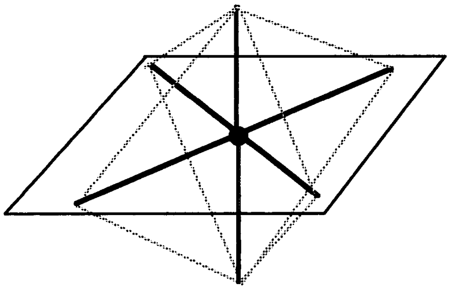

Fig. 1.16 *Six linear objects repelling*

Valence Shell Electron Pair Repulsions (VSEPR)

The shape of a covalent molecule may be predicted by electron pair repulsions in the valence shell. Note that the bonding in the covalent molecule, i.e. the formula of the compound and whether the bonds are single, double or triple, must be known in advance. Consider the valence shell of carbon in methane. A dot cross diagram shows that there are four pairs of electrons, all bond pairs, i.e. one electron of each pair of electrons originates from the carbon atom (dot) and the second electron of each pair of electrons from a hydrogen atom (cross), Fig. 1.17.

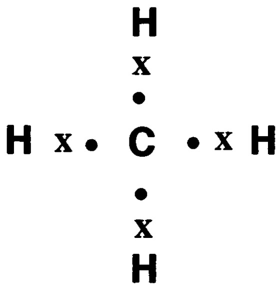

Fig. 1.17 *Dot cross diagram of electron pairs in methane*

The electrons are considered in pairs since they occupy atomic or molecular orbitals in pairs rather than remaining as single electrons. These pairs of electrons repel each other equally. The two-dimensional dot cross diagram cannot show the shape assumed by the four bonded hydrogens around the central carbon but, from the three-dimensional geometry summarised above, a tetrahedral arrangement is expected. The next diagram, Fig. 1.18, attempts to show this tetrahedral arrangement but a model is necessary to show clearly its total symmetry.

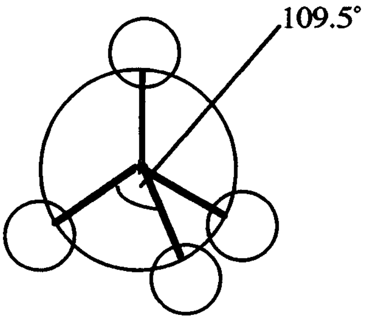

Fig. 1.18 *Tetrahedral shape of methane*

Dot cross diagrams can be used to show the electron pairs in NH_3 and in BF_3, Fig. 1.19.

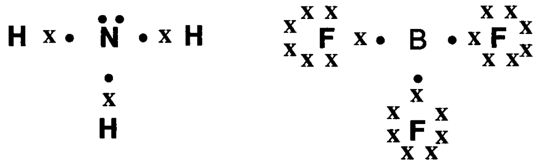

Fig. 1.19 *Dot cross diagram of electron pairs in ammonia and boron trifluoride*

In NH_3 there are three bond pairs and one lone pair in the valence shell of the central nitrogen atom. A lone pair of electrons is one not involved in bonding. All four pairs of electrons, whether they are involved in bonding or not, repel each other spatially and assume a tetrahedral arrangement in the valence shell around the central nitrogen nucleus. However, the repulsion between the electron pairs is not equal. Lone pairs lie closer to the central nucleus than bond pairs, the bond pair being attracted away from the central nucleus by the second atom with which it is shared. The distance between bond pairs is, therefore, greater than the distance between a bond pair and a lone pair which is in turn greater than the distance between two lone pairs which lie relatively close to the central nucleus. Consequently, lone pair-lone pair repulsions are greater in magnitude than bond pair-lone pair repulsions which in turn are greater than bond pair-bond pair repulsions: l.p.-l.p. > l.p.-b.p. > b.p.-b.p.

In ammonia, this means that the three bond pairs are pushed closer together by the lone pair of electrons than they would be if the fourth electron pair were also a bond pair. The H-N-H bond angle is reduced to 107° instead of the regular tetrahedral bond angle of 109.5°. Therefore nitrogen's valence electron pairs are arranged in a distorted tetrahedron. Since the final shape of the ammonia molecule is determined by the position of the atoms bonded to the central nitrogen it has a pyramidal shape, Fig. 1.20, although the lone pair of electrons has to be considered when arranging these atoms.

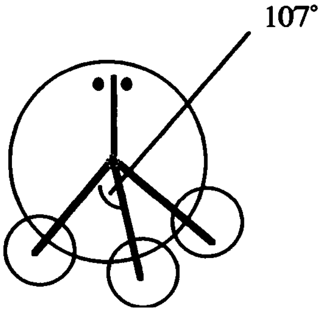

Fig. 1.20 *Pyramidal shape of ammonia*

In BF_3 there are three bond pairs and no lone pairs of electrons in the valence shell of boron. Note that boron does not obey the octet rule in this substance. These electron pairs repel each other spatially to the same extent and according to three-dimensional geometry assume a trigonal planar arrangement with F-B-F bond angles of 120°, Fig.1.21. As the name suggests the molecule is perfectly flat.

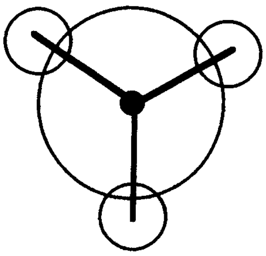

Fig. 1.21 *Trigonal planar shape of boron trifluoride*

Thus, a covalent molecule of general formula AB_3 may have a pyramidal shape or a trigonal planar shape. To assign the correct shape to a particular compound, it is necessary to (i) determine the total number of electron pairs in the valence shell, (ii) determine how many lone pairs and bond pairs are present, and (iii) consider different degrees of electron pair repulsions when predicting bond angles. Multiple bonds must also be considered where they arise (see below).

Dot cross diagrams can be used again to show the arrangement of electron pairs in H_2O and in $BeCl_2$, Fig. 1.22.

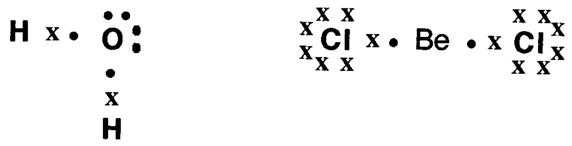

Fig. 1.22 *Dot cross diagram of electron pairs in water and beryllium chloride*

In H_2O there are two bond pairs and two lone pairs of electrons in the valence shell of the central oxygen atom. All four pairs of electrons, whether they are involved in bonding or not, repel each other spatially and assume a tetrahedral arrangement in the valence shell around the central oxygen nucleus. However, the repulsion between the electron pairs is not equal because the lone pairs repel one another more than they repel the bond pairs. The bond pairs repel one another to a smaller extent again. This means that the two bond pairs are pushed closer together by the lone pairs of electrons so that the H-O-H bond angle is reduced to 104.5^o instead of the regular tetrahedral bond angle of 109.5^o. Therefore oxygen's valence electron pairs are arranged in a distorted tetrahedron but even more distorted than that in ammonia because now there are two lone pairs. The final shape of the water molecule is determined by the position of the atoms bonded to the central oxygen. Its shape is v-shaped. Since there are only three atoms in the molecule it must, of course, be planar. The two lone pairs of electrons had to be considered when arranging these atoms. Again the diagram below, Fig. 1.23, does not adequately represent the 104.5^o bond angle and the exact relationship of this shape to the tetrahedral, etc., so a model is necessary to illustrate it correctly. It should be noted that there are v-shaped molecules based on trigonal planar arrangements of electron pairs. (See Table 1.3.)

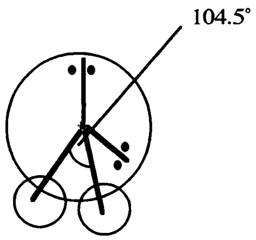

Fig. 1.23 *V-shaped planar water molecule*

In $BeCl_2$ there are two bond pairs and no lone pairs of electrons in the valence shell of beryllium. These repel each other spatially to the same extent and according to three-dimensional geometry assume a linear arrangement with a Cl-Be-Cl bond angle of 180^o, Fig. 1.24.

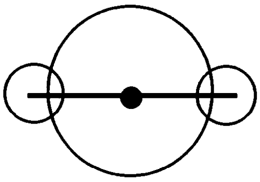

Fig. 1.24 *Linear shape of beryllium chloride*

Thus, a covalent molecule of general formula AB_2 may be v-shaped or linear. To assign the correct shape to a particular AB_2 compound, it is necessary again to (i) determine the total number of electron pairs in the valence shell, (ii) determine how many lone pairs and bond pairs are present, and (iii) consider different degrees of electron pair repulsions when predicting bond angles.

The shape of many covalent molecules can be predicted in a similar manner to that used in these examples. The following is a summary of results with the more important shapes for Leaving Certificate students in bold.

General Formula	Possible shapes	B-A-B bond angle	No. of bond pairs	No. of lone pairs	Example
AB_6	**Octahedral**	**90°**	**6**	**0**	**SF_6**
AB_5	**Trigonal bipyramid**	**120°,90°**	**5**	**0**	**PCI_5**
	Square pyramidal (octaheddrally based)	90°	5	1	IF_5
AB_4	**Tetrahedral**	**109.5°**	**4**	**0**	**CH_4**
	See-saw (trigonal bipyramidally based)	<120°,90°	4	1	$TeCl_4$
	Square planar (octahedrally based)	90°	4	2	ICl_4^-
AB_3	**Trigonal Planar**	**120°**	**3**	**0**	**BF_3** SO_3
	Pyramidal (tetrahedraly based)	**<109.5°**	**3**	**1**	**NH_3**
	T-shaped (trigonal bipyramidally based)	90°	3	2	CIF_3
AB_2	**Linear**	**180°**	**2**	**0**	**$BeCl_2$**
	V-shaped planar (trogonal planar based)	<120°	2	1	$SnCl_2$ SO_2
	V-shaped planar (tetrahefrally based)	**<<109.5°**	**2**	**2**	**H_2O**
	Linear (trigonal bipyramidally based)	180°	2	3	ICl_2^-
AB	Linear Any diatomic molecule must be linear	180°			

Table 1.3 *Shapes of covalent molecules*

Note on charged species

If the central atom bears a positive charge then one of the bond pairs can be considered to have originated from two electrons from the central atom, e.g. in H_3O^+ there are three bond pairs and one lone pair - the shape is pyramidal with an $H\text{-}O^+\text{-}H$ bond angle of 104.5^o.

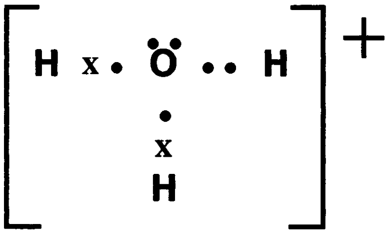

Fig. 1.25 *Dot cross diagram of electron pairs in H_3O^+*

Conversely, if the central atom bears a negative charge then one of the bond pairs can be considered to have originated from two electrons from one of the atoms bonded to the central atom, e.g. in BH_4^-, there are four bond pairs. Both electrons of one of these pairs of electrons can be considered to have originated from a hydride ion. Such a pair constitutes a dative covalent bond. The shape is tetrahedral with an $H\text{-}B^-\text{-}H$ bond angle of 109.5^o.

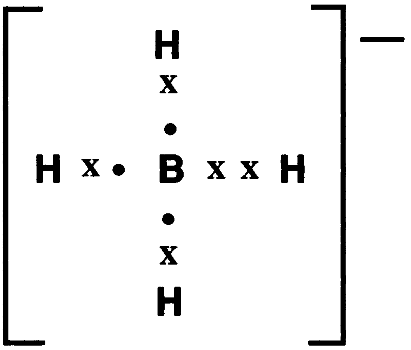

Fig. 1.26 *Dot cross diagram of electron pairs in BH_4^-*

O=C=O

Fig. 1.27 *Bonding in carbon dioxide*

Note on the shapes of more complicated molecules

Ignore the extra pairs of electrons involved in double or triple bonds when predicting the shape of a covalent molecule. The reason for not considering the electrons involved in double or triple bonds is because, whether a bond is single, double or triple, it can have only one orientation with respect to the central atom. The electrons involved in making the second bond between two atoms must join the two atoms along the same line as the first bond and so do not influence the shape. For example, in carbon dioxide there are four bond pairs of electrons in the valence shell of the central carbon atom. Ignoring two of these because they are involved in double bonds would correctly suggest a linear shape for carbon dioxide.

So far only the shapes of molecules which consist of a cluster of atoms about a single central atom have been considered. It is possible to predict the shapes of more complicated covalent molecules using this valence shell electron pair repulsion theory. For example, what shape does the propynoic acid molecule, Fig. 1.28, have?

Consider the shape at each carbon and at the oxygen atom bonded to both carbon and hydrogen in turn from left to right. There is a linear arrangement at the first carbon atom (four bond pairs, two of which are ignored since they constitute part of a triple bond). There is a linear arrangement again at the second carbon atom for the same reason. At the third carbon atom there is a trigonal planar arrangement (four bond pairs, one of which is ignored since there is a double bond) and finally there is a v-shaped planar arrangement at the oxygen atom (four electron pairs, two bond pairs and two lone pairs). Note that the method described here for deducing shape presupposes a knowledge of the bonds present between the various atoms. (See Experiments 1.3 and 1.4.)

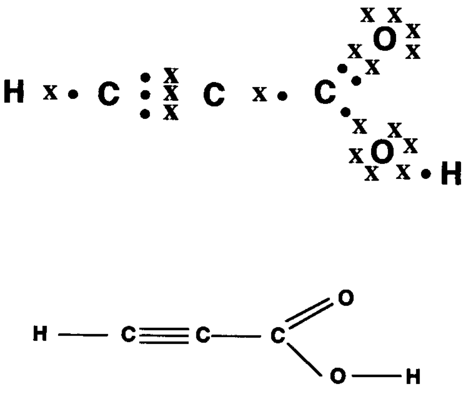

Fig. 1.28 Bonding in propynoic acid

1.4 Experiments

Experiment 1.1

Building Models of the Elements

Student experiment

Materials

Orbit molecular modelling system
Molymod molecular models system

Safety

Wear safety spectacles

Procedure

1. Construct models of the following using orbit models: elemental sulphur, S_8 rings, elemental carbon, diamond and graphite.

2. Using the molymod system, construct models of hydrogen, oxygen, nitrogen gas molecules, showing the single, double and triple bonds.

Discussion

The three-dimensional arrangement of some of these structures cannot be clearly represented on paper so the model building exercise is very important.

Experiment 1.2

Cubic Crystal Model Construction

Student experiment or teacher demonstration

Materials

Polystyrene spheres, 25 mm radius
All-purpose clear adhesive, e.g. UHU or Bostik
Light cardboard
Scissors
Sellotape

Safety

Wear safety spectacles. Avoid contact between adhesive and skin.

Procedure

1. Construct a square frame from strips of cardboard which can just hold four touching polystyrene spheres.

2. Glue the spheres together. When the glue has set the four spheres can be lifted out as a layer.

3. Make a second layer of four spheres in the same way. Then position the second layer above the first so that each of the four spheres lies exactly above one of the spheres in the lower layer. This arrangement represents the simple cubic structure.

4. Construct two other square frames of side 6.4 cm from strips of cardboard. Temporarily attach four spheres to the corners of each of the frames using sellotape. Take a single polystyrene sphere and place it in the centre on top of the four spheres in one of these layers. Glue it in this position to the four lower spheres.

   Position the second layer on top of this single sphere again so that this single sphere touches each of the four spheres in the top layer also. Glue the spheres in place. Remove the cardboard and sellotape. This is the body-centred cubic arrangement.

5. Construct a slightly bigger square cardboard frame which can hold five spheres, four at the vertices of the square and one at the centre. Glue the five spheres together. Make a second layer of five spheres in the same way.

6. Take one of these layers of five spheres and arrange four spheres on top of it in a diamond so that each of the four occupies a position which will be at the centre of each of the vertical faces of the cube under construction, touching three spheres in the lower layer.

7. Arrange the second layer of five spheres vertically in line with the first. This is the face-centred cubic arrangement.

Discussion

These models could be constructed in advance if time did not permit them to be built in class.

Experiment 1.3

Model Building of Compounds

Student experiment

Materials

Orbit molecular modelling system
Molymod molecular models system
Polystyrene spheres, 25 mm and 50 mm
Adhesive and NaCl jig available from laboratory suppliers

Safety

Wear safety spectacles. Avoid contact between adhesive and skin.

Procedure

1. Construct models of the following using orbit models: sodium chloride lattice; covalent molecules - water, methane, ammonia; ice lattice showing hydrogen bonds. Note the shapes of the covalent molecules.

2. Construct models of carbon dioxide and propynoic acid using the molymod system. Note the shapes.

3. Construct a model of sodium chloride using the jig to position a layer of 50 mm polystyrene spheres representing chloride ions, then 25 mm spheres representing sodium ions, followed by further layers of 50 mm and 25 mm spheres. Note the simple cubic packing of the two different ion types. The jig allows easy assembly of the spheres which can be painted different colours for clarity.

Discussion

The three-dimensional arrangement of some of these structures cannot be clearly represented on paper so the model building exercise is very important.

Experiment 1.4

Three-dimensional Geometry

Teacher demonstration or student experiment

Materials

Glycerol, 200 cm^3
Detergent, 200 cm^3
Water, 1.6 l
Wire frameworks which can be immersed in a 2 litre beaker: tetrahedron, trigonal bipyramid and octahedron, with handles.

Safety

Wear safety spectacles. Glycerol is irritating to the eyes.

Procedure

1. Prepare a soap solution with 10% glycerol, 10% detergent (washing-up liquid) in water. Allow to stand for a few hours.

2. Holding by the handle, dip each wire framework in turn in soap solution, withdraw, allow to drain and observe.

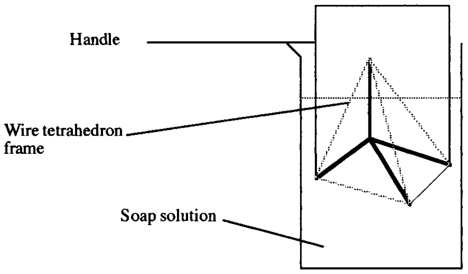

Fig. 1.29 *Tetrahedron in soap film*

Discussion

The unfamiliar tetrahedral, trigonal bipyramidal and octahedral shapes could also be demonstrated with plastic or wooden models.

1.5 References

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CHAPTER 2 SKILLS

2.1 Notes on Nomenclature

Binary Compounds

Binary compounds are made up of two elements. The names of binary compounds contain the two elements, the more electropositive element first, but the second element's name is changed slightly to end in - ide. The -ide ending indicates a binary compound although some hydroxides and ammonium compounds have more than two elements present but their names still end in -ide, e.g. sodium hydroxide and ammonium chloride. Furthermore, not all binary compounds have names ending in -ide, e.g. water, ammonia, etc. Note that solutions of hydrogen halides or hydrogen sulphide in water are named differently from the pure gaseous compounds. For example, hydrochloric acid is HCl(aq) and hydrosulphuric acid is $H_2S(aq)$.

In compounds, the Greek prefixes mono-, di-, tri-, tetra-, penta-, hexa-, hepta-, nona- and deca-, etc., are used to indicate the number of each element or radical in the formula. For example, N_2O_4 is dinitrogen tetroxide. If no prefixes are used, it indicates that the elements have combined according to their normal valency, hence aluminium carbide is Al_4C_3 and it is not necessary to call it tetraaluminium tricarbide.

Variable Valency

Iron chloride can be $FeCl_2$ or $FeCl_3$. To avoid ambiguity these compounds could be called iron dichloride and iron trichloride, respectively, but in fact they are usually referred to as iron(II) chloride and iron(III) chloride. A Roman numeral written in brackets after the name of an element gives the oxidation number of the element in that compound (see section 2.2). Similarly, CuCl and $CuCl_2$ are referred to as copper(I) chloride and copper(II) chloride. This rule can also be applied to compounds of non-metals. The compound of formula SO_3 is sulphur trioxide as explained above but it could also be called sulphur(VI) oxide.

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Compounds Containing Oxygen

There are currently two systems for naming compounds and radicals or ions containing oxygen (apart from the simple binary compounds of oxygen dealt with above). The first system presented below is the traditional one. It can be described as semi-systematic, and its importance lies in its continued widespread use in industry and education. IUPAC has specified a second system for naming these compounds but it has not been adopted to any appreciable extent in industry or by chemical suppliers.

Traditional System

Apart from binary compounds, compounds containing oxygen have common names ending in -ite or -ate. An -ite compound has fewer oxygen atoms than the corresponding -ate compound, e.g. sodium sulphite and sodium sulphate are Na_2SO_3 and Na_2SO_4, respectively, and potassium nitrite and potassium nitrate are KNO_2 and KNO_3, respectively.

These compounds are called ternary (three) compounds because there are two elements associated with a central atom of chlorine, sulphur, nitrogen, etc. They are often oxyacid series, e.g. HClO, $HClO_2$, $HClO_3$, $HClO_4$, and HNO_3 and HNO_2 or their salts. The name of the most common acid of the series ends in -ic and its salts end in -ate. An acid which is in the same series, but where the central atom is in a higher oxidation state than in the most common acid, has the prefix per- and its name also ends in -ic. An acid which is in the same series, but where the central atom is in a lower oxidation state than in the most common acid, has a name ending in -ous. If an acid with the central atom in an even lower oxidation state exists, this acid has a prefix hypo- and its name ends in -ous. Sulphuric and nitric acids have different numbers of oxygen atoms according to the rules of this system and there is no way of establishing the formula of the compound from its name.

IUPAC System

In IUPAC nomenclature, however, the various suffixes and prefixes in all oxyacids are replaced by an -ic ending combined with the oxidation state of the central atom given in Roman numerals in brackets as shown below. The formula of the compound can be deduced from its name.

	Common name	**IUPAC name**
$HClO$	hypochlorous acid	chloric(I) acid
$HClO_2$	chlorous acid	chloric(III) acid
$HClO_3$	chloric acid	chloric(V) acid
$HClO_4$	perchloric acid	chloric(VII) acid

In salts of oxyacids, the traditional endings change from -ous to -ite and from -ic to -ate. In IUPAC nomenclature, however, the ending -ate is used for all oxygen-containing salts combined with the oxidation state given in Roman numerals in brackets as shown below.

	Common name	**IUPAC name**
$NaClO$	sodium hypochlorite	sodium chlorate(I)
$NaClO_2$	sodium chlorite	sodium chlorate(III)
$NaClO_3$	sodium chlorate	sodium chlorate(V)
$NaClO_4$	sodium perchlorate	sodium chlorate(VII)

In oxyacids where there is more than one replaceable hydrogen, more than one series of salts can be formed. For example, H_3PO_4, phosphoric acid, can form three sets of salts: the phosphates where all three hydrogens are replaced, the hydrogenphosphates where two hydrogens are replaced, and the dihydrogen-phosphates where only one hydrogen has been replaced. In IUPAC nomenclature, however, the ending -ate is used for all the salts combined with the oxidation state given in Roman numerals in brackets as shown below.

	Common name	**IUPAC name**
Na_3PO_4	sodium phosphate	trisodium phosphate(V)
Na_2HPO_4	sodium hydrogenphosphate	disodium hydrogenphosphate(V)
NaH_2PO_4	sodium dihydrogenphosphate	sodium dihydrogenphosphate(V)

Stable Ions and Free Radicals

Certain clusters of atoms bonded together often remain intact through a series of chemical reactions. There are two types of such clusters, stable ions and free radicals. Stable ions of this type include the positive ammonium ion and the negative nitrate, nitrite, sulphate, sulphite, carbonate, hydrogencarbonate, hydroxide and phosphate ions. They are stable in the sense that they exist in aqueous solution or in crystals, etc.

Free radicals have at least one unpaired electron which makes them very reactive entities, e.g. Cl, O, CH_3, NO, etc. An unpaired electron is often, but not always, indicated in the formula by a dot, e.g. $Cl^{\bullet}$, $CH_3^{\bullet}$. The electron configurations of chlorine and oxygen will show one and two unpaired electrons, respectively. Note that the chloride ion and the chlorine free radical are two different species, as are the oxide ion and the oxygen free diradical. It is convenient to consider the overall chemical properties, the charge on the stable ion or free radical and the valency of the stable ion or free radical rather than the properties, charges and valencies of their component atoms.

Name	Radical formula	Valency	Ion formula
Ammonium		1	NH_4^+
Sulphate		2	SO_4^{2-}
Sulphite		2	SO_3^{2-}
Nitrate		1	NO_3^-
Nitrite		1	NO_2^-
Carbonate		2	CO_3^{2-}
Hydrogencarbonate		1	HCO_3^-
Phosphate		3	PO_4^{3-}
Hydroxide		1	OH^-
Chlorine	Cl	1	
Oxygen	O	2	
Methyl	CH_3	1	
Ethyl	C_2H_5	1	
Phenyl	C_6H_5	1	
Benzoate	C_6H_5COO	1	

Table 2.1 *Common stable ions and free radicals*

Exercise 2.1

Complete Table 2.2(a) with unambiguous names of the binary compounds whose formulae are given.

Formula	Name
CO_2	
CO	
NO	
NO_2	
BF_3	
Ag_2O	
LiH	
SiH_4	
$HCl_{(aq)}$	
$HCl_{(g)}$	
CaO	
$FeCl_2$	
$FeCl_3$	
CuCl	
$CuCl_2$	
Mg_2Si	

Table 2.2(a) *Exercise 2.1*

Formula	Name
CO_2	Carbon dioxide
CO	Carbon monoxide
NO	Nitrogen monoxide
NO_2	Nitrogen dioxide
BF_3	Boron trifluoride
Ag_2O	Silver(I) oxide
LiH	Lithium hydride
SiH_4	Silicon hydride
$HCl_{(aq)}$	Hydrochloric acid
$HCl_{(g)}$	Hydrogen chloride
CaO	Calcium oxide
$FeCl_2$	Iron(II) chloride
$FeCl_3$	Iron(III) chloride
CuCl	Copper(I) chloride
$CuCl_2$	Copper(II) chloride
Mg_2Si	Magnesium silicide

Table 2.2(b) *Answers*

Exercise 2.2

Sulphuric acid = H_2SO_4
Chloric acid = $HClO_3$
Phosphoric acid = H_3PO_4
Nitric acid = HNO_3
Carbonic acid = H_2CO_3

Give the IUPAC name for the following compounds: HClO; $HClO_2$; H_2SO_3; $MgSO_3$; HNO_2; $Ca(NO_2)_2$; K_2CO_3; $KHCO_3$; $CaHPO_4$; LiH_2PO_4.

Answers

Chloric(I) acid; chloric(III) acid; sulphuric(IV) acid; magnesium sulphate(IV); nitric(III) acid; calcium nitrate(III); potassium carbonate;
potassium hydrogencarbonate; calcium hydrogenphosphate(V);
lithium dihydrogenphosphate(V).

2.2 Valency and Oxidation Numbers

Valency

The valency of an element or ion is the number of electrons such a species tends to donate, accept or share when forming chemical bonds. Valency enables one to predict the ratio in which species combine and hence to write formulae for many compounds.

Some elements and each of the ions listed above have a fixed valency. The alkali and alkaline earth metals tend to have fixed valencies of one and two, respectively. The valency of an ion corresponds to the size of its charge - valencies by definition are always positive.

Some elements have more than one valency - more than one compound can therefore result when these elements combine with other species. Transition metals are characterised by having variable valencies. For example, copper may have valencies of one, two and three, iron exhibits valencies of two and three, and higher, etc. (See Table 2.3.)

Valence states of first row d-block elements

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
		1	1	1	1	1	1	1	
	2	2	2	2	2	2	2	2	2
3	3	3	3	3	3	3	3	3	
	4	4	4	4	4	4	4		
		5	5	5		5			
			6	6	6				
				7					

Table 2.3 *Valence states of first row d-block elements*

The electron configurations of the transition metals often suggest to us which valence states are likely to exist and, of those which do exist, which are likely to be the most stable. It is important to bear in mind that when the first row transition metals lose electrons, the 4s electrons are lost first. In the case of copper, the Cu^+ oxidation state arises when the only 4s electron is lost and the Cu^{2+} valence state arises when a second electron is lost from the 3d subshell. The Cu^{3+} valence state is known but uncommon. However, the Cu^+ ion might be expected upon inspection of the electron configurations to be more stable than the Cu^{2+} ion. However, Cu^{2+} compounds are, in fact, more common and more stable than Cu^+ which are very easily oxidised to Cu^{2+}compounds.

$Cu = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^{10}$
$Cu^+ = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^0, 3d^{10}$
$Cu^{2+} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^0, 3d^9$

$Fe = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^6$
$Fe^{2+} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^0, 3d^6$
$Fe^{3+} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^0, 3d^5$

From these electron configurations, one would expect the Fe^{3+} ion with its set of completely filled or exactly half-filled subshells to be more stable than the Fe^{2+} ion. While this is a correct assumption about the relative stabilities of isolated Fe^{3+} and Fe^{2+} ions, it does not mean that Fe^{3+} compounds are more common or more stable than Fe^{2+} compounds. Transition metal ions are stabilised to different extents by the ions or neutral species with which they bond. The formation of coloured compounds is another characteristic of transition metals in various valence states. While certain colours are commonly associated with certain transition elements in certain valence states, e.g. Cu^{2+} salts are often blue, the colour observed is not just a property of the particular valence state of the particular transition metal. The colour depends to a very great extent on the electrical properties of the ions or neutral substances complexed to the transition metal ion, e.g. green and purple Cu^{2+} compounds also exist. Other elements have very

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Valency	1	2											3	4	3	2	1	0
	H																	He
	Li	Be											B	C	N	O	F	Ne
	Na	Mg											Al	Si	P	S	Cl	Ar
	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
	Fr	Ra																

Table 2.4 *Normal valencies of main group elements*

variable valency and therefore it is more difficult to predict the ratio in which they combine with other species. The non-metals, including phosphorus, sulphur and chlorine exhibit variable valency. Despite the existence of variable valency, the most common valency for the main group elements can easily be read from the position of the element in the periodic table. Groups 1 and 2 as already mentioned have valencies of one and two, respectively. Groups 13 and 14 have valencies of three and four, while Groups 15, 16 and 17 have valencies of three, two and one, respectively. The elements of group 18 are usually assigned a valency of zero, because they do not easily combine with other elements. A few compounds of these elements do exist but the valencies of the inert gas elements are not predictable.

Valency and Formulae

A knowledge of valency allows a student to write formulae for many inorganic compounds. Refer to Tables 2.3 and 2.4.

Worked Example 1
Write the formula for silicon hydride.

Valency of Si = 4
Valency of H = 1

Four H are needed to balance one Si ⇒ SiH_4

Worked Example 2
Write the formula for calcium chloride.

Valency of Ca = 2
Valency of Cl = 1

Two Cl are needed to balance one Ca ⇒ $CaCl_2$

Worked Example 3
Write the formula for aluminium oxide, which is the main colourless constituent of the precious gem stones, emerald, ruby and sapphire. Impurities impart the characteristic colours.

Valency of Al = 3
Valency of O = 2

Two Al are needed to balance three O ⇒ Al_2O_3

Take the lowest common multiple of the two valencies to find the total number of electrons transferred or shared in the bonding. In this case the number of electrons transferred or shared is 2 x 3 = 6. The formula of aluminium oxide can also be worked out using a table as follows.

	Al	**O**	
Valency	3	2	
No. atoms required to obtain l.c.m.	x 2	x 3	Formula = Al_2O_3
L.c.m. of valencies	6	6	

Table 2.5 *Formula of aluminium oxide*

Worked Example 4
Write the formula for the oxide of carbon, where the elements exhibit their normal group valencies.

Valency of C = 4
Valency of O = 2

Two O are needed to balance one C ⇒ CO_2

Take the lowest common multiple of the two valencies to find the total number of electrons transferred or shared in the bonding. In this case the number of electrons transferred or shared is 2 x 2 = 4. The formula of carbon oxide can also be worked out using a table as follows.

	C	**O**	
Valency	4	2	
No. atoms required to obtain l.c.m.	x 1	x 2	Formula ⇒ CO_2
L.c.m. of valencies	4	4	

Table 2.6 *Formula of carbon dioxide*

This example illustrates a weakness in the method some students apply to arrive at a formula. They simply reverse the valencies of the two elements. Although this method regularly gives the correct formula, in this case it would lead to a formula of C_2O_4.

Exercise 2.3

Write the formulae for each of the following: sodium chloride (common table salt); calcium oxide; lithium bromide (an anti-depressant used to treat severe depression); gallium oxide; magnesium nitride; aluminium chloride; arsenic(III) oxide (a virulent poison); sodium hydride; calcium fluoride (used in water supplies to counteract tooth decay); barium chloride; zinc oxide (total sun block).

Answers

$NaCl$; CaO; $LiBr$; Ga_2O_3; Mg_3N_2; $AlCl_3$; As_2O_3; NaH; CaF_2; $BaCl_2$; ZnO.

The valencies of free radicals and stable ions are very useful. Table 2.1, p. 25, shows common free radicals and stable ions, their charges and valencies. Free radicals are unstable as they have an unpaired electron which tends to pair off with an electron from another atom or group of atoms to produce a stable molecule. When a stable ion occurs in a compound its charge must be balanced by that on an oppositely charged ion or ions.

Now we can write the correct formulae for a large number of substances by simply matching the valencies of the two parts in the name of the compound using the information above.

Worked Example 5

Write the formula for potassium sulphate.

Valency of potassium = 1
Valency of sulphate = 2
Two K needed to balance one sulphate ⇒ K_2SO_4

Worked Example 6

Write the formula for calcium hydroxide.

Valency of calcium = 2
Valency of hydroxide = 1

Two OH are needed to balance one Ca ⇒ $Ca(OH)_2$

Worked Example 7

The lowest common multiple method can also be used. Write the formula for calcium phosphate.

	Ca	PO_4	
Valency	2	3	
No. atoms required to obtain l.c.m.	x 3	x 2	Formula = $Ca_3(PO_4)_2$
L.c.m. of valencies	6	6	

Table 2.7 *Formula of calcium phosphate*

Exercise 2.4

Write the formula of each of the following: barium sulphate (used as 'barium meal' for X-raying soft tissue of the alimentary canal); magnesium nitrate; calcium phosphate; sodium sulphite; potassium hydrogencarbonate (a constituent of some indigestion remedies); beryllium hydroxide; ammonium chloride (smelling salts); aluminium sulphate; calcium carbonate (chalk, marble, limestone); ammonium phosphate.

Answers

$BaSO_4$; $Mg(NO_3)_2$; $Ca_3(PO_4)_2$; Na_2SO_3; $KHCO_3$; $Be(OH)_2$; NH_4Cl; $Al_2(SO_4)_3$; $CaCO_3$; $(NH_4)_3PO_4$.

Oxidation Numbers

Related to the concept of valency is that of oxidation state. This is the number of electrons lost or gained by an atom of an element in a compound or ion treating all the bonds as ionic, i.e. assigning the electrons to the more electronegative element of the bond. Oxidation states of atoms which have 'gained' electrons are negative and atoms which have 'lost' electrons have positive oxidation states. In fact, in compounds other than ionic, while whole electrons have not been transferred, electron density has actually been transferred towards the electronegative atoms.

Oxidation numbers of an atom in a molecule of a compound can be predicted using the following rules.

1. The sum of the oxidation numbers in a neutral compound must be zero and must add to give the overall charge if the species is ionic.

2. An atom of a free element has an oxidation state of zero since it cannot have lost electrons

to, or gained electrons from, another atom of the same element, each having the same electronegativity.

3. The oxidation state of the alkali metals in compounds is always +1 and similarly the alkaline earth metals in compounds always have oxidation state of +2.

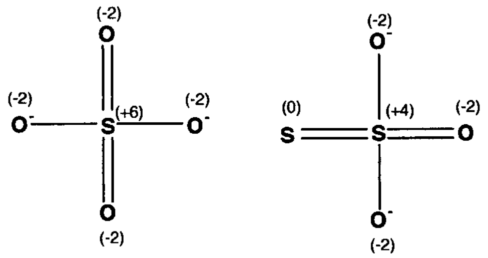
4. The oxidation state of hydrogen in most compounds is +1. There is one group of compounds which is an important exception. In the metal hydrides, hydrogen has an oxidation state of -1 because hydrogen is more electronegative than the metal element and is thus assigned the bonding electrons when determining oxidation states.

5. The oxidation state of oxygen in most compounds is -2. The compounds OF_2 and the peroxides and superoxides are important exceptions. In oxygen difluoride, OF_2, the oxygen atom is bonded to the only other element which is more electronegative than it. Therefore, the fluorine is assigned the bonding electrons when determining oxidation states, giving oxygen an oxidation state of +2. In peroxides, each oxygen atom is bonded to another oxygen atom and to another more electropositive element. Since the two oxygen atoms have the same electronegativity value neither can obtain electrons from the other so bonding electrons can only be assigned to each oxygen from the electropositive atom, giving oxygen in peroxides an oxidation state of -1. In the superoxide KO_2, it follows from Rule 3 that if the oxidation number of the potassium ion is +1 then the oxidation number of oxygen must be - 0.5.

6. The oxidation number of a halogen in most binary compounds is -1. Exceptions include Cl_2O and ICl.

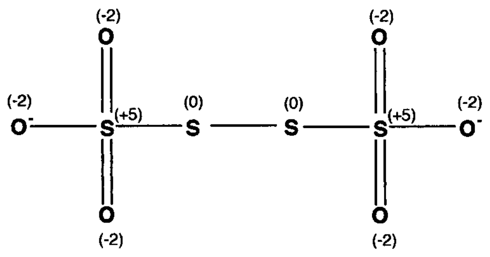
Oxidation states can be fractional as the KO_2 example above shows. Here are two other examples which might be encountered in Leaving Certificate chemistry. What are the oxidation states of each element in the compounds Fe_3O_4 and $Na_2S_4O_6$? In Fe_3O_4, we know that oxygen is more electronegative than iron and assign oxygen its common oxidation state of -2. Thus, the four oxygens have an oxidation state of -8. This implies that the three iron atoms between them have a total oxidation number of +8 and that each individual iron atom has an oxidation number of +8/3. Actually, in Fe_3O_4, which is an ionic compound and as such does not have definite molecules, two of every three of the iron ions are Fe^{3+} and the third is Fe^{2+}. Its formula may be written $FeO.Fe_2O_3$.

In $Na_2S_4O_6$, each of the sodium atoms is given the oxidation state of +1 as sodium is the most electropositive element present. The overall oxidation state of the $S_4O_6^{2-}$ ion is therefore -2. Oxygen is more electronegative than sulphur and is therefore assigned its common oxidation state of -2. Thus, the six oxygens have an oxidation state of -12. This implies that the four sulphur atoms between them have a total oxidation number of +10 and that each individual sulphur atom has an average oxidation number of +10/4 or +2.5. In $Na_2S_4O_6$, two of the sulphur atoms actually exist in an oxidation state of five and the other two in oxidation state zero, Fig. 2.1.



Sulphate ion

Thiosulphate ion



Tetrathionate ion

Fig 2.1 *Oxidation states in some sulphur-containing ions*

What are the valencies and oxidation states of carbon in each of the compounds, carbon dioxide, methane, methanol and methanal?

The valency of carbon in each case is 4 since its four valence electrons are shared in each case. However, its oxidation number in carbon dioxide is +4 having bonded with two electronegative oxygens. In methane the oxidation number of carbon is -4 having bonded with more electropositive hydrogen. In methanol the oxidation number of carbon is -2, where carbon is bonded to more electronegative oxygen and more electropositive hydrogen. Comparing the oxidation numbers of the carbon in methane with the carbon in methanol shows that electron density has been drawn away from the carbon by the more electronegative oxygen atom. In methanal the oxidation number of carbon is zero, where carbon is bonded to more electronegative oxygen and more electropositive hydrogen again but now even more electron density has been drawn away from the carbon atom compared with methanol. The carbon atom is losing electrons as it is oxidised from methanol to methanal.

Thus, valency gives the number of electrons involved in bonding but oxidation numbers provide information about their distribution.

Oxidation numbers also provide information about oxidation and reduction of species in redox reactions. Since oxidation is defined as loss of electrons and reduction as gain of electrons, an increase in the oxidation number of an element indicates that it has been oxidised and a decrease in oxidation number indicates reduction. For example, in the biological oxidation of glucose in respiration the carbon undergoes an increase in oxidation number from zero in glucose to +4 in carbon dioxide, indicating oxidation of the carbon.

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

2.3 Chemical Equations

Balancing Chemical Equations

Balanced chemical equations give the formulae for the reacting chemicals on the left and the formulae of the products of the reaction on the right. Additionally, the correct ratio of moles of each of these substances to one another needed for complete reaction is given. From Avogadro's law, if some of the reactants and products are gaseous, the ratio of the volumes of the different gases is given by the balanced equation also, provided that the volumes are all measured at the same conditions of temperature and pressure. What the balanced chemical equation most certainly does not give is the ratio of masses of reactants and products.

In a balanced equation there are equal numbers of each type of atom on both sides of the equation. This must be so since atoms cannot be interconverted in a chemical reaction and neither can they be destroyed or created so there must be the same number of each type at the beginning and end of a chemical reaction.

It was **Thomas Graham** (1805-1869), also remembered for his experiments on gaseous diffusion, who first wrote chemical equations linearly in the 1840s and included the ratios of equivalents of reactants and products. Sometimes it is helpful to write only part of a chemical equation. For example, in redox reactions some ions do not participate in the oxidation or reduction processes. These are called spectator ions and it is sometimes helpful to write the chemical reaction omitting the spectator ions. The remaining ionic reactant and product species in the balanced equation must balance (i) in terms of atoms, (ii) in terms of charge, and (iii) in terms of electron transfer. For example, the reaction between potassium manganate(VII) and disodium ethanedioate under acidic conditions is represented by the following balanced equation.

$$2KMnO_4 + 5(COONa)_2 + 8H_2SO_4 \rightarrow$$
$$2MnSO_4 + 5Na_2SO_4 + K_2SO_4 + 8H_2O + 10CO_2$$

Omitting the spectator ions, none of which undergoes an oxidation number change, gives

$$2MnO_4^- + 5(COO)_2^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2$$

Inspection of this balanced ionic equation shows that (i) there is the same number of each type of atom on the left and on the right of the equation, (ii) the total charge on all species on the left is +4 and the total charge on all species on the right is +4, and (iii) the change in oxidation number of both manganese atoms is -10 and the change in oxidation number of the ten carbon atoms is +10 so the equation is also balanced in terms of electron transfer in the oxidation and reduction steps. It may be helpful to break down this ionic equation further to give the separate oxidation and reduction steps, or half-equations.

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

$$(COO)_2^{2-} \rightarrow 2CO_2 + 2e^-$$

Note that each of these half-reactions is itself balanced in terms of (i) atoms and (ii) charge. Note also that in order for the charge transfers to balance in the redox reaction the manganese half-reaction must occur twice while the carbon half-reaction occurs five times.

Balancing Equations by Inspection

Before stoichiometric calculations can be carried out, a balanced equation is required.

Worked Example 1

Balance the equation

$$Mg + HCl \rightarrow MgCl_2 + H_2(\uparrow)$$

In this equation there is one Mg atom on each side. There is one H atom on the left, but two on the right. There is one Cl atom on the left, but two on the right. Therefore, more H and Cl must be used on the left to make the products on the right. Two rules must be obeyed.

(i) The formulae must not be altered as this would change the chemicals taking part in the reaction, e.g. changing CO to CO_2 is not allowed. This point must be stressed to students.

(ii) The quantity of each substance may be changed. The quantity of a substance may be doubled by placing a 2 in front of the formula of the substance, tripled by placing a 3, etc.

In this example we must double the quantity of H on the left so a 2 is placed in front of HCl. This automatically doubles the amount of Cl also, as required. The balanced equation is

$$Mg + 2HCl \rightarrow MgCl_2 + H_2$$

This procedure is called balancing by inspection and although the instructions are quite tedious to write out, the steps required in a given example are usually quite obvious.

Exercise 2.5

Balance the following equations.

1. $CH_4 + O_2 \rightarrow CO_2 + H_2O$
2. $Al + Cl_2 \rightarrow AlCl_3$
3. $SO_2 + O_2 \rightarrow SO_3$
4. $P + O_2 \rightarrow P_2O_5$
5. $NaOH + H_2SO_4 \rightarrow Na_2SO_4 + H_2O$
6. $Na + H_2O \rightarrow NaOH + H_2$
7. $Ca(OH)_2 + HNO_3 \rightarrow Ca(NO_3)_2 + H_2O$
8. $Ca(HCO_3)_2 \rightarrow CaCO_3 + H_2O + CO_2$
9. $C_8H_{18} + O_2 \rightarrow CO_2 + H_2O$
10. $NaOH + SiO_2 \rightarrow Na_2SiO_3 + H_2O$
11. $Al + O_2 \rightarrow Al_2O_3$
12. $Al_2O_3 + NaOH \rightarrow NaAlO_2 + H_2O$

Answers

1. $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
2. $2Al + 3Cl_2 \rightarrow 2AlCl_3$
3. $2SO_2 + O_2 \rightarrow 2SO_3$
4. $4P + 5O_2 \rightarrow 2P_2O_5$
5. $2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$
6. $2Na + 2H_2O \rightarrow 2NaOH + H_2$
7. $Ca(OH)_2 + 2HNO_3 \rightarrow Ca(NO_3)_2 + 2H_2O$
8. $Ca(HCO_3)_2 \rightarrow CaCO_3 + H_2O + CO_2$
9. $2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$
10. $2NaOH + SiO_2 \rightarrow Na_2SiO_3 + H_2O$
11. $4Al + 3O_2 \rightarrow 2Al_2O_3$
12. $Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$

Exercise 2.6

Using the rules for valency and nomenclature above, write equations for the following reactions and balance them.

1. When magnesium carbonate is heated, it decomposes to give carbon dioxide and magnesium oxide.
2. Hydrogen gas and oxygen gas react explosively to give water vapour.
3. Hydrochloric acid and ammonium hydroxide react to form ammonium chloride and water.
4. Nitrogen and oxygen react together to give nitrogen(IV) oxide.
5. Nitrogen gas and hydrogen gas give the compound ammonia (NH_3) in the fertiliser industry.

Answers

1. $MgCO_3 \rightarrow MgO + CO_2$
2. $2H_2 + O_2 \rightarrow 2H_2O$
3. $HCl + NH_4OH \rightarrow NH_4Cl + H_2O$
4. $N_2 + 2O_2 \rightarrow 2NO_2$
5. $N_2 + 3H_2 \rightarrow 2NH_3$

Balancing Redox Equations

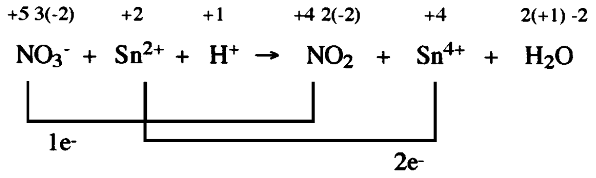
An ability to deduce half-equations is the basis of one method for balancing redox equations.

Worked Example 1

To balance the equation

$$NO_3^- + Sn^{2+} + H^+ \rightarrow NO_2 + Sn^{4+} + H_2O$$

first assign oxidation numbers to each species to determine which elements are undergoing oxidation number change.



It is clear that nitrogen and tin are undergoing change in oxidation number. Write balanced half-equations for the species involving these two elements using the equation given and the number of electrons transferred in the oxidation and reduction steps as a guide. It may sometimes be necessary, although it is not in this example, to introduce H^+ ions, OH^- ions or H_2O molecules to either side of the half-equation in order to balance it, even if they do not feature in the original equation presented for balancing. If they do not feature in the original equation these introductions will cancel in the final step.

$$NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O$$

$$Sn^{2+} \rightarrow Sn^{4+} + 2e^-$$

Taking the lowest common multiple of the number of electrons transferred in each of these steps, in this case two, rewrite the original equation so that the electron transfers in the oxidation and reduction steps balance, taking the first half-equation twice and the second once. This means that, in order for the charge transfers to balance in the redox reaction, the nitrogen half-reaction must occur twice while the tin half-reaction occurs once.

$$2NO_3^- + 4H^+ + Sn^{2+} + 2e^- \rightarrow 2NO_2 + 2H_2O + Sn^{4+} + 2e^-$$

Check that the number of electrons on each side is equal and cancel them and any other species common to both sides.

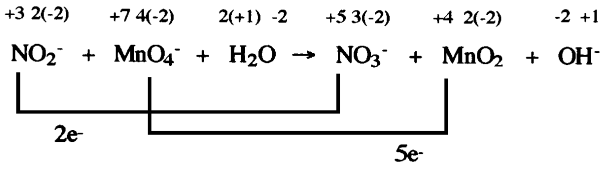
$$2NO_3^- + 4H^+ + Sn^{2+} \rightarrow 2NO_2 + 2H_2O + Sn^{4+}$$

Worked Example 2

Balance the equation

$$NO_2^- + MnO_4^- + H_2O \rightarrow NO_3^- + MnO_2 + OH^-$$

Assigning oxidation numbers, it is clear that nitrogen and manganese are the elements undergoing oxidation number change.



Now the half-reactions must be deduced. The manganese half-reaction is easily deduced. Note that it balances in terms of atoms and charge and that it involves the transfer of three electrons.

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$$

To write the nitrogen half-reaction it is necessary to introduce one species on each side of the equation which does not appear on that side of the original equation.

$$NO_2^- + 2OH^- \rightarrow NO_3^- + H_2O + 2e^-$$

Note that this half-equation is balanced in terms of atoms and charge and involves a transfer of two electrons. This half-reaction must therefore occur three times for every twice the manganese half-reaction occurs so that the electron transfers balance.

$$3NO_2^- + 2MnO_4^- + 4H_2O + 6OH^- + 6e^- \rightarrow$$
$$3NO_3^- + 2MnO_2 + 3H_2O + 8OH^- + 6e^-$$

Cancel out the species occurring on both sides of the equation. Now it is clear why it was acceptable to add OH^- ions on the left hand side and water on the right hand side of the nitrogen half-reaction - they cancel at the stage of combining the half-reactions. The balanced equation is

$$3NO_2^- + 2MnO_4^- + H_2O \rightarrow 3NO_3^- + 2MnO_2 + 2OH^-$$

Exercise 2.7
Balance the following equations for redox reactions which occur in aqueous solution using oxidation numbers and/or half-reactions.

1. $NO_3^- + I_2 + H^+ \rightarrow NO_2 + IO_3^- + H_2O$
2. $HBrO + H_2O \rightarrow H^+ + Br^- + O_2$
3. $Cr_2O_7^{2-} + HNO_2 + H^+ \rightarrow Cr^{3+} + NO_3^- + H_2O$
4. $IO_4^- + I^- + H^+ \rightarrow I_2 + H_2O$
5. $MnO_4^- + C_2O_4^{2-} + H^+ \rightarrow Mn^{2+} + CO_2 + H_2O$
6. $MnO_4^- + Cl^- + H^+ \rightarrow 2Mn^{2+} + Cl_2 + H_2O$

Answers

1. $10NO_3^- + I_2 + 8H^+ \rightarrow 10NO_2 + 2IO_3^- + 4H_2O$
2. $2HBrO + 2H_2O \rightarrow 2H_3O^+ + 2Br^- + O_2$
3. $Cr_2O_7^{2-} + 3HNO_2 + 5H^+ \rightarrow 2Cr^{3+} + 3NO_3^- + 4H_2O$
4. $IO_4^- + 7I^- + 8H^+ \rightarrow 4I_2 + 4H_2O$
5. $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$
6. $2MnO_4^- + 10Cl^- + 16H^+ \rightarrow 2Mn^{2+} + 5Cl_2 + 8H_2O$

2.4 References

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CHAPTER 3

THE MOLE

3.1 Historical Background to Calculations in Chemistry

For calculations to make sense in chemistry it was, and still is, very important to understand the nature of chemicals and how they combine.

In 1662, **Robert Boyle** (1635-1703) verified experimentally that the volume of a fixed mass of gas was inversely proportional to the pressure at constant temperature. He was the first scientist who applied the laws of physics to chemistry.

In 1787, **Jacques Alexandre César Charles** (1746-1823) proposed a relationship between the temperature and the volume of a fixed mass of gas at constant pressure. He said that all gases expanded at the same rate when heated, a fact now known as Charles's law. Charles stated that the rate of expansion of a gas was $^1/_{273}$ of its volume at 0 ^{o}C for each degree Celsius rise in temperature. This implied that the volume of a gas would be zero at -273 ^{o}C and that no temperature lower than this could exist. In 1848 **Lord Kelvin** (1824-1907) proposed an absolute temperature scale with its zero at -273 ^{o}C. On this scale, known as the absolute or Kelvin scale, temperature is defined to be proportional to the product of the pressure and volume of a fixed mass of the ideal gas (see p. 40). It follows from this definition that, if the pressure of the gas is kept constant, its temperature, on the absolute (Kelvin) scale, is proportional to its volume.

In 1792, **Jeremias Benjamin Richter** (1762-1807) published the first of the three volumes of his *Anfangsgründe der Stöchyometrie* (The Foundations of Stoichiometry) and in doing so introduced a new term into chemistry from the Greek words *stoicheion* (element) and *metron* (measure). Richter studied the proportions by mass in which various acids and bases combined and compiled his results into tables of data from which other analysts could read the combining masses of these acids and bases. He also studied the reactions between salts and tried to deduce the composition of the products from the composition of the reactants. Stoichiometry has developed since Richter's time but it is still concerned with the composition of compounds and the proportions in which various elements and compounds combine.

John Dalton (1766-1844), the English chemist who proposed the first modern theory of atomic structure, then went on to discuss how he thought atoms combined to form compounds. He suggested that atoms combined in pairs to form simple compounds, i.e. they combined in one to one ratios to form the simplest possible binary compounds of the form AB. From (rather inaccurate) combining masses he found that in the formation of water, assumed to be HO, the ratio by mass of hydrogen to oxygen was 1:6; in the formation of ammonia, assumed to be NH, the ratio of nitrogen to hydrogen by mass was 4:1. In 1803, having assigned hydrogen a mass of one, Dalton drew up a table of relative atomic masses with nitrogen assigned a value of 4 and oxygen a value of 6, etc. Over the following years, Dalton changed the values of relative atomic masses for some of the elements, as more experimental data became available. He also accepted that compounds other than diatomic ones existed, e.g. where two different compounds formed from the same elements, e.g. CO and CO_2, although he continued to assume water and ammonia were diatomic. In addition, not all scientists assigned a relative atomic mass of one to hydrogen, and experiments by different scientists about this time suggested different values for the relative atomic masses of some elements, even when the same scale was used consistently. For example, relative atomic masses of 8 and 16 for oxygen were recorded in different experiments on combining masses. Consider the two reactions below. In the first, 8 g of oxygen combine with 1 g of hydrogen but in the second, 16 g of oxygen combine with 1 g of hydrogen.

$$H_2 + {}^1/_2O_2 \rightarrow H_2O$$

$$H_2 + O_2 \rightarrow H_2O_2$$

Since the concepts of valency and the existence of molecules were not understood at the time, contradictory results of this kind could not be correctly interpreted. In addition to his atomic theory, Dalton had also put forward his law of partial pressures of gases in 1801: provided that they do not react chemically, the pressure exerted by a mixture of gases in a container is the sum of their partial pressures, i.e. the pressure which each gas would exert if it alone occupied the container.

William Hyde Wollaston (1766-1828) introduced the term equivalent mass in 1808 in an attempt to explain the problem of more than one relative atomic mass for the same element. The equivalent mass of an element or compound is the mass of it which combines with a specified mass of hydrogen or oxygen. He used oxygen as his standard for a scale of relative atomic masses, assigning it a value of 10, and calculated the equivalent masses of various other elements and compounds. He devised a slide rule on which the equivalent masses were engraved. The various relative atomic masses calculated from different experiments were, according to him, multiples of the equivalent mass of an element. However, since different chemists were using different references for their scale of relative masses, Wollaston's idea of equivalent mass did not succeed in making the picture any less confusing although the equivalent mass term survived right up almost until today and calculations were performed with equivalents rather than moles until quite recently. In modern chemistry the equivalent mass of an element is the mass of it in grams which combines with 1 g of hydrogen, i.e. it is the gram molecular mass divided by the valency.

The Swedish chemist **Jöns Jacob Berzelius** (1779-1848) continued the work of Dalton and attempted to produce an accurate table of relative atomic masses by using precision in all measurements in his experiments. He understood that compounds are not necessarily diatomic but do consist of simple whole number ratios of atoms. Berzelius assigned hydrogen a mass of 1 and measured the atomic masses of 45 of the 49 elements known at the time (1818) relative to this standard. He also drew up a second series of relative atomic masses based on oxygen having a mass of 100, so even within Berzelius's own results, more than one relative atomic mass for the same element existed.

Joseph Louis Gay-Lussac (1778-1850) showed in 1808 that gases combine in simple proportions by volume. He showed experimentally that:

2 volumes carbon monoxide + 1 volume oxygen
→ 2 volumes carbon dioxide;

1 volume hydrogen + 1 volume chlorine
→ 2 volumes hydrogen chloride;

2 volumes hydrogen + 1 volume oxygen
→ 2 volumes water vapour.

He summarised his findings in a law, now known as the Gay-Lussac law, which states that when gases combine chemically, the volumes of the reactants and the product(s) if they are gaseous are in simple whole number ratios, all volumes measured under the same conditions of temperature and pressure.

These experimental findings caused great discussion. Each of these equations suggested at the time that atoms had to split - otherwise one oxygen particle could not produce two carbon dioxide particles or two water vapour particles and one hydrogen particle or one chlorine particle could not make two hydrogen chloride particle. Some chemists, including Dalton, rejected Gay-Lussac's findings totally because they appeared to contradict the indivisibility of atoms theory. Others, including Berzelius, tried to make them fit as well as they could into the accepted theories of atomic structure and atomic combination.

The Italian chemist **Amadeo Avogadro** (1776-1856) suggested in 1811 that equal volumes, V, of different gases at the same temperature and pressure contained equal numbers of particles, N. Comparing the densities of two different gases, ρ_1 and ρ_2, was therefore equivalent to comparing the masses of their particles, m_1 and m_2, if equal volumes contain equal numbers of molecules.

$$\frac{\rho_1}{\rho_2} = \frac{\frac{m_1N_1}{V_1}}{\frac{m_2N_2}{V_2}}$$

$$= \frac{m_1}{m_2}$$

For oxygen and hydrogen, this ratio of masses is about 16:1 but when oxygen gas reacts with hydrogen gas the ratio of their combining masses is about 8:1. This caused great confusion in early chemistry because, while nearly every chemist used a value of 1 for the atomic mass of hydrogen, some experimenters took the relative atomic mass of oxygen as 8 from the combining masses of hydrogen and oxygen in the formation of water and others took it as 16 from other experiments. Here the work of Avogadro also suggested 16 as the relative atomic mass of oxygen. Avogadro suggested a way of reconciling the apparently contradictory results from various experiments on combining masses and the ratio of masses deduced above from gas densities. He put forward the ideas of integral molecules and elementary molecules which are equivalent to the modern terms molecules and atoms respectively. Thus, hydrogen’s molecules (integral molecules) had a relative atomic mass of 2 while its atoms (elementary molecules) were assigned a mass of 1. Oxygen’s integral molecule had a relative atomic mass of 32 and its elementary molecule had a mass of 16. This assumption would account for both the ratio of densities and the combining masses of hydrogen and oxygen and other elements.

Unfortunately, Avogadro's hypothesis was rejected because nobody understood how, or why, two similar atoms would bond together to form a molecule. In particular, the very influential Berzelius opposed Avogadro's theory on these grounds, so right through a period of almost fifty years total chaos existed about chemical calculations when the correct explanation had actually already been put forward by Avogadro, with the experimental results of Gay-Lussac supporting it.

William Thomson (1824-1907), who was born in Belfast and who later was knighted and became Lord Kelvin, recognised the concept of an absolute zero of temperature and defined the absolute scale of temperature in 1848. The absolute zero of temperature corresponds to a temperature of -273.15 ^{o}C and is the temperature at which the average kinetic energy of atoms and molecules is a minimum. The unit of temperature on this scale is the kelvin. The kelvin is one of the base units of the SI system. As the kelvin is the SI unit of temperature it must be used in all calculations involving other physical quantities.

At the Karlsruhe Chemical Congress of 1860, **Stanislao Cannizzaro** (1826-1910), another Italian, proposed the adoption of Avogadro’s hypothesis without being able to provide an explanation for the existence of diatomic gaseous elements. Although the chemists who attended the meeting did not immediately accept the proposal it soon became widely known and a sufficient number of influential chemists of the time did adopt Avogadro’s ideas and spread the information. Thus, the distinction between atoms and molecules was accepted at last.

August Wilhelm von Hofmann (1818-1892), a German chemist, who had come to England in 1845 to direct the Royal College of Chemistry, used in his lectures a new measure called a crith (from the Greek, *krithe*, barley-corn) to help his calculations. One crith was taken to be the weight of one litre of hydrogen gas at 0 ^{o}C and at a pressure of 760 mm Hg (0.0906 g). This was the first time an amount of a chemical was specified.

Edward Frankland (1825-1899) who succeeded Hofmann at the Royal College of Chemistry used the concept of valency in his lectures in 1852, i.e.

the combining power of an element, but the term valency apparently first appeared in Chemical News, an English Journal, in 1866. The crith of Hofmann was popularised in England by Frankland at this time.

In 1865 **Josef Loschmidt** (1821-1895) calculated, using the kinetic theory of gases and experiments on diffusion, the diameter of an ‘air’ molecule and the number of molecules in a millilitre of gas. He obtained values of about 1 x 10^{-10} m for the diameter of the ‘air’ molecule and 2.7 x 10^{19} molecules in a millilitre.

Combining the relationships between volume, pressure and temperature with Avogadro's hypothesis had given the equation of state for the ideal gas: $pV = nRT$, where p, V and T are the pressure, volume and absolute temperature of the gas, n is the ratio of the mass of the sample to the relative molecular mass of the substance (in modern terms the number of moles in the sample) and R is the gas constant. In 1873 **Johannes van der Waals** (1837-1923) modified the equation of state to allow for the finite sizes of molecules and for intermolecular attractions.

The term mole was probably introduced in 1896 by the chemist **Wilhelm Ostwald** (1853-1932). It is a particularly appropriate term, derived from the Latin word, *moles*, meaning heap or pile. Although the crith, the weight of one litre of hydrogen gas at 0 °C and at a pressure of 760 mm Hg (0.0906 g), had gained stature, the standard was changed to an oxygen standard by international agreement in 1897. This was because oxygen formed more stable compounds with more elements than did hydrogen. The standard quantity was then taken to be 32 g of oxygen gas at standard temperature and pressure and occupying 22.4 l. A relative atomic mass on this scale was a gram atom or mole and similarly a relative molecular mass was a gram molecule or mole.

The first accurate value for the Avogadro number, 6.5 x 10^{23} was given by **Jean Perrin** (1870-1942) in 1908 following an application of kinetic theory to a suspension of gamboge (a gum) particles in water. Several experiments were subsequently designed and provided more and more accurate values for the Avogadro number. The Avogadro number is a dimensionless number but the Avogadro constant (symbol L), is the number of particles in a mole and is the Avogadro number divided by the mole and is now taken to be 6.022045 x 10^{23} mol^{-1}.

The mole was defined in terms of the Avogadro number as one of the seven basic units in the SI system in 1961. A mole is the amount of a substance which contains as many elementary entities as there are carbon atoms in 0.012 kg of carbon-12. The elementary entity must be specified and may be an atom, a molecule, an ion, a radical, an electron, etc., or a specified group of such particles. A mole contains the Avogadro number of the specified elementary particles. A mole of a gas at standard temperature and pressure occupies a volume of 22.4 dm^3 or litres. The symbol for a mole is mol.

At this time also the carbon-12 isotope was adopted by the international physics and chemistry communities as the standard for relative atomic masses instead of oxygen. This was because, as mass spectrometry became the ultimate tool in accurate measurements of isotope masses and relative abundances, the carbon-12 isotope had a very convenient set of reference traces.

One mole = 12 g of carbon-12 or molar mass in grams of any other substance

= 6 x 10^{23} particles

= 22.4 l of ideal gas at s.t.p.

3.2 Kinetic Theory

The kinetic theory describes the behaviour of matter according to the laws of mechanics and statistics. The ideas included in modern kinetic theory were proposed and refined by a number of scientists. Robert Boyle stated the mathematical relationship between the pressure and volume of a sample of a gas at constant temperature from observation. **Daniel Bernoulli** (1700-1782) is best remembered for his studies on the physics of fluids, but was also the first to attempt to give a mathematical treatment of the behaviour of gases with changing temperature and pressure. **James Joule** (1818-1889) demonstrated the equivalence of heat and mechanical energy and in doing so established a greater understanding of the concept of heat. William Thomson, Lord Kelvin, helped to make the work of Joule, a brewer, known and accepted in the scientific community. He established the absolute scale for measuring temperature. **James Clerk Maxwell** (1831-1879) and **Ludwig Boltzmann** (1844-1906) both investigated statistically the distribution of speeds of molecules in a sample of gas and share the credit for the derivation of the kinetic theory equation

$$pV = \frac{N m \overline{c^2}}{3}$$

where p and V are, respectively, the pressure and volume of the sample of gas which contains N molecules, each of mass m moving with a root mean square velocity of $\sqrt{\overline{c^2}}$. The kinetic theory equation, derived mathematically, can be combined with the equation of state for the ideal gas to show that the temperature of a gas is proportional to the average kinetic energy, E_k, of the molecules.

$$pV = \frac{N m \overline{c^2}}{3} \quad \text{and } pV = nRT$$

$$\text{Therefore,} \quad \frac{N m \overline{c^2}}{3} = nRT$$

Therefore, since n, N, and R are all constants in a sample of gas,

$$m\overline{c^2} \propto T$$

$$\text{But,} \quad {}^1\!/\!_2 m\overline{c^2} = \overline{E}_k$$

$$\Rightarrow \quad \overline{E}_k \propto T$$

This is borne out experimentally because at high temperatures chemical reactions proceed very quickly since the high kinetic energies of the colliding particles ensure sufficient energy in collisions for bond breaking and reforming. The kinetic theory equation is also consistent with Avogadro's law, Boyle's law, Charles's law, Graham's law of diffusion, Brownian motion, etc., and thus there is indirect evidence in support of the kinetic theory of gases. The kinetic theory is very useful in chemistry on a purely descriptive level as well as at a mathematical level. While the kinetic theory applies to liquids, solids and gases, it is most useful for gases where the intermolecular forces are least and the mathematical equations are simplest.

The kinetic theory envisages all matter as being composed of large numbers of particles which are in constant motion and therefore have kinetic energy. Various physical and chemical properties can be explained in terms of the kinetic theory. Gas particles possess the highest quantities of kinetic energy and have the greatest freedom of movement, with large intermolecular spaces. Gases have no fixed shape and are compressible. Gas reactions are fast because the particles are in rapid motion and collide energetically. However, the bulk gas does not travel as quickly as this speed might suggest because collisions between the molecules retard the speed in a particular direction. In fact, in a sample of air, a molecule makes about five billion collisions every second. So the rate of diffusion of carbon dioxide through air is significantly smaller than its molecular speed. Neither do all the molecules of the gas travel at the same speed. In a sample of gas, containing a very large number of molecules travelling in various directions and undergoing frequent collisions, James Clerk Maxwell proposed that most molecules should have speeds close to the root mean square speed and rather few would have speeds far above or below the root mean square speed, Fig. 3.1.

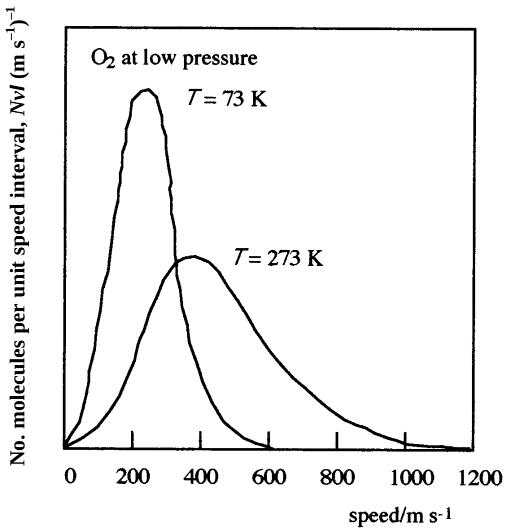


Fig 3.1 *Distribution of speed in molecules at different temperatures*

The curve is not symmetrical because molecules cannot have a speed lower than zero, but there is no theoretical upper speed limit (other than the speed of light in vacuum). As the temperature increases, however, the root mean square speed increases and so does the number of particles with higher speeds so the shape of the curve in Fig. 3.1 changes. This explains the increase in chemical reactivity at higher temperatures – a greater proportion of molecules have higher speeds.

Particles in a liquid have less kinetic energy but are still in constant motion, although in closer contact with one another. Liquids have no shape and are virtually incompressible.

Particles in a solid have the least kinetic energy. The particles tend to vibrate at fixed points in a structure where they are in contact with other particles. Solids have definite shape and are essentially incompressible. Reactions involving solids are slow because only the particles at the surface can participate in collisions with a reactant and these particles may not possess sufficient energy for a collision to lead to reaction.

The concept of the ideal gas has important applications in the kinetic theory. The ideal gas is an imaginary gas which obeys the gas laws perfectly at all conditions of temperature and pressure. Real gases approximate to ideal behaviour at low pressures. Mathematical equations to describe gas behaviour are more easily derived for imaginary substances which in theory never condense but the gas laws can be applied without modification to real gases at normal temperatures and pressures without serious error. The ideal gas is one where a small volume of gas contains a very large number of particles which are point masses moving randomly and obeying Newton's laws of motion. Collisions between the molecules or collisions between the molecules and the walls of the container occur very frequently and are elastic, i.e. do not involve a loss of energy. There are no intermolecular forces except during collisions.

Real gases condense into liquids because of attractive intermolecular forces which do not exist in the ideal gas and because their molecules have real volumes, while the molecules of the ideal gas are point masses. The ideal gas can achieve the temperature of absolute zero because the volume occupied by its point masses can theoretically be zero. However, a real gas, where the molecules have actual physical size, could not have zero volume at zero temperature even if it had not condensed before reaching that temperature as all real gases do. (See ‘Intermolecular Forces’, p. 11 and Experiment 3.1, p. 48.)

3.3 Ideas Leading Towards An Understanding of the Mole Concept

The Mole Concept

The following dialogue and comment is an extract reprinted with permission from ‘The Mole’ by Doris Kolb, in the Journal of Chemical Education, Volume 55, Number 11, November 1978.

‘Student: How do you know how much material to use in a chemical reaction?

Teacher: Well, ordinarily you want to use amounts that are chemically equivalent, or approximately so. Suppose we wanted to react this 10 g sample of aluminium with iodine. How much iodine do you think we would need?

Student: About 10 g?

Teacher: That would make the reactants equal in mass, but try to think in terms of atoms. An iodine atom is much bigger than an aluminium atom. It weighs almost five times as much.

Student: Then I guess we would use five times as much iodine. How about 50 g?

Teacher: That would be about right if each aluminium atom reacted with only one iodine atom, but don't forget that an aluminium atom can combine with three iodine atoms.

Student: In that case I guess we would need three times fifty grams of iodine. That would be about 150 g. Gosh! That seems like a lot of iodine for only 10 g of aluminium!

Although the word mole was not used in that dialogue, the mole concept certainly was. The discussion could not have taken place without it. There is probably no concept in the entire first year chemistry course more important for students to understand than the mole. There are also few things that give them quite so much trouble.'

Alternatives to Counting

When large numbers of small objects must be quantified they can be counted, but the larger the number of objects involved and the smaller those objects the more tedious, if not impossible, this counting becomes. So it is with atoms and molecules. Counting is not just tedious but simply out of the question since atoms and molecules are so small - in 1998 instruments have only recently been developed which can view individual atoms and then only the larger heavier ones. Such equipment is too expensive and in any case is unnecessary since there is a better way of solving the problem of measuring quantities of atoms and molecules accurately.

When large numbers of small objects must be quantified they can be measured by weighing. If the mass of a single object is known, any larger mass can be divided by the unit mass to find the number of objects present. It may or may not be necessary to know the number of objects present - often the mass will suffice. There are many everyday examples of weighing small objects instead of counting them to obtain exact quantities. A bank teller, for example, doesn't count coins. The coins are separated according to type and weighed. The mass of £5 worth of 20p coins is known, the mass of £10 worth of 50p coins is known, etc. In a hardware shop, screws, nails, nuts, etc., are often sold by mass instead of being counted. While the vendor does not need to know the number of nails in a kilogram, the buyer probably does. Loose sweets, grapes, cocktail sausages, etc., are rarely counted out in shops - you buy a certain mass of material which will always contain the same number of small objects provided those objects are uniform of course. The more accurate the balance, the more accurate the count.

Large numbers of small objects can also be quantified by measuring volumes. There are several everyday examples of this. Golf balls at a driving range are sold by the bucketful. Popcorn in cinemas is not counted out piece by piece. When the carton is full you accept that you have a certain portion and you are satisfied that another carton of the same size filled to the same level has a very similar quantity of popcorn as yours. If the pieces of popcorn were all identical you could be even more satisfied with this way of measuring. In recipes, particularly in US cookbooks, quantities of sugar, flour, etc., are often given as volumes. The volume used is the 'cup' because most cups used to hold approximately the same volume. This idea was, and still is, very convenient where an accurate kitchen scales is not available. In modern times, most US kitchens have a measuring cup which removes the uncertainty of different shapes and sizes. We buy milk, orange juice, petrol, central heating oil, etc., by volume, satisfied in each case of having obtained definite quantities. It would be possible to calculate the number of objects present in a certain volume if the volume of an individual unit were known but allowance would have to be made for packing - in most cases the individual objects would not completely fill the space they occupy.

Collective terms

Pair -	2
Dozen -	12
Score -	20
Gross -	144
Mole -	6.022×10^{23}

The mole is just another collective term. One dozen golf balls has a different mass to a dozen oranges but there are twelve of each in a dozen. One mole of water molecules and one mole of helium atoms have different masses but there are 6.022×10^{23} particles in each.

How Big is Avogadro's Number?

A cube of rock salt with a side of length 3 cm contains Avogadro's number of sodium ions and Avogadro's number of chloride ions.

A glass containing 18 cm^3 of water holds Avogadro's number of water molecules.

A strip of magnesium ribbon of length 12 m contains Avogadro's number of magnesium atoms.

But just how many particles can there be stuffed into these dimensions? Once more quoting from The Mole by Doris Kolb, in the Journal of Chemical Education, Volume 55, Number 11, November 1978.

'When written in its exponential form, 6.02×10^{23}, Avogadro's number looks extremely large, but to most people it does not appear to be nearly so huge as it really is. It may seem somewhat larger when written in the form 602 000 000 000 000 000 000 000, or when recognised as being equal to 602 000 x a million x a million x a million, but the number is actually too gigantic for the mind to comprehend.

The fact that you can hold Avogadro's number of atoms in the palm of your hand belies the size of the number because atoms are so incredibly small. To convey the magnitude of Avogadro's number we need to use more tangible units.

If you had Avogadro's number of tiny grains of sand, for example, you could spread them out evenly over the entire state of California, and you would end up with a layer of sand as high as a ten-storey building.

If you could divide Avogadro's number of sheets of paper into a million equal piles, the stacks would be so tall they would stretch all the way from here to the sun, and even beyond it*.

Avogadro's number of marshmallows spread uniformly over all 50 of the United States would yield a blanket of marshmallows more than 600 miles deep.

If Avogadro's number of pennies were distributed equally among all the people on earth (currently** around 4 billion), each one would have enough money to spend a million dollars every hour, day and night, throughout his lifetime, and still he would not spend half of it....

Avogadro's number is so enormous it defies comprehension. On the other hand, one need not be able to comprehend Avogadro's number in order to use it. There is no reason why 6×10^{23} cannot be treated the same way we would 6 thousand, or 6 hundred, or a dozen. The important thing to remember is that, overwhelming though its size may be, Avogadro's number is still a real and finite number.

Students sometimes wonder why Avogadro chose such a strange number. He didn't choose it, of course. No one did. Avogadro's number is the number of atoms in a gram atomic weight of any element. The number was predetermined when the gram was established as a basic unit of mass.'

* Actuallly several hundred times further than the sun.

** The present population of the world is about 5 billion.

How Was Avogadro's Number Measured?

A wide variety of chemical and physical procedures have been applied to the calculation of the Avogadro constant. Some are very simple in principle while others are quite advanced. A few of the simpler methods are described here.

Using the charge on the electron and electrolysis experiments

Robert Millikan measured the charge on the electron in the famous oil drop experiment of 1909. The charge on a mole of electrons was known to be about 96 500 coulombs, or one faraday. The charge on a mole of electrons was easily measured in electrolysis experiments, e.g. by measuring the charge required to plate one mole of a monovalent metal. The Avogadro constant, *L*, was then calculated as follows.

$$L = \frac{\text{total charge on one mole of electrons}}{\text{charge on one electron}}$$

Using the most accurate modern data available for the Faraday constant (*F*) and the charge on the electron

$$L = \frac{96485}{1.602189 \times 10^{-19}}$$

$$= 6.022 \times 10^{23}\ \text{mol}^{-1}$$

This value is not accepted today as the most accurate which can be obtained and that calculated in 1909 was less accurate again because of errors in the value of the Faraday constant and in Millikan's value for the charge on the electron used at that time.

From radioactivity

The principle of this method for calculating the Avogadro constant is that as a sample of radioactive radium-226 disintegrates by emitting α-particles, the number of disintegrations in a certain period of time can be measured accurately using a Geiger counter. Following emission from the radium-226 nuclei, the α-particles combine with electrons in the material they pass through, forming helium gas. The volume of helium gas obtained by α-particle emission from a sample of radium-226 is measured over the same period of time as the disintegrations are counted. This was first done by **Sir James Dewar** (1843-1923) in 1910. There were two methods of counting α-particles available at the time; observing the scintillations caused by the radiation and using the ionising effects of the radiation. The latter had been used by 1908 by **Hans Geiger** (1882-1947) to develop an early form of Geiger-Müller tube. The corresponding number of moles of helium gas, *n*, can be calculated by using the equation of state: $pV = nRT$. The Avogadro constant, *L,* can be calculated as follows.

$$L = \frac{\text{no. of disintegrations every second in sample}}{\text{no. of moles helium formed every second}}$$

For accuracy the experiment should be conducted over a long period of time because, although the activity of radium-226 is high (8.15×10^{12} Bq mol^{-1}), the corresponding volume of helium collected per second is still very small. First attempts gave a crude value of 7×10^{23} mol^{-1} for the Avogadro constant. Using more carefully collected data

$$L = \frac{\text{no. of disintegrations every second in sample}}{\text{no. of moles helium formed every second}}$$

$$= \frac{8.15 \times 10^{12}}{1.35 \times 10^{-11}}$$

$$= 6.04 \times 10^{23}\ \text{mol}^{-1}$$

Using X-ray diffraction

The volume occupied by a mole of crystalline silicon can be obtained by careful measurement of density and molar mass. The molar mass is determined by mass spectrography for accuracy. The volume occupied by a single atom of silicon, i.e. the volume per atom in the crystal rather than the volume of an atom, can be calculated by measurements taken from X-ray diffraction of the silicon crystal (see p. 6). The Avogadro constant can then be calculated as follows.

$$L = \frac{\text{volume occupied by one mole of Si atoms}}{\text{volume occupied by one Si atom}}$$

The reliability of this method depends on the use of a crystal of silicon of high purity. This method, combined with the most modern optical interferometry techniques, gives the currently most accurate value for the Avogadro constant of 6.022045 x 10^{23} mol^{-1}.

Surface film

There is no simple procedure which could be used to obtain a good estimate of the Avogadro constant in the school laboratory but perhaps there is still some merit in an experiment which gives some approximation of it.

In this experiment a small volume of a dilute solution (0.005% v/v) of a fatty acid, e.g. octadec-9-enoic acid (oleic acid, $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$) in a volatile solvent, e.g. ether, is dropped onto the surface of water. The solvent quickly evaporates and the fatty acid molecules arrange themselves in an approximately circular monomolecular layer on the water surface with their hydrophilic polar carboxylic acid functional groups in contact with the water surface and the hydrophobic non-polar hydrocarbon chains sticking straight up out of the water. The molecules are assumed to be in lateral contact with one another, attracted to each other by van der Waals forces. The extent of the monomolecular layer can be easily seen by sprinkling talcum powder on the water surface before dropping on the fatty acid.

The approximate length of the fatty acid molecule can be calculated since the concentration of the fatty acid solution is known, the average volume of a drop added to the water is known and so the volume of acid in a drop can be equated with the volume of the cylinder of fatty acid molecules on the water surface.

Quantity	**Result**
Concentration of oleic acid solution	0.005% v/v
Average volume of drop of oleic acid solution	0.05 cm^3
Average radius of oleic acid film	2.47 cm
Molar mass of oleic acid	282 g
Density of oleic acid	0.89 g cm^{-3}

Table 3.1 *Experimental results*

Volume of cylinder = volume of 0.005% of drop of solution

$$\pi r^2 h = \frac{0.005 \times 0.05}{100}$$

$$\pi(2.47)^2 h = 2.5 \times 10^{-6}\ \text{cm}^3$$

$$h = 1.3 \times 10^{-7}\ \text{cm}$$

The fatty acid molecule is presumed to be cylindrical, with its length approximately four times its diameter as can be seen in a model of the structure, and the volume of a single molecule can be calculated.

Radius of cylindrical molecule

$$= 1.3 \times 10^{-7} \div 8$$

$$= 1.625 \times 10^{-8}\ \text{cm}$$

Volume per molecule

$$= \pi r^2 h$$

$$= \pi\,(1.625 \times 10^{-8})^2 \times 1.3 \times 10^{-7}$$

$$= 1.078 \times 10^{-22}\ \text{cm}^3$$

The volume of a mole of fatty acid molecules can be calculated from the density of the material and its molecular mass.

$$\text{Volume/mol} = \frac{\text{molar mass}}{\text{density}}$$

$$= \frac{282}{0.89}$$

$$= 317 \text{ cm}^3$$

$$L = \frac{\text{vol. occupied by 1 mole of fatty acid mols.}}{\text{vol. occupied by one fatty acid mol.}}$$

$$= \frac{317}{1.078 \times 10^{-22}}$$

$$= 2.9 \times 10^{24} \text{ mol}^{-1}$$

Any answer between 6 x 10^{22} and 6 x 10^{24} mol^{-1} is acceptable given the various sources of error which include the following.

The accuracy with which a 0.005% solution can be prepared and stored when the solvent is very volatile is questionable. The method by which the volume of an average drop of this solution can be measured, e.g. using a burette, is also open to error due to evaporation. The measurement of the radius of the cylinder of fatty acid on the water leads to further errors because it is only very approximately circular. Assumptions are also made, perhaps wrongly, that the layer of fatty acid is monomolecular and that the length is approximately four times the diameter of the molecule since models do not necessarily use atoms and bond lengths built to the same scale. Furthermore, the purity of the oleic acid sample used may not be such that the use of the molar mass and density of pure oleic acid is appropriate. Pure oleic acid is, unfortunately, very expensive (see Experiment 3.2).

3.4 Units, Accuracy, Calculating Machines

The SI system (Système International d'Unités) is an internationally agreed coherent set of units. A coherent set of units is one where the product or quotient of any two units in the system gives the unit of the resultant quantity without the need to introduce any constants, e.g. velocity = displacement/time and the unit for velocity is the metre/second. There are seven base units of the SI system. These are given in Table 3.2.

Unit	Symbol	Physical quantity
metre	m	length
kilogram	kg	mass
second	s	time
ampere	A	electric current
kelvin	K	temperature
mole	mol	amount of substance
candela	cd	luminous intensity

Table 3.2 *Basic units of SI*

The radian (plane angle) and steradian (solid angle) are supplementary units.

There are many derived units obtained from the base units by defining relationships. For example, volume is the product of the length, the breadth and the height of an object, i.e. it is the product of three lengths so the unit of volume is the metre cubed, m^3. Density is the ratio of mass to volume and therefore the unit of density is the kg m^{-3}. Eighteen or so of these derived units have been given special names, e.g. the unit of pressure is derived from the force per unit area and has been given the name pascal, symbol Pa. If the unit is named after a scientist the unit is written in lower case but the symbol has a capital first letter, e.g. joule, J; pascal, Pa; newton, N; coulomb, C; etc.

In conjunction with the SI system a set of decimal multiples and submultiples are recommended if the unit itself is too large or too small in a given case. Hence, centimetres, millipascals, and micrograms are all part of the SI system (see Table 3.3).

Submultiple	Prefix	Symbol	Multiple	Prefix	Symbol
10^{-18}	atto	a	10^{1}	deca	da
10^{-15}	femto	f	10^{2}	hecto	h
10^{-12}	pico	p	10^{3}	kilo	k
10^{-9}	nano	n	10^{6}	mega	M
10^{-6}	micro	µ	10^{9}	giga	G
10^{-3}	milli	m	10^{12}	tera	T
10^{-2}	centi	c	10^{15}	peta	P
10^{-1}	deci	d	10^{18}	exa	E

Table 3.3 *Submultiples and multiples used in conjunction with the SI system*

In chemistry, as explained earlier, the SI system is used very widely but note that grams are much more commonly used than kilograms in calculations and most chemical formulae refer to masses in grams. For example, the density of a substance is often given in chemistry in the unit g cm^{-3} while the standard SI unit for density is kg m^{-3}.

In Europe, SI units have been universally adopted in all scientific and engineering work. They are also becoming more and more familiar in everyday life as distances are measured in metres, masses in kilograms, gas bills feature cubic metres, etc. In the United States, however, the metric system has not been introduced into everyday transactions such as buying flour, milk, gas (petrol), etc. The terms pounds, pints and miles are still in the everyday language. However, science and engineering in the US are adopting the SI system, albeit slowly. The Imperial system of units is used in the US to a much wider extent in manufacturing and other industries than is the case in Europe, although the National Institute of Standards and Technology has been using and recommending the adoption of the SI system in the United States since 1964.

Decimal Places and Significant Figures[4]

In any measured quantity, where the error is not specifically stated, the accuracy is indicated by the number of significant figures used. For example, a value given as 5.765 is taken to be accurate to four significant figures, while a value given as 8.5×10^3 is taken to be accurate to only two significant figures.

While a knowledge of errors and their computation is not necessary at Leaving Certificate level it is important that students are aware of the concept of accuracy in reporting results of calculations. The following guidelines for students are suggested.

In a one-step calculation the answer should be given to the same number of significant figures as in the least accurate value given in the original data. For example, calculate the sum of the masses of chemicals A and B from the three masses given.

Mass of chemical A and its container	=	104.678 g
Mass of container	=	32.9 g
Mass of chemical B	=	78.54 g

The total mass of the chemicals A and B = 104.678 - 32.9 + 78.54 = 150.318 g. The least accurate value from the given data is the mass of the container which is given to three significant figures. Accordingly, the answer should be given to three significant figures also, i.e. 150 g.

It is quite common, but incorrect, practice for answers to calculations in chemistry to be simply rounded off to one or two decimal places. For example, what is the density of a piece of iron of mass 70.75 g and volume 9 cm^3?

$$\text{Density} = \frac{\text{mass}}{\text{volume}}$$

$$= \frac{70.75}{9}$$

$$= 7.861111111 \text{ g cm}^{-3}$$

It is not unusual to see answers like this routinely rounded off to two decimal places. It is obvious that the accuracy of the answer does not extend to the ninth decimal place given on the calculator display but neither is the answer reliable to the second decimal place because the volume was measured to only one significant figure, thus the acceptable answer is 8 g cm^{-3}.

If the calculation involves several steps, at each stage keep at least one more significant figure in the answer than in the data given and then at the final stage round off to the number of significant figures in the quantity in the data with the least number of significant figures. For example, 11.00 g of iron and 11.00 g of sulphur are heated together to form iron(II) sulphide. Which reactant is limiting and what mass of iron(II) sulphide is formed? The relative atomic masses of iron and sulphur are 56 and 32, respectively.

$$Fe + S \rightarrow FeS$$

$$\text{No. of moles Fe} = \frac{11.00}{56}$$

$$= 0.19643$$

$$= 0.20$$

$$\text{No. of moles S} = \frac{11.00}{32}$$

$$= 0.34375$$

$$= 0.34$$

The iron is limiting. Only 0.20 mol of S can react and from the balanced equation 0.20 mol of FeS is formed.

$$\text{Mass of FeS} = 0.19643 \times 88$$

$$= 17.28584$$

The mass of FeS formed would usually be given as 17.29 g, i.e. rounded off to the number of significant figures given for the masses. More correctly, it should be given as 17 g, i.e. rounded off to the number of significant figures given for the least accurate quantities, the relative atomic masses.

Rounding off relative atomic masses to integral values is standard practice at Leaving Certificate level and indeed at third level except for all but the most accurate calculations. Integral values for relative atomic masses for all of the elements are taken, ignoring the more accurate values available from the periodic table, except in the cases of chlorine and copper which are taken as having relative atomic masses of 35.5 and 63.5 respectively.

Calculator

The electronic calculator was first permitted for use in Certificate examinations in Ireland in 1975. The calculators were then not allowed in examinations for a few years but were permitted again in 1978. The calculators available at that time were somewhat bulkier than the modern slimline models, they had l.e.d. displays and therefore had a greater power demand than the modern models with their low-power liquid crystal displays. Students had to have spare penlight batteries then - solar powered models were very uncommon. If students think that calculations in chemistry are tedious nowadays, maybe it would help to remind them that their teachers probably had to do them all 'long ago' without a calculator!

In chemistry the student should be able to use the adding, subtracting, multiplying and dividing operators, the inverse function, the square and square root functions, the exponential function, the $\log_{10}$ and antilog functions. They should be aware of the calculation priority sequence of their particular model, for example in a pH calculation involving logs or antilogs. Most modern scientific calculators have so many additional functions and modes of operation and display that the students can become confused and cannot master or operate quickly and without mistakes even this limited list of functions. Sometimes the calculator becomes stuck in a statistical mode or a fixed number of decimal places mode from which the student cannot escape. The student should know how to reset the calculator to normal operational mode. Some students are naturally curious and will press enough buttons to succeed in escaping anyway but it should be a process they are able to repeat easily and have acquired by design not accident. They should be encouraged to keep the instruction manual for the calculator and practise the calculations in it, especially for the particular functions mentioned above.

3.5 Experiments

Experiment 3.1

To Demonstrate Brownian Motion (See Module 1, Atomic Structure & Trends in the Periodic Table of the Elements)

Experiment 3.2

To Estimate the Avogadro Constant

Teacher demonstration

Materials

Molecular model of octadec-9-enoic acid (oleic acid)
Oleic acid
Ether
Talcum powder
Water
Water trough
Glass or plastic 1 cm^3 pipette
50 cm^3 and 100 cm^3 volumetric flask
Burette
Beaker
Metre stick or ruler

Safety

Oleic acid is an irritant. Ether is extremely flammable. Wear safety glasses.

Procedure

1. Prepare a 0.005% solution of oleic acid in ether by measuring out 0.5 cm^3 of oleic acid with a 1 cm^3 pipette, transferring it directly to a 50 cm^3 volumetric flask and diluting it to 50 cm^3 with ether in the usual way. This is a 1% (v/v) solution. Clean the pipette by rinsing a number of times with ether and then allow time for the ether to evaporate. Then measure out 0.5 cm^3 of the 1% solution with the 1 cm^3 pipette, transfer it directly to a 100 cm^3 volumetric flask and again dilute it to 100 cm^3 with ether in the usual way. This second solution is 0.005% (v/v). Stopper tightly.

2. Put 10 cm^3 of the 0.005% solution of oleic acid into a burette. Fill the part below the tap and take the reading. Allow, say, 50 drops to flow out of the burette into a beaker and take the new reading. From the difference in volumes calculate the volume of an average drop of the solution.

3. Put water to a depth of a few cm in the trough and sprinkle the surface lightly with talcum powder.

4. Allow one drop of the 0.005% oleic acid solution to fall onto the water surface. The solvent evaporates quickly and a roughly circular film of oil can be seen on the water surface, its boundary marked by talcum powder. Measure the diameter of the oil film a number of times and find the average diameter.

5. Calculate from the results the length of the oleic acid molecule (see p. 44). Repeat Steps 3, 4 and 5 a number of times and average the results.

7. From the model of oleic acid, estimate the ratio of the length of the molecule to its radius, assuming it occupies a space which is roughly cylindrical. Hence calculate the volume of an oleic acid molecule.

8. Calculate the volume occupied by a mole of oleic acid given that its density is 0.89 g cm^{-3} and its molar mass is 282 g. Calculate the Avogadro constant, *L*, as follows.

$$L = \frac{\text{volume occupied by 1 mol of oleic acid}}{\text{volume occupied by one oleic acid molecule}}$$

Discussion

The various sources of error should be pointed out to the student.

3.6 References

1. Changing Celsius to Kelvin is Not Just a Unit Conversion, B.H. Nordstrom, *Journal of Chemical Education,* 70, 1993.

2. A Mole of M&M's, C. Merlo and K. E. Turner, *Journal of Chemical Education,* 70, 1993.

3. Amount and the Mole, Barry O'Brien, *Chemistry in Action, 50, 1997.*

4. Measuring with a Purpose, P. A. Metz and J. R. Pribyl, *Journal of Chemical Education,* 72, 1995.

CHAPTER 4

CHEMICAL CALCULATIONS

4.1 Calculations

Some students find it helpful to practise questions as named procedures, particularly when new to the subject. They need to memorise and practise the general procedure but retain the ability to cope with variations. They must learn to recognise the named procedure from the phraseology of the question and practise working procedures in reverse, e.g. find the density of a gas from its molecular mass and find the molecular mass of a gas from its density. Students need to note, however, that not all problems can be neatly categorised and that many may involve several named procedures.

- Try underlining the key part of the question.

- Try boxing answers to intermediate stages.

- Do label the answers to intermediate stages with the name of the substance it refers to and the units.

- In complicated titrations or other procedures sketch the stages of the experiment to help follow the logic of the problem. This is not done in this booklet because the calculations are mostly introductory but it can be a very helpful tool.

- Practise, practise, practise.

- Only certain procedures can be examined, so if the student has been practising, he or she must have done a similar question already. The one in hand just seems unfamiliar.

- Check the calculations.

- Re-read the question. Have you omitted anything?

- Take relative atomic masses from the periodic table (they may be given on the examination paper) and not atomic numbers (unless appropriate).

4.2 Relationships and Interrelationships

Relationships

In chemical calculations the unit of mass usually used is the gram. Occasionally, if the calculation is based on an industrial process, kilograms or tonnes may be involved. The relationship between the gram, kilogram and tonne is given below and the student will probably find it easiest to convert to grams, calculate in grams using the familiar formulae, and reconvert the answer back to kilograms or tonnes. One of the reasons that the standard SI unit of mass, the kilogram, is not used in the standard textbook formulae is because most laboratory experiments involve smaller masses than this amount.

For measurement of volume, chemical calculations use the l or the cm^3. The unit of volume in each formula below should be memorised. Again, one of the reasons that the SI unit of volume, the cubic metre, m^3, has not been fully adopted is that it is too large a volume for most laboratory experiments. One exception to this rule is in the ideal gas equation where standard SI units are used throughout and volumes therefore must be in m^3. Students need to be aware of the relationship between m^3, cm^3 and l. They should also know that the litre is the equivalent of the cubic decimetre and that the millilitre is the equivalent of the cm^3.

It is useful to know that standard pressure in SI units is 1.01325 x 10^5 Pa (N m^{-2}) or in the alternative but not SI units, 760 mm Hg, 1.01 bar or 1 atmosphere. Standard pressure is often approximated to 1 x 10^5 Pa.

Standard temperature is 273.15 K, usually approximated to 273 K. Standard temperature and pressure are sometimes abbreviated to s.t.p.

Molar volume of a gas at s.t.p. is taken to be 22.4 l (only strictly true for the ideal gas).

The Avogadro constant is taken as 6 x 10^{23} mol^{-1}.

The following are some important relationships frequently used in chemical calculations.

$$\text{Density (g cm}^{-3}) = \frac{\text{mass (g)}}{\text{volume (cm}^3)}$$

$$\text{No. of moles} = \frac{\text{mass (g)}}{\text{molar mass (g mol}^{-1})}$$

$$\text{No. of moles} = \frac{\text{volume (l)}}{\text{molar volume (l mol}^{-1})}$$

$$\text{No. of moles} = \frac{\text{number of molecules}}{\text{Avogadro constant (mol}^{-1})}$$

$$\text{No. of moles} = \text{molarity (mol l}^{-1}) \text{ x volume (l)}$$

$$\text{Concentration (g l}^{-1}) = \text{molarity (mol l}^{-1}) \text{ x molar mass (g mol}^{-1})$$

$$\frac{\text{Molarity}_1 \text{ (mol l}^{-1}) \text{ x volume}_1 \text{ (cm}^3)}{n_1} = \frac{\text{molarity}_2 \text{ (mol l}^{-1}) \text{ x volume}_2 \text{ (cm}^3)}{n_2}$$

{n_1 is the no. of moles of reactant 1 which react with n_2 moles of reactant 2}

$$\text{Percentage yield} = \frac{\text{actual yield (g) x 100}}{\text{theoretical yield (g)}}$$

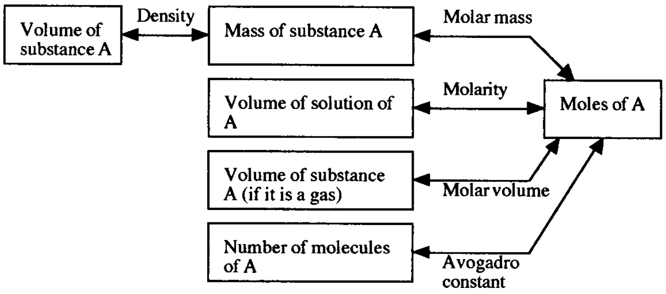
$$= \frac{\text{actual yield (mol) x 100}}{\text{theoretical yield (mol)}}$$

The following are important conversion factors frequently required in calculations.

1 000 000 g = 1000 kg = 1 tonne (t)
1 000 000 cm^3 = 1000 l = 1 m^3
101325 Pa (N m^{-2}) = 760 mm Hg = 1 atmosphere = 1.01 bar

Interrelationships

In some calculations it is necessary to deduce one set of data about a substance from other data about the same substance. A student should be expected to be able to manipulate the interrelationships given below.



4.3 Relative Atomic Mass and Percentage Abundance of Isotopes

Worked Example 1

The element neon is composed of two isotopes, 91% with relative atomic mass 20 and 9% with relative atomic mass 22. Calculate the relative atomic mass of neon from this information.

In a sample of 100 neon atoms

	Total mass
91 have mass 20	91 x 20 = 1820
9 have mass 22	9 x 22 = 198
Total mass	= 2018

100 atoms of neon have mass 2018

Relative atomic mass of neon is 20.2.

Relative atomic mass has no units.

Worked Example 2

Calculate the relative atomic mass of cadmium from its mass spectrum, assuming each ion displayed has unit charge (see Fig. 4.1).

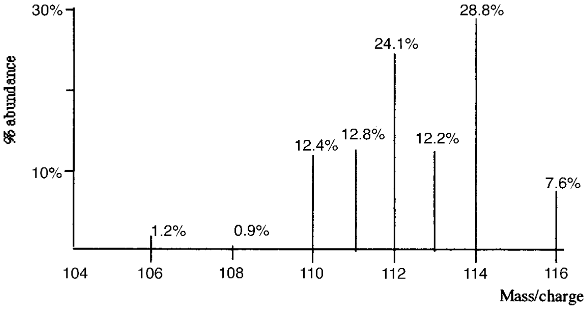


Fig. 4.1 *Mass spectrum of cadmium (Mass/charge = relative atomic mass/charge on ion)*

The mass spectrum displays eight isotopes.

In a sample of 100 cadmium atoms

		Total mass
1.2 have mass 106	1.2 x 106 =	127.2
0.9 have mass 108	0.9 x 108 =	97.2
12.4 have mass 110	12.4 x 110 =	1364.0
12.8 have mass 111	12.8 x 111 =	1420.8
24.1 have mass 112	24.1 x 112 =	2699.2
12.2 have mass 113	12.2 x 113 =	1378.6
28.8 have mass 114	28.8 x 114 =	3283.2
7.6 have mass 116	7.6 x 116 =	881.6
	Total mass =	11251.8

100 atoms of cadmium have mass 11251.8

$$\text{Average mass of cadmium atom} = \frac{11251.8}{100}$$

$$= 112.5 \text{ g}$$

Relative atomic mass of cadmium is 112.5

Relative atomic mass has no units.

Of course, there cannot be 0.9 of an atom of cadmium. This fraction of an atom is only a mathematical idea which arises in the very small sample of 100 atoms which we use to solve the problem. In order to have whole numbers of each isotope it would be necessary to consider a larger sample of cadmium. Since the ratio is the same, mathematically it is unnecessary to consider a larger sample.

Worked Example 3

Calculate the percentage composition of a sample of copper which has a relative atomic mass of 63.55 and which contains isotopes of mass number 63 and 65.

The students should recognise that this question is the reverse of Question 1 and reversing the solution to Question 1 gives the answer.

Relative atomic mass of copper is 63.55

$\Rightarrow$ average mass of copper atom = 63.55

$\Rightarrow$100 atoms of copper have a mass of (63.55 x 100) = 6355

In a sample of 100 copper atoms there are x atoms of mass 63 and (100 - x) of mass 65.

		Total mass
x have mass 63	x x 63 =	$63x$
(100 - x) have mass 65	(100 - x) x 65=	$6500 - 65x$
	Total mass =	$6500 - 2x$

$$\Rightarrow 6500 - 2x = 6355$$

$$145 = 2x$$

$$x = 72.5$$

In the copper sample 72.5% of the atoms have mass number 63 and 27.5% have mass number 65.

Exercise 4.1

Q.1. Calculate the relative atomic mass of boron which has a percentage composition of 18.6% ^{10}B and 81.4% ^{11}B. Explain why the atomic radii of both isotopes are equal.

Q.2. Distinguish between mass number and relative atomic mass. Calculate the percentage composition of the element lithium which has two isotopes of mass numbers 6 and 7 and has a relative atomic mass of 6.941.

Answers

Q.1. 10.8. Atomic radii are only influenced by interactions between the positively charged protons in the nucleus and the electrons in the electron cloud.

Q.2. 5.9% ^{6}Li and 94.1% ^{7}Li.

4.4 Gas Laws

Worked Example 1

What volume is occupied by a gas at a pressure of 1.01×10^5 Pa if it has a volume of 205 cm^3 at a pressure of 2.02×10^5 Pa?

Since the question involves only pressures and volumes, we may assume that the temperature is constant throughout and therefore can apply Boyle's law.

$$p_1V_1 = p_2V_2$$

$$2.02 \times 10^5 \times 205 = 1.01 \times 10^5 \times V_2$$

$$\frac{2.02 \times 10^5 \times 205}{1.01 \times 10^5} = V_2$$

$$V_2 = 410 \text{ cm}^3$$

Note that the gas occupies a greater volume at the lower pressure.

There is no need to convert cm^3 to m^3 in this type of question. Since the units on the two sides of the equation are equal any conversion factor used will cancel. The volume calculated for V_2 will therefore have the same units as V_1.

Worked Example 2

What is the new volume of a gas heated to 200 ^{o}C if it has a volume of 2.00 l at a temperature of 100 ^{o}C?

Since the question involves only temperatures and volumes, we may assume that the pressure is constant throughout and therefore that volume is proportional to temperature.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\frac{2}{373} = \frac{V_2}{473}$$

$$V_1 = 2.54 \text{ l}$$

Note that the gas occupies a greater volume at the higher temperature.

Again there is no need to convert l to m^3 in this type of question. Since the units on the two sides of the equation are equal any conversion factor used will cancel. The volume calculated will therefore have the same units as V_1. Degrees Celsius must be converted to kelvins. (See section 3.1.)

Worked Example 3

A gas occupies a volume of 3.00 l at a temperature of 25 ^{o}C and a pressure of 800 mm Hg. What volume will the gas occupy at s.t.p.?

Since the question involves temperatures, pressures and volumes, we will apply the general gas law.

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

The standard conditions of temperature and pressure are discussed on p. 52. Degrees Celsius must be converted to kelvins, but the pressure units and volume units given can be used directly provided they are used consistently on both sides of the equation.

$$\frac{800 \times 3}{298} = \frac{760 \times V_2}{273}$$

$$V_2 = \frac{800 \times 3 \times 273}{298 \times 760}$$

$$V_2 = 2.89 \text{ l}$$

Worked Example 4

A gas at a temperature of 227 °C occupies a container of volume 0.821 l at a pressure of 1.000 atmosphere. What is the pressure in pascals? How many moles of gas are present? Take the universal gas constant, R, to be 8.314 J K^{-1} mol^{-1}.

The formula required here is the equation of state of the ideal gas, $pV = nRT$, and all quantities must be in standard SI units. Give three significant figures in the answer.

$$227\ ^{o}\text{C} = 500 \text{ K}$$

$$0.821 \text{ l} = 0.821 \times 10^{-3} \text{ m}^3$$

$$1.000 \text{ atmosphere} = 1.01 \times 10^{5} \text{ Pa}$$

$$pV = nRT$$

$$1.01 \times 10^{5} \times 0.821 \times 10^{-3} = n \times 8.314 \times 500$$

$$n = 0.020 \text{ mol}$$

Worked Example 5

In an experiment to measure the relative molecular mass of a volatile liquid, 0.475 g of the liquid was vaporised at a temperature of 100 °C. The volume occupied by the vapour was 93.0 cm^3 at a pressure of 101 kPa. How many moles of vapour are present? Hence calculate the relative molecular mass of the liquid. If the liquid is an element, identify it. Take R, the universal gas constant, to be 8.31 J K^{-1} mol^{-1}.

The formula required here is again the equation of state of the ideal gas, $pV = nRT$, and all quantities must be in standard SI units. Keep four significant figures in the intermediate stages of the calculation and give three significant figures in the final answer.

$$100\ ^{o}\text{C} = 373 \text{ K}$$

$$93 \text{ cm}^3 = 93 \times 10^{-6} \text{ m}^3$$

$$101 \text{ kPa} = 1.01 \times 10^{5} \text{ Pa}$$

$$pV = nRT$$

$$1.01 \times 10^{5} \times 93 \times 10^{-6} = n \times 8.31 \times 373$$

$$n = \frac{1.01 \times 10^{5} \times 93 \times 10^{-6}}{8.31 \times 373}$$

$$n = 0.003030 \text{ mol}$$

$$n = \frac{m}{M_r}$$

$$0.003030 = \frac{0.475}{M_r}$$

$$M_r = \frac{0.475}{0.003030}$$

$$= 157$$

Relative molecular mass has no units.

The only volatile liquid element is bromine, Br_2 (see p. 2). It has a relative molecular mass of 159.81. This answer is, allowing for experimental error, reasonably close to this.

Worked Example 6

Calculate a value for R, the universal gas constant, given that one mole of a gas occupies a volume of 22.4 l at s.t.p.

Convert l to m^3 and °C to K; the answer will then be in standard SI units of J K^{-1} mol^{-1}.

$$pV = nRT$$

$$1.01 \times 10^5 \times 22.4 \times 10^{-3} = 1 \times R \times 273$$

$$R = \frac{1.01 \times 10^5 \times 22.4 \times 10^{-3}}{1 \times 273}$$

$$= 8.29 \text{ J K}^{-1} \text{ mol}^{-1}$$

Worked Example 7

What volume of oxygen, at s.t.p., is required to burn 2 l of methane measured at s.t.p. according to the equation

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

According to Avogadro's law equal volumes of gases at the same temperature and pressure contain equal numbers of molecules. Therefore, if two molecules of oxygen are required to burn every methane molecule, according to the balanced equation, then the volume of oxygen gas required must be twice the volume of methane burned. So, the answer is 4 l.

Note: according to Gay-Lussac's law, gases combine in simple proportions by volume provided they are measured under the same conditions of temperature and pressure.

Worked Example 8

Ammonia is burned in oxygen according to the equation

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

What is the final volume of the mixture if 4 l of ammonia are burned in 10 l of oxygen at a certain temperature and pressure? You may assume the reaction goes to completion.

According to Avogadro's law, 4 l of ammonia will require 5 l of oxygen for complete combustion. There will therefore be 5 l of unused oxygen in the container at the end of the reaction. Also, for every 9 l of reactants, 10 l of products are formed according to the balanced equation. So the final volume is 15 l.

Worked Example 9

C_xH_y is a hydrocarbon. On combustion in excess oxygen, 750 cm^3 of the hydrocarbon produced 3 l of carbon dioxide and 3.75 l of water vapour. All measurements were made at the same temperature and pressure. What is the formula of the hydrocarbon?

Construct a 'balanced' equation.

$$C_xH_y + ?O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$$

C_xH_y	xCO_2	$\frac{y}{2}H_2O$
0.75 l	3 l	3.75 l
1	4	5

According to Avogadro's law, at constant temperature and pressure, the ratio of the volumes is equal to the ratio of the numbers of moles. Divide by the smallest volume to get a simple ratio. Rewrite the balanced equation.

$$C_xH_y + ?O_2 \rightarrow 4CO_2 + 5H_2O$$

Therefore $x = 4$, $\frac{y}{2} = 5$ and ? = 6 $^1/_2$.

The hydrocarbon is C_4H_{10}.

Exercise 4.2

Q.1. What is the pressure exerted by a sample of gas which occupies a volume of 265 cm^3, if it occupies a volume of 355 cm^3 at a pressure of 101 kPa and at the same temperature?

Q.2. What is the temperature of a gas which occupies a volume of 2.00 l if the same gas has a volume of 2.87 l at a temperature of 27 °C and the same pressure?

Q.3. A gas occupies a container which has a volume of 250 cm^3 and registers a pressure of 5 atmosphere at a temperature of -15 °C. If the gas is released into a chamber where the final pressure is atmospheric pressure and where the final temperature is 0 °C, what volume does the gas occupy in the chamber?

Q.4. How many moles are present in a 560 cm^3 sample of a gas which is at a temperature of 25 ^{o}C and exerts a pressure of 2 atmospheres? Take *R*, the universal gas constant, to be 8.314 J K^{-1} mol^{-1}.

Q.5. Describe the apparatus used to measure the relative molecular mass of a volatile liquid. The relative molecular mass of a solvent used to remove nail varnish was determined as follows. A sample of the solvent of mass 0.79 g was vaporised at a temperature of 100 ^{o}C and at atmospheric pressure which was recorded as 755 mm Hg. The vapour occupied a volume of 277 cm^3 under these conditions. Calculate the number of moles of the solvent present and its relative molecular mass. Identify which of the two commonly used solvents for removing nail varnish, propanone, CH_3COCH_3 or ethyl ethanoate, $CH_3COOC_2H_5$, the sample actually was. Take *R*, the universal gas constant, to be 8.31 J K^{-1} mol^{-1}.

Q.6. Calculate a value for *R*, the universal gas constant, given that 3.00 mol of helium occupy a volume of 67.2 l at a temperature of 20.0 ^{o}C and a pressure of 108.7 kPa. Why is helium the real gas which is considered to come closest in behaviour to that of the ideal gas?

Q.7. What volume of oxygen gas is required to combine with 7.00 l of sulphur dioxide gas according to the equation

$$SO_2 + {}^1/_2O_2 \rightarrow SO_3$$

Q.8. What is the final volume of the reaction mixture when 2 l of nitrogen gas and 6 l of hydrogen gas react according to the following equation and there is 25% conversion to ammonia?

$$N_2 + 3H_2 \rightarrow 2NH_3$$

Q.9. What is the molecular formula of an aromatic hydrocarbon given that 560 cm^3 of the vaporised hydrocarbon when burned in excess oxygen produces 3.36 l of carbon dioxide gas and 1.68 l of water vapour? What volume of oxygen gas was consumed at constant temperature?

Answers

Q.1. 135 kPa.
Q.2. 209 K or -64 ^{o}C.
Q.3. 1323 cm^3.
Q.4. 0.05 mol.
Q.5. 9.0 x 10^{-3}, 88, $CH_3COOC_2H_5$.
Q.6. 8.31 J K^{-1} mol^{-1}. Helium has the smallest molecules and the least degree of intermolecular attraction.
Q.7. 3.5 l.
Q.8. 7 l.
Q.9. C_6H_6, 4.20 l.

4.5 Calculations Based on the Definition of the Mole

Worked Example 1

How many atoms are there in 280 cm^3 of oxygen gas at s.t.p.?

This question relates the number of particles present to the volume occupied by a sample of a gas. It can be solved by setting up a ratio, using the definition of the mole, to supply a second piece of information relating the number of particles to the volume of the gas.

x molecules → 280 cm^3

6 x 10^{23} molecules → 22 400 cm^3 (molar volume)

$$\frac{x}{6 \times 10^{23}} = \frac{280}{22400}$$

$$x = \frac{280 \times 6 \times 10^{23}}{22400}$$

$$= 7.50 \times 10^{21} \text{ molecules}$$

Since oxygen is diatomic the number of atoms is

$$2 \times 7.50 \times 10^{21}$$

$$= 1.50 \times 10^{22}$$

Note that there has to be consistency between the units of volume of the gas sample and the units for molar volume, usually given as 22.4 l. In the calculation the cm^3 unit was used for the molar volume and the sample volume.

Note also that the number of particles in a sample can only be calculated in this way for gaseous samples.

Worked Example 2

How many moles are there in 13.25 g of anhydrous sodium carbonate (Na_2CO_3)?

This question relates the number of moles present to the mass of a sample. It can be solved by setting up a ratio, using the definition of the mole to supply a second piece of information relating the number of moles to the mass of the substance.

x mol → 13.25 g

1 mol → 106 g (molar mass)

$$\frac{x}{1} = \frac{13.25}{106}$$

$$x = \frac{13.25 \times 1}{106}$$

$$= 0.1250$$

Worked Example 3

What is the density of carbon dioxide gas (i) at s.t.p. and (ii) at room temperature? Molar volume at s.t.p. is 22.4 l and is 24.0 l at room temperature.

$$\text{Density} = \frac{\text{mass}}{\text{volume}}$$

$$= \frac{\text{molar mass}}{\text{molar volume}}$$

$$\text{(i) Density} = \frac{44}{22.4}$$

$$= 1.96 \text{ g l}^{-1} \text{ at s.t.p.}$$

$$\text{(ii) Density} = \frac{44}{24}$$

$$= 1.8 \text{ g l}^{-1} \text{ at room temperature}$$

Worked Example 4

What is the density of air at s.t.p.? Take the composition of air to be 20% oxygen and 80% nitrogen.

$$\text{Density} = \frac{\text{mass}}{\text{volume}}$$

$$= \frac{\text{molar mass}}{\text{molar volume}}$$

One mole of gaseous particles occupies 22.4 l at s.t.p. whether the gas is a mixture or otherwise. The molar mass of a mixture is the weighted average of the contributions from its constituents.

In this case, in a sample of 100 air molecules

	Total mass
80 have mass 28	80 x 28 = 2240
20 have mass 32	20 x 32 = 640
	Total mass 2880

100 molecules of air have mass = 2880

Average mass of an ‘air molecule’ = 28.80

$$\text{Density of air} = \frac{\text{molar mass}}{\text{molar volume}}$$

$$= \frac{28.80}{22.4}$$

$$= 1.29 \text{ g l}^{-1}$$

Worked Example 5

What is the volume occupied at s.t.p. by a sample of ozone gas, O_3, which has a mass of 1.5×10^{-3} g?

This question relates the mass to the volume occupied by a sample of a gas. Again it can be solved by setting up a ratio, using the definition of the mole, to supply a second piece of information relating the mass to the volume of the gas.

$$1.5 \times 10^{-3} \text{ g} \rightarrow x \text{ l}$$

$$48 \text{ g (molar mass)} \rightarrow 22.4 \text{ l (molar volume)}$$

$$\frac{1.5 \times 10^{-4}}{48} = \frac{x}{22.4}$$

$$x = \frac{1.5 \times 10^{-3} \times 22.4}{48}$$

$$= 7.0 \times 10^{-4}$$

The volume is 7.0×10^{-4} l

Worked Example 6

What mass of sodium contains the same number of atoms as 7.1 g of chlorine gas?

$$\text{Number of moles } Cl_2 = \frac{\text{mass (g)}}{\text{molar mass (g mol}^{-1})}$$

$$n = \frac{m}{M_r}$$

$$= \frac{7.1}{71}$$

$$= 0.10$$

Remember, however, that the particles in chlorine gas are diatomic molecules so there are 0.20 mol of chlorine atoms present. Sodium metal consists of single atoms so 0.20 mol of sodium are required.

$$\text{Then } n = \frac{m}{M_r}$$

$$\frac{0.20}{1} = \frac{m}{23}$$

$$m = 0.20 \times 23$$

$$= 4.6 \text{ g}$$

4.6 g of sodium metal contains the same number of atoms as there are chlorine atoms in 7.1 g of chlorine gas.

Worked Example 7

What is the mass in grams of a single oxygen atom?

This question relates the mass to the number of particles present in a sample. Once more, it can be solved by setting up a ratio, using the definition of the mole, to supply a second piece of information relating the mass to the number of particles present.

$$1 \text{ atom of oxygen} \rightarrow x \text{ g}$$

$$6 \times 10^{23} \text{ atoms} \rightarrow 16 \text{ g (molar mass)}$$

$$\frac{1}{6 \times 10^{23}} = \frac{x}{16}$$

$$x = \frac{16 \times 1}{6 \times 10^{23}}$$

$$x = 2.67 \times 10^{-23}$$

The mass is 2.7×10^{-23} g

Worked Example 8

If the recommended daily dietary intake of the element calcium for a normal healthy female in the age group 20 - 40 years is 1000 mg, how many atoms of calcium should be consumed daily?

1000 mg = 1 g

$$x \text{ atoms of calcium} \rightarrow 1 \text{ g}$$

$$6 \times 10^{23} \text{ atoms} \rightarrow 40 \text{ g (molar mass)}$$

$$\frac{x}{6 \times 10^{23}} = \frac{1}{40}$$

$$x = \frac{1 \times 6 \times 10^{23}}{40}$$

$$= 1.5 \times 10^{22}$$

The number of atoms is 1.5×10^{22}

Exercise 4.3

Q.1. Define a mole.

Q.2. What is the volume of a mole of oxygen gas at standard temperature (0 °C) and standard pressure (101 325 Pa)?

Q.3. What is the volume of a mole of any gas at standard temperature (0 °C) and standard pressure (101 325 Pa)?

Q.4. What number of atoms is present in a mole of gold?

Q.5. What number of particles is present in a mole of any substance?

Q.6. What number of molecules is present in a mole of oxygen?

Q.7. What number of atoms is present in a mole of oxygen?

Q.8. What is the molar mass of gold?

Q.9. What is the molar mass of oxygen gas?

Q.10. What is the molar mass of sulphuric acid, H_2SO_4?

Q.11. What is the molar mass of calcium nitrate, $Ca(NO_3)_2$?

Q.12. A packet of fruit gums contains 144 mg of calcium. How many calcium atoms does it contain?

Q.13. What is the density at s.t.p. of laughing gas, N_2O, used by dentists as an anaesthetic?

Q.14. How many moles are there in 3.0 g of magnesium oxide?

Q.15. What is the density of a mixture of 25% NO_2 and 75% N_2O_4 by volume at s.t.p.?

Q.16. Experiments in Australia have shown that a single cow releases 500 l of methane gas into the atmosphere from its digestive system every day. This high level of methane release by cattle and other ruminants presents an important environmental problem leading to a global warming risk. Assuming that the methane released into the atmosphere is measured at normal atmospheric pressure (1.01×10^5 Pa) and at a temperature of 20.0 °C, calculate the volume occupied by 500 l of methane at s.t.p. and hence calculate the number of moles of methane released by a single cow per day.

Q.17. What is the volume occupied by 8.0 g of sulphur dioxide at s.t.p.?

Q.18. What mass of aluminium metal contains the same number of atoms as there are in 31.75 g of crystalline iodine?

Q.19. What is the mass in grams of a single hydrogen molecule?

Q.20. If the recommended daily allowance (RDA) for an adult of vitamin C (ascorbic acid, $C_6H_8O_6$) is 30 mg, how many ascorbic acid molecules should be consumed daily?

Answers

Q.1. The quantity of a substance which contains the same number of particles as there are atoms in 12 g of the carbon-12 isotope.
Q.2. 22.4 l.
Q.3. 22.4 l.
Q.4. 6×10^{23} atoms.
Q.5. 6×10^{23} particles.
Q.6. 6×10^{23} molecules.
Q.7. 1.2×10^{24} atoms.
Q.8. 197 g.
Q.9. 32 g.
Q.10. 98 g.
Q.11 164 g.
Q.12. 2.16×10^{21} atoms.
Q.13. 1.96 g l^{-1}.
Q.14. 0.075 mol.
Q.15. 3.6 g l^{-1}.
Q.16. 466 l; 20.8 mol per day.
Q.17. 2.8 l.
Q.18. 6.750 g.
Q.19. 3×10^{-24} g.
Q.20. 1.0×10^{20} molecules.

4.6 Calculations on Chemical Composition

Percentage Composition

Worked Example 1

What is the percentage composition of (i) ethyne, C_2H_2; (ii) benzene, C_6H_6; (iii) caffeine, $C_8H_{10}N_4O_2$?

(i)

$$\%\text{ carbon} = \frac{\text{mass of carbon} \times 100}{\text{molar mass}}$$

$$= \frac{12 \times 2 \times 100}{26}$$

$$= 92\%$$

$$\%\text{ hydrogen} = \frac{\text{mass of hydrogen} \times 100}{\text{molar mass}}$$

$$= \frac{1 \times 2 \times 100}{26}$$

$$= 8\%$$

(ii)

$$\%\text{ carbon} = \frac{\text{mass of carbon} \times 100}{\text{molar mass}}$$

$$= \frac{12 \times 6 \times 100}{78}$$

$$= 92\%$$

$$\%\text{ hydrogen} = \frac{\text{mass of hydrogen} \times 100}{\text{molar mass}}$$

$$= \frac{1 \times 6 \times 100}{78}$$

$$= 8\%$$

(iii)

$$\%\text{ carbon} = \frac{\text{mass of carbon} \times 100}{\text{molar mass}}$$

$$= \frac{12 \times 8 \times 100}{194}$$

$$= 49\%$$

$$\%\text{ hydrogen} = \frac{\text{mass of hydrogen} \times 100}{\text{molar mass}}$$

$$= \frac{1 \times 10 \times 100}{194}$$

$$= 5\%$$

$$\%\text{ nitrogen} = \frac{\text{mass of nitrogen} \times 100}{\text{molar mass}}$$

$$= \frac{14 \times 4 \times 100}{194}$$

$$= 29\%$$

$$\%\text{ oxygen} = \frac{\text{mass of oxygen} \times 100}{\text{molar mass}}$$

$$= \frac{16 \times 2 \times 100}{194}$$

$$= 16\%$$

Worked Example 2

How many magnesium atoms are there in a chlorophyll-a molecule ($C_{55}H_{72}O_5N_4Mg_x$) if chlorophyll-a contains 2.69% magnesium by mass? Molar mass of chlorophyll-a is (868 + 24x).

$$\%\text{ magnesium} = \frac{\text{mass of magnesium} \times 100}{\text{molar mass}}$$

$$2.69 = \frac{24 \times x \times 100}{(868 + 24x)}$$

$$(2.69 \times 868) + (2.69 \times 24x) = 2400x$$

$$2334.92 + 64.56x = 2400x$$

$$2334.92 = 2335.44\,x$$

$$x = 0.9998$$

$$= 1$$

There is one magnesium atom in the chlorophyll-a molecule.

Exercise 4.4

Q.1. What is the percentage composition of the poison, strychnine, $C_{21}H_{22}N_2O_2$?

Q.2. What is the percentage composition of the analgesic, aspirin, $C_9H_8O_4$?

Q.3. What is the percentage composition of the mineral, olivine, $Mg_3Si_4O_{10}(OH)_2$?

Q.4. How many iron atoms are there in haemoglobin, the respiratory pigment present in red blood corpuscles, given that the molecular mass of the giant haemoglobin molecule is 64232 + 56x and that it contains 0.35% iron by mass?

Q.5. As an industrialist you have the option of purchasing and transporting three different iron ores from different sources to your blast furnace for the extraction of iron metal. Which of the following ores contains the highest percentage of iron by mass? To the nearest integer what is the percentage iron in each ore?

Ore A contains 45% of Fe_2O_3 as its only iron-containing compound.

Ore B contains 35% of Fe_3O_4 as its only iron-containing compound.

Ore C contains 25% Fe_2O_3 and 18% $CuFeS_2$ as its only two iron-containing compounds.

Answers

Q.1. C = 75.4% H = 6.6%
N = 8.4% O = 9.6%.

Q.2. C = 60.0% H = 4.4% O = 35.6%.

Q.3. Mg = 19.0% Si = 29.6%
O = 50.8% H = 0.5%.

Q.4. Four iron atoms.

Q.5. Ore A has the highest percentage of iron. Ore A contains 32% iron, ore B 25% and ore C 23%.

Water of Crystallisation and Degree of Hydration

Worked Example 1

What is the percentage water of crystallisation (i) in sodium carbonate, $Na_2CO_3.10H_2O$ and (ii) in turquoise, the semiprecious birthstone, which has the formula $CuAl_6(PO_4)_4(OH)_8.4H_2O$?

$$\text{(i) \% water of crystallisation} = \frac{\text{mass of water x 100}}{\text{molar mass}}$$

$$= \frac{18 \text{ x } 10 \text{ x } 100}{286}$$

$$= 63\%$$

Note that it is the molar mass of the hydrated sodium carbonate and not the molar mass of anhydrous sodium carbonate which must be used in the calculation.

$$\text{(ii) \% water of crystallisation} = \frac{\text{mass of water x 100}}{\text{molar mass}}$$

$$= \frac{18 \text{ x } 4 \text{ x } 100}{813.5}$$

$$= 8.9\%$$

Worked Example 2

What is (i) the percentage water of crystallisation and (ii) the average degree of hydration, x, of a sample of sodium carbonate, $Na_2CO_3.xH_2O$, which had partially effloresced, if the mass of a 5.00 g sample is reduced to a mass of 2.05 g upon being heated strongly with a Bunsen burner?

(i) % water of crystallisation

$$= \frac{\text{mass of water in sample x 100}}{\text{mass of sample}}$$

$$= \frac{(5.00 - 2.05) \text{ x } 100}{5.00}$$

$$= 59\%$$

(ii)

$$\frac{\text{mass of water in sample}}{\text{mass of Na}_2\text{CO}_3\text{ in sample}} = \frac{\text{mass of water in 1 mol of sample}}{\text{mass of Na}_2\text{CO}_3\text{ in 1 mol of sample}}$$

$$\frac{2.95}{2.05} = \frac{18x}{106}$$

$$x = \frac{2.95 \times 106}{2.05 \times 18}$$

$$= 8.5$$

Note that the degree of hydration of a crystalline sample is nearly always a whole number. However, if the sample has lost water of crystallisation, the molecules on the surface of the sample could have a lower degree of hydration than those in the bulk of the sample and the average degree of hydration need not be a whole number.

Exercise 4.5

Q.1. A sample of Epsom salts, a laxative, $MgSO_4.xH_2O$ was analysed by a student to determine its percentage water of crystallisation and the degree of hydration, x. The 7.00 g sample was heated strongly in a crucible until a constant mass of 3.41 g was recorded. Calculate the percentage water of crystallisation and the value of x in the sample.

Q.2. Plaster of Paris, $CaSO_4.xH_2O$, is used to make first casts in sculpture, and in medicine to make casts for broken bones. It is obtained by heating gypsum, $CaSO_4.2H_2O$ to 120-130 ^oC. Calculate the degree of hydration of plaster of Paris given that 400 g of gypsum, $CaSO_4.2H_2O$, upon being heated, yielded 337.21 g of plaster of Paris, $CaSO_4.xH_2O$.

Answers

Q.1. 51.29%. x = 7.

Q.2. x = ½.

Empirical Formula and Percentage Composition

Worked Example 1

What is the empirical formula of nicotine, given that its percentage composition by mass is 74.0% carbon, 8.7% hydrogen and 17.3% nitrogen?

In a sample of 100 g of nicotine there are 74 g of carbon atoms, 8.7 g of hydrogen atoms and 17.3 g of nitrogen atoms.

Element	**Mass (g)**	**No. of moles ($n = \frac{m}{A_r}$)**	**Simplest ratio**
C	74.0	$\frac{74.0}{12} = 6.167$	$\frac{6.167}{1.236} = 4.99$ $= 5$
H	8.7	$\frac{8.7}{1} = 8.7$	$\frac{8.7}{1.236} = 7.04$ $= 7$
N	17.3	$\frac{17.3}{14} = 1.236$	$\frac{1.236}{1.236} = 1$

Since the ratio of the atoms in any sample of the compound is the same as the ratio of the atoms in a single molecule, the empirical formula of nicotine is therefore C_5H_7N. The relative molecular mass of a compound with this formula is 81. The relative molecular mass of nicotine is in fact 162 so the molecular formula of nicotine is $C_{10}H_{14}N_2$.

Exercise 4.6

Q.1. Mustard gas was the first substance to be used in chemical warfare. It was released by the Germans in World War I during the First Battle of Ypres, 1914. What is the empirical formula of mustard gas given its percentage composition: 39.3% carbon, 4.4% hydrogen, 38.8% chlorine and 17.5% sulphur?

Q.2. What is the degree of hydration of gypsum given that it contains 23.3% calcium, 55.8% sulphate ion and 20.9% water of crystallisation by mass and that 172 g of gypsum contains one mole of calcium sulphate?

Answers

Q.1. $C_6H_8Cl_2S$.
Q.2. $CaSO_4.2H_2O$.

Empirical Formula and Combining Masses

Worked Example 1

Black antimony sulphide has been used as a mascara pigment since at least Egyptian times. In fact the symbol for the element antimony, Sb, comes from the Latin *stibium* meaning ‘mark’. What is the empirical formula of antimony sulphide if 10.00 g of antimony combines with sulphur to form 13.93 g of antimony sulphide?

10.00 g of antimony combined with 3.93 g of sulphur. Calculate the ratio of moles in which they combine.

Element	**Mass (g)**	**No. of moles ($n = \frac{m}{A_r}$)**	**Simplest ratio**	
Sb	10.0	$\frac{10.0}{122}$ = 0.082	$\frac{0.082}{0.082}$ = 1	2
S	3.9	$\frac{3.93}{32}$ = 0.123	$\frac{0.123}{0.082}$ = 1.5	3

If a whole number ratio is not obtained upon dividing the actual number of moles by the smallest number of moles, the figures can usually be scaled up to a set of whole numbers. Since the ratio of the atoms in any sample of the compound is the same as the ratio of the atoms in a single molecule, the empirical formula of antimony sulphide is therefore Sb_2S_3.

Exercise 4.7

Q.1. What is the empirical formula of gallium arsenide, used as a light absorber in solar panels, if a 2 g sample of gallium combined with arsenic to produce 4.14 g of gallium arsenide?

Q.2. Silver iodide is used to seed clouds to obtain artificial rainfall. If 2.50 g of silver combined with 2.94 g of iodine to produce silver iodide what is its empirical formula?

Q.3. In an experiment, 5.00 g of a brick red oxide of copper yields 4.44 g of copper metal upon reduction. What is the empirical formula of the compound?

Answers

Q.1. GaAs. Q.2. AgI. Q.3. Cu_2O.

4.7 Equations and Reacting Masses p- Stoichiometry

The following balanced equation represents a general chemical reaction where exactly n_1 moles of chemical A react completely with n_2 moles of chemical B to produce n_3 moles of chemical C and n_4 moles of chemical D.

$$n_1\text{A} + n_2\text{B} \rightarrow n_3\text{C} + n_4\text{D}$$

The ratio of the numbers of moles of any two chemicals in such a balanced equation is fixed and therefore it is possible, given the number of moles of one reactant used or product made, to calculate the number of moles of any other one of the reactants used or products made by simply referring to the balanced equation.

It is important to remember that in these calculations the balanced equation gives the ratio of moles and not the ratio of masses. If information about reacting masses is required, and it often is, such calculations can be done in three stages.

Stage 1

Data about one reactant or product, A, must be given in moles or converted to moles using the interrelationships shown on p. 52.

Stage 2

The balanced equation for the reaction is consulted to relate the number of moles of the first reactant (or product), A, to the number of moles of another reactant (or product), B.

Stage 3

Data on B is converted again using the interrelationships shown on p. 52 to give the required answer. This can be summarised as follows.

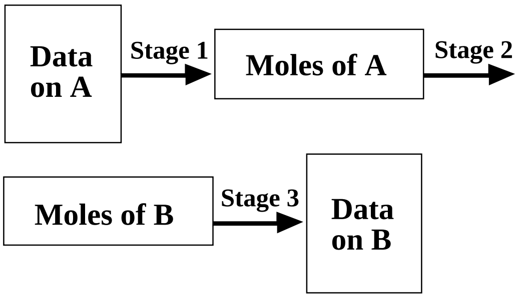


Fig. 4.2 *Stoichiometric calculations*

Worked Example 1

(i) What mass of sodium chromate is required to react completely with 16.55 g of lead(II) nitrate according to the chemical equation given below?

(ii) What mass of lead(II) chromate, the artists' pigment chrome yellow, is produced in the process?

(iii) What mass of sodium nitrate by-product is obtained?

$$Pb(NO_3)_2 + Na_2CrO_4 \rightarrow PbCrO_4 + 2NaNO_3$$

(i) Stage 1

$$n = \frac{m}{M_r}$$

$$= \frac{16.55}{331}$$

$$= 0.05 \text{ mol } Pb(NO_3)_2$$

Stage 2

From balanced equation

$Pb(NO_3)_2$: Na_2CrO_4
1 mol : 1 mol
⇒ 0.05 mol : 0.05 mol

Stage 3

$$n = \frac{m}{M_r}$$

$$m = 0.05 \times 162$$

$$= 8.1 \text{ g}$$

8.1 g of Na_2CrO_4 needed for reaction with 16.55 g of $Pb(NO_3)_2$

(ii) Stage 1

$$n = \frac{m}{M_r}$$

$$= \frac{16.55}{331}$$

$$= 0.05 \text{ mol } Pb(NO_3)_2$$

Stage 2

From balanced equation

$Pb(NO_3)_2$: $PbCrO_4$
1 mol : 1 mol
⇒ 0.05 mol : 0.05 mol

Stage 3

$$n = \frac{m}{M_r}$$

$$m = 0.05 \times 323$$

$$= 16.15 \text{ g}$$

16.15 g of $PbCrO_4$, chrome yellow, produced in the reaction of 16.55 g of $Pb(NO_3)_2$

(iii) Stage 1

$$n = \frac{m}{M_r}$$

$$= \frac{16.55}{331}$$

$$= 0.05 \text{ mol } Pb(NO_3)_2$$

Stage 2

From balanced equation

$Pb(NO_3)_2$: $NaNO_3$
1 mol : 2 mol
⇒ 0.05 mol : 0.1 mol

Stage 3

$$n = \frac{m}{M_r}$$

$$m = 0.1 \times 85$$

$$= 8.5\text{ g}$$

8.5 g of $NaNO_3$ produced in the reaction of 16.55 g of $Pb(NO_3)_2$

Worked Example 2

When copper(II) nitrate is heated strongly it decomposes to form copper(II) oxide, nitrogen(IV) oxide and oxygen gas.

(i) Write formulae for each reactant and product and hence write a balanced equation for the reaction.

(ii) What mass of copper(II) nitrate must be decomposed by heat to produce 200 g of copper(II) oxide by this reaction?

(iii) What is the total volume of gas produced, measured at s.t.p.? What proportion of the gas by volume is oxygen?

(i) Formulae

Copper(II) nitrate	$Cu(NO_3)_2$
Copper(II) oxide	CuO
Nitrogen(IV) oxide	NO_2
Oxygen gas	O_2

$$2Cu(NO_3)_2 \rightarrow 2CuO + 4NO_2 + O_2$$

(ii) Stage 1

$$n = \frac{m}{M_r}$$

$$= \frac{200}{79.5}$$

$$= 2.52\text{ mol CuO}$$

Stage 2

From balanced equation

$Cu(NO_3)_2$: CuO
1 mol : 1 mol
⇒ 2.52 mol : 2.52 mol

Stage 3

$$n = \frac{m}{M_r}$$

$$m = 2.52 \times 187.5$$

$$= 472.5\text{ g}$$

473 g of $Cu(NO_3)_2$ needed to produce 200 g of CuO

(iii) Stage 1

$$n = \frac{m}{M_r}$$

$$= \frac{200}{79.5}$$

$$= 2.52\text{ mol CuO}$$

Stage 2

From balanced equation

$Cu(NO_3)_2$: CuO : NO_2 : O_2
2 mol : 2 mol : 4 mol : 1 mol

2.52 mol : 2.52 mol : 5.04 mol : 1.26 mol

When 2.52 mol of $Cu(NO_3)_2$ reacts, 5.04 mol of NO_2 and 1.26 mol of O_2 are produced, giving a total of 6.30 mol of gas.

Stage 3

$$\text{No. of moles} = \frac{\text{volume (l)}}{\text{molar volume (l)}}$$

$$\text{Volume} = 6.30 \times 22.4$$
$$= 141 \text{ l}$$

Oxygen gas constitutes one fifth of this volume according to Avogadro's law since it contributes one fifth of the total number of moles of gas present.

Worked Example 3

In the anaerobic respiration of glucose in yeast the products are ethanol and carbon dioxide. This reaction takes place when yeast uses glucose in fruit juices or malt to produce ethanol in alcohol manufacture.

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$$

(i) What mass of ethanol was produced in the fermentation of glucose if 120 l of carbon dioxide gas were collected at room temperature? Take molar volume at room temperature to be 24 l.

(ii) What volume of pure ethanol, density 0.785 g cm^{-3}, was produced?

(i) Stage 1

$$\text{No. of moles } CO_2 = \frac{\text{volume (l)}}{\text{molar volume (l)}}$$

$$= \frac{120}{24}$$

$$= 5.0$$

Stage 2

From the balanced equation

C_2H_5OH : CO_2
1 mol : 1 mol
5.0 mol : 5.0 mol

Stage 3

$$n = \frac{m}{M_r}$$

$$m = 5.0 \times 46$$

$= 230$ g of ethanol produced

(ii)

$$\text{Density} = \frac{\text{mass}}{\text{volume}}$$

$$\text{Volume} = \frac{\text{mass}}{\text{density}}$$

$$= \frac{230}{0.785}$$

$= 293\ cm^3$ ethanol

Exercise 4.8

Q.1. What volume of oxygen gas at s.t.p. is required to react with 100 g of heptane according to the following equation?

$$C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O$$

Q.2. Hydrochloric acid added to sodium hydrogencarbonate produces sodium chloride, water and carbon dioxide. Write a balanced equation for the reaction. If exactly one tonne of sodium hydrogencarbonate is sufficient to neutralise the acid, what mass of hydrogen chloride was present? What volume of carbon dioxide at s.t.p. was produced?

Q.3. Calcium oxide and carbon dioxide are produced by roasting calcium carbonate. Write a balanced equation for the reaction. What mass of calcium carbonate upon roasting will give 3.24 l of carbon dioxide gas at room temperature? What mass of calcium oxide is produced in the process? Molar volume at room temperature is 24 l.

Q.4. Trinitroglycerine is a high explosive which, when detonated, undergoes the following reaction.

$$4C_3H_5N_3O_9 \rightarrow 6N_2 + 12CO_2 + 10H_2O + O_2$$

What mass of trinitroglycerine is required to produce, upon detonation, 500 l of nitrogen gas measured at s.t.p.? What mass of water is produced in the same reaction?

Answers

Q.1. 246.4 l oxygen gas.

Q.2. $HCl + NaHCO_3 \rightarrow NaCl + CO_2 + H_2O$
435 kg HCl. 2.7 x 10^5 l.

Q.3. $CaCO_3 \rightarrow CaO + CO_2$
13.5 g; 7.56 g.

Q.4. 3.38 kg. 670 g.

4.8 Introduction to Volumetric Analysis

Chemicals often react in solution, i.e. both reactants and products are dissolved in a solvent which does not itself necessarily participate in the reaction but acts as the medium in which the reactants move, collide and react. The concentration of the solution can determine the speed of the reaction - in very dilute solutions there can be an appreciable delay before reacting molecules with sufficient energy for reaction meet. Most collisions will be between a particle of one of the reactants and a solvent molecule. If the activation energy for the reaction is low, the rate of reaction can still be effectively instantaneous, even in quite dilute solutions. This is the case in the reaction between acid and base in aqueous solution. Whenever a collision between an acid and a base occurs in dilute aqueous solution there will be a high probability of its being successful in leading to a reaction because the activation energy is low and, consequently, the reaction of acid and base in dilute solution is considered instantaneous. Some redox reactions and reactions where complexes are formed (e.g. the reaction between EDTA and calcium or magnesium ions) are also effectively instantaneous in aqueous solution.

Any of these reactions can be used in volumetric analysis to determine the concentration of a solution by reacting a known volume of it with a known volume of a standard solution. A standard solution is one whose concentration is known. This type of analysis is called a titration and is carried out by adding one solution to a known volume of the other until the reaction is just complete, i.e. until the end point is reached. An indicator of some kind can be used to show by a colour change or otherwise when the end point is reached.

In acid-base reactions, for example, a chemical indicator which changes colour according to the pH of the solution can be used to detect the end point because there is a sharp change in pH in an acid-base neutralisation just at the end point. Alternatively, a pH meter could be used to detect the sharp change in the pH at end point in an acid-base titration. In other titrations, a chemical which will only react at the end point forming a distinctly coloured product, can act as an indicator. For example, in redox reactions involving iodine, starch is used as an indicator. Iodine combines reversibly with starch to form a blue black complex. Starch is added as the end point approaches and the intense colour is observed. At the end point, when the availability of the iodine is reduced to zero, the colour of the starch-iodine complex suddenly disappears.

Calculation gives the concentration of the ‘unknown’ , i.e. of the solution whose concentration was unknown.

We know from the stoichiometry of the balanced equation for a reaction that

$$n_1\text{A} + n_2\text{B} \rightarrow n_3\text{C} + n_4\text{D}$$

i.e. that n_1 (mol) of A react with n_2 (mol) of B. In solution the number of moles of a substance present is given by the following relationship.

Number of moles = molarity (mol l^{-1}) x volume (l).
Therefore, n_1 = molarity$_1$ (mol l^{-1}) x volume$_1$ (l)
and n_2 = molarity$_2$ (mol l^{-1}) x volume$_2$ (l).

So

$$\frac{n_1}{n_2} = \frac{\text{molarity}_1\ (\text{mol l}^{-1}) \times \text{volume}_1\ (\text{l})}{\text{molarity}_2\ (\text{mol l}^{-1}) \times \text{volume}_2\ (\text{l})}$$

$$= \frac{\text{molarity}_1\ (\text{mol l}^{-1}) \times \text{volume}_1\ (\text{cm}^3) \times 10^{-3}}{\text{molarity}_2\ (\text{mol l}^{-1}) \times \text{volume}_2\ (\text{cm}^3) \times 10^{-3}}$$

$$= \frac{\text{molarity}_1\ (\text{mol l}^{-1}) \times \text{volume}_1\ (\text{cm}^3)}{\text{molarity}_2\ (\text{mol l}^{-1}) \times \text{volume}_2\ (\text{cm}^3)}$$

$$= \frac{M_1V_1}{M_2V_2}$$

i.e.

$$\frac{n_1}{n_2} = \frac{M_1V_1}{M_2V_2}$$

$$\Rightarrow \quad \frac{M_1V_1}{n_1} = \frac{M_2V_2}{n_2}$$

It is not appropriate to give titrimetric calculations in isolation from the theory of acid-base reactions, redox reactions and complexometric reactions. Therefore, the following examples deal only with a few basic manipulations of data common to all work with chemical solutions and do not attempt to cover calculations in the topic of volumetric analysis in a comprehensive way.

Worked Example 1

How many moles of HCl are contained in 50 cm^3 of 0.2 M HCl?

$$\text{No. of moles} = \frac{\text{molarity (mol l}^{-1}) \times \text{volume (cm}^3)}{1000}$$

$$= \frac{0.2 \times 50}{1000}$$

$$= 0.01$$

Worked Example 2

What is the concentration in g l^{-1} of ammonium chloride in a 0.01 M solution?

Concentration (g l^{-1})

$$= \text{molarity (mol l}^{-1}) \times \text{molar mass (g mol}^{-1})$$

$$= 0.01 \times 53.5$$

$$= 0.535 \text{ g l}^{-1}$$

Worked Example 3

What mass of anhydrous sodium carbonate is required to prepare 250 cm^3 of a 0.05 M solution?

$$\text{No. of moles} = \frac{\text{molarity (mol l}^{-1}) \times \text{volume (cm}^3)}{1000}$$

$$= \frac{0.05 \times 250}{1000}$$

$$= 0.0125$$

$$n = \frac{m}{M_r}$$

$$m = 0.0125 \times 106$$

$$= 1.325 \text{ g}$$

Worked Example 4

What is the combined concentration of calcium and magnesium ions, in mol l^{-1}, in a 100 cm^3 sample of hard water if a volume of 22.25 cm^3 of 0.01 M EDTA (H_2) is required to react with the calcium and magnesium ions (X^{2+}) according to the balanced equation

$$H_2Y^{2-} + X^{2+} \rightarrow YX^{2-} + 2H^+$$

From the balanced equation the EDTA reacts in the ratio 1:1 with the metal ions.

$$\frac{M_1V_1}{n_1} = \frac{M_2V_2}{n_2}$$

$$\frac{0.01 \times 22.25}{1} = \frac{M_2 \times 100}{1}$$

$$M_2 = \frac{0.01 \times 22.25 \times 1}{100 \times 1}$$

$$= 2.2 \times 10^{-3} \text{ mol } l^{-1}$$

Ca^{2+} and Mg^{2+}

Exercise 4.9

Q.1. How many moles of copper sulphate are contained in 20 cm^3 of 0.50 M $CuSO_4$ solution?

Q.2. How many moles of sodium ions are contained in 100 cm^3 of 1.5 M Na_2CO_3 solution?

Q.3. How many moles of iodate ion are contained in 2 l of 0.1 M KIO_3 solution?

Q.4. What is the concentration, in g l^{-1} of potassium hydroxide, of a 0.25 M solution of KOH?

Q.5. What is the concentration, in g l^{-1} of potassium iodide, of a 0.005 M solution of KI?

Q.6. What is the concentration in g l^{-1} of (i) sodium ion and (ii) chloride ion, in a 2 M solution of NaCl?

Q.7. What mass of sodium ethanedioate, $Na_2C_2O_4$, is required to prepare 500 cm^3 of a 0.05 M solution?

Q.8. How many grams of silver nitrate, $AgNO_3$, are required to prepare 250 cm^3 of a 0.1 M solution?

Q.9. How many grams of glucose, $C_6H_{12}O_6$, must be dissolved in water to prepare 2 l of a 0.25 M solution?

Q.10. A tomato food contains, among other salts, 49 g of potassium oxide, K_2O, in 500 cm^3 of aqueous solution. What is the molarity of the solution in terms of potassium ion?

Q.11. 'Dioralyte' is a commercial preparation to treat the loss of fluids and salts which occurs as the result of diarrhoea. A sachet of Dioralyte contains, among other salts, 0.3 g of potassium chloride and 0.47 g of sodium chloride. If, according to the instructions on the packet, the sachet is dissolved in 200 cm^3 of solution, what is the molarity of the solution in terms of (i) potassium ion, (ii) sodium ion, and (iii) chloride ion?

Q.12. A solution of sodium chloride was titrated with a solution of silver nitrate until the end point was reached. Calculate the concentration of the silver solution in (i) mol l^{-1} of $AgNO_3$, and (ii) in g l^{-1} of $AgNO_3$, if a volume of 25 cm^3 of the 0.10 M sodium chloride solution required 23.3 cm^3 of the silver nitrate solution according to the balanced equation

$$AgNO_3 + NaCl \rightarrow AgCl(\downarrow) + NaNO_3$$

Q.13. In an experiment to determine the concentration of a vinegar, a sample of the vinegar was diluted by a factor of ten and titrated in 25 cm^3 portions with 0.10 M sodium hydroxide solution. The following reaction occurs.

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

If the average titre was 27.2 cm^3, what was the concentration of the original vinegar solution in (i) mol l^{-1}, (ii) g l^{-1}, and (iii) % w/v, of ethanoic acid?

Q.14. A window cleaning solution contains ammonia. It reacted with sulphuric acid in a titration thus:

$$2NH_4OH + H_2SO_4 \rightarrow (NH_4)_2SO_4 + 2H_2O$$

The solution was titrated in 25 cm^3 portions with 0.05 M sulphuric acid. For neutralisation the average titre was 12.4 cm^3. What mass of ammonia, NH_3, is dissolved in 250 cm^3 of this cleaning solution?

Answers

Q.1. 0.01 mol.
Q.2. 0.30 mol Na^+.
Q.3. 0.2 mol.
Q.4. 14 g l^{-1}.
Q.5. 0.8 g l^{-1}.
Q.6. (i) 46 g l^{-1} Na^+. (ii) 71.0 g l^{-1} Cl^-.
Q.7. 3.4 g.
Q.8. 4 g.
Q.9. 90 g.
Q.10. 2.1 mol l^{-1} K^+.
Q.11. (i) 0.02 mol l^{-1} K^+.
(ii) 0.04 mol l^{-1} Na^+.
(iii) 0.06 mol l^{-1} Cl^-.
Q.12. (i) 0.11 mol l^{-1}. (ii) 18 g l^{-1}.
Q.13. (i) 1.1 mol l^{-1}. (ii) 66 g l^{-1}. (iii) 6.6% w/v.
Q.14. 0.2 g NH_3 per 250 cm^3.

4.9 Limiting Reactant and Percentage Yield

Limiting Reactant

In a chemical reaction, the reactants are not always mixed in stoichiometric quantities, i.e. there may be an excess of one reactant. The reactant which is not in excess and which is completely used up in the reaction is called the limiting reactant. The quantities of products obtained are related to the number of moles of the limiting reactant. To determine which reactant is the limiting one, the balanced equation for the reaction and the quantities of the reactants must be compared.

Worked Example 1

Ammonium chloride and calcium hydroxide react together to form ammonia according to the balanced equation

$$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + CaCl_2 + 2H_2O$$

If 5.4 g of ammonium chloride are mixed with 6.9 g of calcium hydroxide, determine which is the limiting reactant and calculate (i) how many moles and (ii) what mass of ammonia gas are expected to be produced.

$$n = \frac{m}{M_r}$$

For NH_4Cl $\quad n = \frac{5.4}{53.5}$

$$= 0.10 \text{ mol}$$

For $Ca(OH)_2$ $n = \frac{6.9}{74}$

$$= 0.09 \text{ mol}$$

Stoichiometric ratio of ammonium chloride to calcium hydroxide from balanced equation:

$$\begin{array}{ccc} NH_4Cl & : & Ca(OH)_2 \\ 2 & : & 1 \end{array}$$

So 0.10 mol of NH_4Cl would require 0.05 mol of $Ca(OH)_2$ for complete reaction. There is more than enough $Ca(OH)_2$ for complete reaction. $Ca(OH)_2$ is in excess and NH_4Cl is limiting.

Looking at the situation another way, 0.09 mol of $Ca(OH)_2$ would require 0.18 mol of NH_4Cl for complete reaction. There is only 0.1 mol of NH_4Cl available, so clearly this is the limiting reactant.

(i) Since only 0.1 mol of NH_4Cl and 0.05 mol of $Ca(OH)_2$ react, from the balanced equation 0.1 mol of ammonia is produced.

(ii) Since

$$n = \frac{m}{M_r}$$

$$m = 0.1 \times 17$$

$$= 1.7 \text{ g}$$

The mass of ammonia obtained is 1.7 g.

Worked Example 2

In a reaction 20.0 cm^3 of propan-2-ol was oxidised to propanone in a solution containing 30.0 g sodium dichromate, $Na_2Cr_2O_7.2H_2O$, dissolved in excess sulphuric acid, according to the balanced equation

$$3CH_3CH(OH)CH_3 + Na_2Cr_2O_7 + 4H_2SO_4$$
$$\rightarrow 3CH_3COCH_3 + Cr_2(SO_4)_3 + Na_2SO_4 + 7H_2O$$

Determine which reactant is in excess and calculate how many moles of propanone could be expected to be formed in this reaction. Take the density of propan-2-ol to be 0.786 g cm^{-3}.

$$\text{Density} = \frac{\text{mass}}{\text{volume}}$$

$$\text{Mass} = \text{density} \times \text{volume}$$

$$\text{Mass of propan-2-ol} = 0.786 \times 20.0$$

$$= 15.72 \text{ g}$$

$$n = \frac{m}{M_r}$$

$$\text{For propan-2-ol } n = \frac{15.72}{60}$$

$$= 0.262 \text{ mol}$$

$$\text{For sodium dichromate } n = \frac{30.0}{298}$$

$$= 0.101 \text{ mol}$$

Stoichiometric ratio of propan-2-ol to sodium dichromate from balanced equation is

$CH_3CH(OH)CH_3$: $Na_2Cr_2O_7$
3 : 1

So 0.262 mol of propan-2-ol would require only 0.087 mol of $Na_2Cr_2O_7$ (or of $Na_2Cr_2O_7.2H_2O$) for complete reaction. There is more than enough $Na_2Cr_2O_7$ for complete reaction. Therefore, $Na_2Cr_2O_7.2H_2O$ is in excess and propan-2-ol is limiting.

Looking at the situation another way, 0.101 mol of $Na_2Cr_2O_7.2H_2O$ would require 0.303 mol of propan-2-ol for complete reaction. There are only 0.262 mol of propan-2-ol available so clearly this is the limiting reactant and the $Na_2Cr_2O_7.2H_2O$ is in excess.

Since only 0.262 mol of propan-2-ol and 0.087 mol of $Na_2Cr_2O_7.2H_2O$ react, from the balanced equation 0.262 mol of propanone are expected to be produced.

Exercise 4.10

Q.1. In the reaction

$$2Al + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2$$

33.75 g of aluminium metal is dissolved in 500 cm^3 of 3M sulphuric acid. Which reactant is limiting? Calculate how many moles of aluminium sulphate could be produced and what volume of hydrogen gas, measured at s.t.p., could be obtained in the reaction.

Q.2. In the extraction of zinc metal from its ore, zinc blende (ZnS), 50 tonnes of the ore were roasted in air to produce zinc oxide which was then reduced using 5.0 tonnes of coke. The reactions are as follows.

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

and $ZnO + C \rightarrow Zn + CO$

Assuming that the first reaction goes to completion, what is the maximum yield of zinc metal which can be expected?

Answers

Q.1. Sulphuric acid. 0.5 mol; 33.6 l.

Q.2. 27 tonne.

Percentage Yield

In a chemical reaction not all the reactants which could react necessarily do so, and not all the product formed is necessarily recovered at the end of the reaction. For either or both of these reasons the yield of product obtained in a reaction might be less than that expected. The reactant might not react fully because the process was an equilibrium process, a high enough temperature was not reached, sufficient time for complete reaction was not allowed or sufficient reagent with which the reactant could react was not present, etc. Also, the product might be lost, despite great care to recover as much as possible, e.g. on the filter paper in a filtration step, in the condenser in a distillation process, by evaporation if it is volatile, in the reaction mixture if it has to be extracted into a solvent, by decomposition if it is unstable, etc.

Worked Example 1

In a reaction 23.0 g of ethanol was oxidised to ethanoic acid using an excess of oxidising reagent according to the equation given. After purification the mass of ethanoic acid obtained was 23.2 g. Calculate the percentage yield of ethanoic acid.

$$3C_2H_5OH + 2Na_2Cr_2O_7 + 8H_2SO_4$$
$$\rightarrow 3CH_3COOH + 2Cr_2(SO_4)_3 + 2Na_2SO_4 + 11H_2O$$

$$\text{Percentage yield} = \frac{\text{actual yield in grams x 100}}{\text{theoretical yield in grams}}$$

$$= \frac{\text{actual yield in moles x 100}}{\text{theoretical yield in moles}}$$

The theoretical yield is obtained with reference to the balanced equation. In theory every mole of ethanol produces one mole of ethanoic acid.

$$n = \frac{m}{M_r}$$

$$\text{For ethanol used} \quad n = \frac{23.0}{46}$$

$$= 0.50 \text{ mol}$$

⇒ quantity of ethanoic acid expected in theory

$$= 0.50 \text{ mol}$$

For ethanoic acid obtained

$$n = \frac{23.2}{60}$$

$$= 0.387 \text{ mol}$$

$$\text{Percentage yield} = \frac{\text{actual yield in moles x 100}}{\text{theoretical yield in moles}}$$

$$= \frac{0.387}{0.50}$$

$$= 77\%$$

Exercise 4.11

Q.1. A reaction takes place between hydrazine and butanone as follows.

$$C_2H_5COCH_3 + NH_2NH_2 \xrightarrow{H^+}$$
$$C_2H_5C(NNH_2)CH_3 + H_2O$$

Calculate which reactant is limiting and hence calculate the percentage yield of butanone hydrazone if 20 cm^3 of butanone and 8.0 cm^3 of anhydrous hydrazine are allowed react in the presence of an acid catalyst and 12.9 g of the product is recovered. The density of butanone is 0.803 g l^{-1} and the density of anhydrous hydrazine is 1.011 g l^{-1}.

Q.2. 25 cm^3 of a solution of 0.10 M sodium thiosulphate and 100 cm^3 of a solution of 0.10 M hydrochloric acid were mixed. The following reaction occurred.

$$Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + S(\downarrow) + SO_2(\uparrow) + H_2O$$

The sulphur precipitated was filtered off after ten minutes, dried and weighed. A mass of 0.042 g was recorded. Determine which reactant is in excess. What is the percentage yield of sulphur? Suggest two ways to account for the low percentage yield.

Q.3. In a reaction 20.0 cm^3 of ethanol, density 0.785 g cm^{-3}, was oxidised to ethanal using 28 g of sodium dichromate oxidising reagent ($Na_2Cr_2O_7.2H_2O$) according to the equation given. After purification, the mass of ethanal obtained was 8.2 g. Show which reactant is in excess. Calculate the percentage yield of ethanal.

$$3C_2H_5OH + Na_2Cr_2O_7 + 4H_2SO_4 \rightarrow 3CH_3CHO + Cr_2(SO_4)_3 + Na_2SO_4 + 7H_2O$$

Answers

Q.1. The butanone is limiting; 67%.

Q.2. The hydrochloric acid is in excess; 53%. The reaction may not have gone to completion after ten minutes and the colloidal sulphur is very fine and some may have passed through the filter paper.

Q.3. The ethanol is in excess; 66%.

This completes the introduction to calculations in chemistry. The student will also be expected to solve problems in specific areas, e.g. thermochemistry, chemical equilibrium, pH, electrochemistry, etc. These are best practised together with the appropriate theory rather than in isolation from it.

APPENDIX

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MODULE 6

Alcohols, Aldehydes, Ketones and Carboxylic Acids

CONTENTS

Chapter 1 **Alcohols**

Chapter 2 **Aldehydes and Ketones**

Chapter 3 **Carboxylic Acids**

CHAPTER 1

ALCOHOLS

1.1 Introduction to Chemical Composition

Monohydric alcohols are compounds of the general formula ROH, where R is an alkyl, substituted alkyl, or aryl group. All alcohols have a hydroxyl (-OH) group and this group mainly dictates the chemical and physical characteristics of alcohols. Thus, the hydroxyl group is termed the functional group in alcohols. The R group attached to the hydroxyl group may be an alkyl group which is open-chain or ring in nature. It may contain multiple bonds, a halogen or indeed an aromatic group, Fig. 1.1. When a hydroxyl group is attached directly to a benzene ring or a derivative of benzene a phenol is formed, Fig. 1.1.

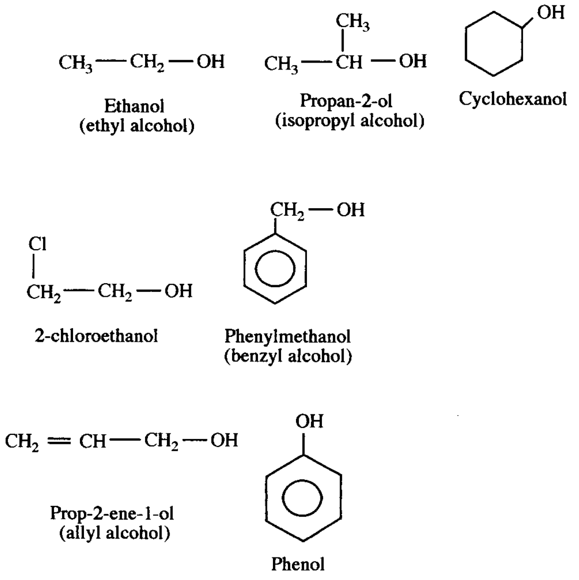


Fig. 1.1

Origin of the Name Alcohol

The word alcohol comes from the Arabic *al-kuhul*, which refers to a substance called kohl, a fine powder of antimony used in eye make-up. Any fine powder became known as alcohol but later, alchemists applied the name alcohol to any essence obtained as a result of distillation.

1.2 Classification of Alcohols

It is worthwhile at this point to classify alcohols as primary (1°), secondary (2°), or tertiary (3°). A primary alcohol has two hydrogens on the hydroxyl-bearing carbon, a secondary alcohol has only one hydrogen on the hydroxyl-bearing carbon, and a tertiary alcohol has no hydrogen on the hydroxyl-bearing carbon, Fig. 1.2.

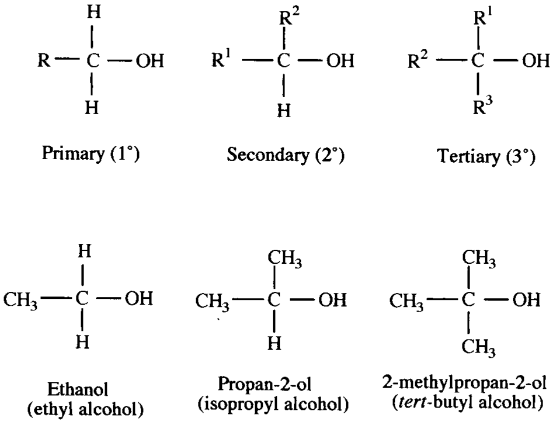
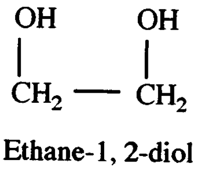


Fig. 1.2

The chemical behaviour of primary, secondary and tertiary alcohols shows some variation. This is usually in the mechanism of a reaction type or in a reaction rate. However, these differences are consistent with, and can be explained by, consideration of their structural differences. These differences will be referred to and explained as they arise in the material treated below.

Diols and Triols

Diols (dihydric alcohols) are alcohols which contain two -OH groups attached to the carbon chain. The simplest dihydric alcohol is ethane-1,2-diol (ethylene glycol), Fig. 1.3.

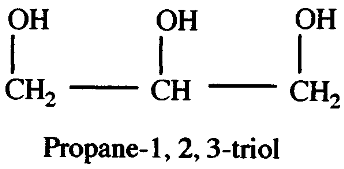


$\overset{OH}{CH_2} - \overset{OH}{CH_2}$

Fig. 1.3

It is used commercially as a permanent antifreeze in car engine cooling systems. It is miscible with water in all proportions and a 50% solution of it freezes at -34 ^{o}C. It is a syrupy liquid which has a sweet taste but is very toxic. [The simplest theoretical diol is $CH_2(OH)_2$. However, it is unstable and forms $CH_2O + H_2O$.] (See also section 1.6.)

Triols (trihydric alcohols) have three -OH groups on the carbon chain. The simplest of these is propane-1,2,3-triol (glycerol or glycerine), Fig. 1.4.



$\overset{OH}{CH_2} - \overset{OH}{CH} - \overset{OH}{CH_2}$

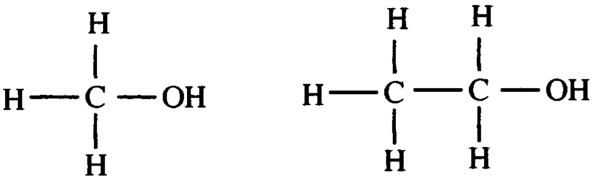
Fig. 1.4

It is completely miscible with water and is colourless, syrupy and has a sweet taste. It is used as a lubricant in watches and in stamp pad inks and in moist paints used by artists. Glycerol is also used as a lubricant in pumps for the petroleum industry as it will not dissolve in hydrocarbons. Being non-toxic it is used for the same reason in the food processing industry.

1.3 Aliphatic Alcohols

Naming of Aliphatic Alcohols

Saturated monohydric aliphatic alcohols (alkanols) form a homologous series of the general formula $C_nH_{2n+1}OH$ ($n \geq 1$). They can be viewed essentially as alkanes where one of the hydrogen atoms has been replaced by a hydroxyl group (-OH). Their names are derived from that of the parent alkane with an 'ol' replacing the final 'e' to signify the presence of the hydroxyl functional group. Thus, the name of the alcohol derived from methane is methanol, the alcohol derived from ethane is ethanol, etc., Fig. 1.5.



$H - \overset{H}{\underset{H}{C}} - OH \qquad H - \overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} - OH$

Fig. 1.5

The names of the first ten members are given in Table 1.1. Isomerism in alcohols up to C_4 is then considered.

IUPAC Name	Common Name	Formula
Methanol	Methyl alcohol	CH_3OH
Ethanol	Ethyl alcohol	C_2H_5OH
Propanol	Propyl alcohol	C_3H_7OH*
Butanol	Butyl alcohol	C_4H_9OH*
Pentanol	Pentyl alcohol	$C_5H_{11}OH$*
Hexanol	Hexyl alcohol	$C_6H_{13}OH$*
Heptanol	Heptyl alcohol	$C_7H_{15}OH$*
Octanol	Octyl alcohol	$C_8H_{17}OH$*
Nonanol	Nonyl alcohol	$C_9H_{19}OH$*
Decanol	Decyl alcohol	$C_{10}H_{21}OH$*

Table 1.1 *Names of alcohols*
*(*More than one structurally isomeric alcohol exists for this formula.)*

A number is commonly included in the name to indicate the position of the hydroxyl group in the carbon chain, thus removing ambiguities that arise due to structural isomerism (treated below for alcohols up to C_4). Thus, propan-1-ol (1-propanol) has the hydroxyl group attached to carbon no. 1 of the propane carbon skeleton and propan-2-ol (2-propanol) has the hydroxyl group attached to carbon no. 2 of the propane skeleton. Both alcohols can be represented by the formula C_3H_7OH, Fig. 1.7.

Structure of Aliphatic Alcohols - Building Up the Aliphatic Alcohols (C_1 - C_4)

When considering isomerism in alcohols it is convenient to view alcohols in terms of alkanes where one of the hydrogens has been replaced by a hydroxyl group. Thus, methanol has only one possible isomeric structure as all of the hydrogens in methane are identical. It is noted that the geometry about the -OH-bearing carbon is tetrahedral. Similarly, ethanol has only one isomer as all six hydrogens in ethane occupy identical environments, Fig. 1.6.

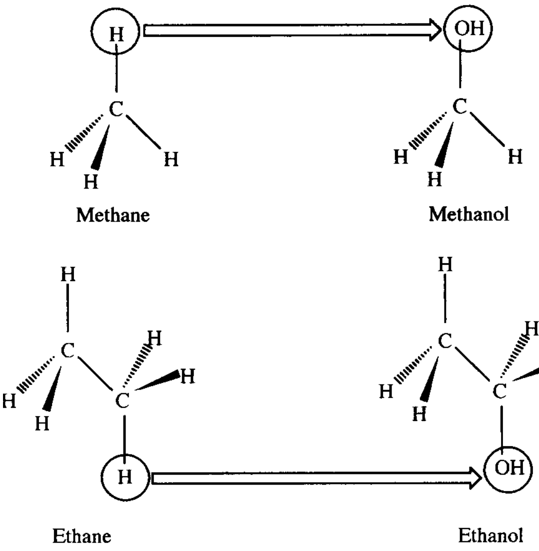


Fig. 1.6

Propane has hydrogens in two distinct environments, thus two structures of propanol are possible. When the hydroxyl group is attached to carbon no. 1 in the propane skeleton we get propan-1-ol (1-propanol or *n*-propyl alcohol) (the '*n*-' notation denotes the normal straight-chain configured compound while the 'iso-' notation denotes the 'isomeric' compound). When the hydroxyl group is attached to carbon no. 2 of the propane skeleton we get propan-2-ol (2-propanol or isopropyl alcohol), Fig. 1.7.

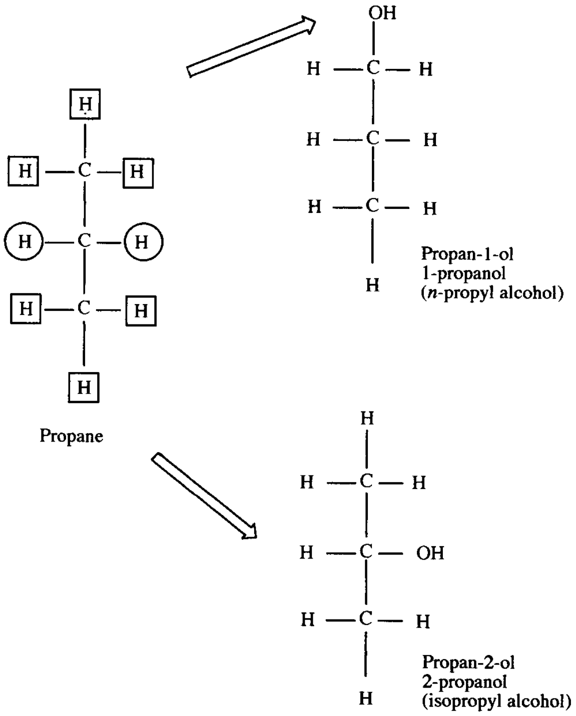


Fig. 1.7

When considering the possible isomers of butanol we examine the two structural isomers of butane and, from the number of differing hydrogen environments present, see how many different isomers of butanol are possible. In Fig. 1.8 we see that four different isomers of the formula C_4H_9OH are possible.

Two of these are primary alcohols (butan-1-ol and 2-methylpropan-1-ol), one is a secondary alcohol (butan-2-ol) and one a tertiary alcohol (2-methylpropan-2-ol), Fig. 1.8.

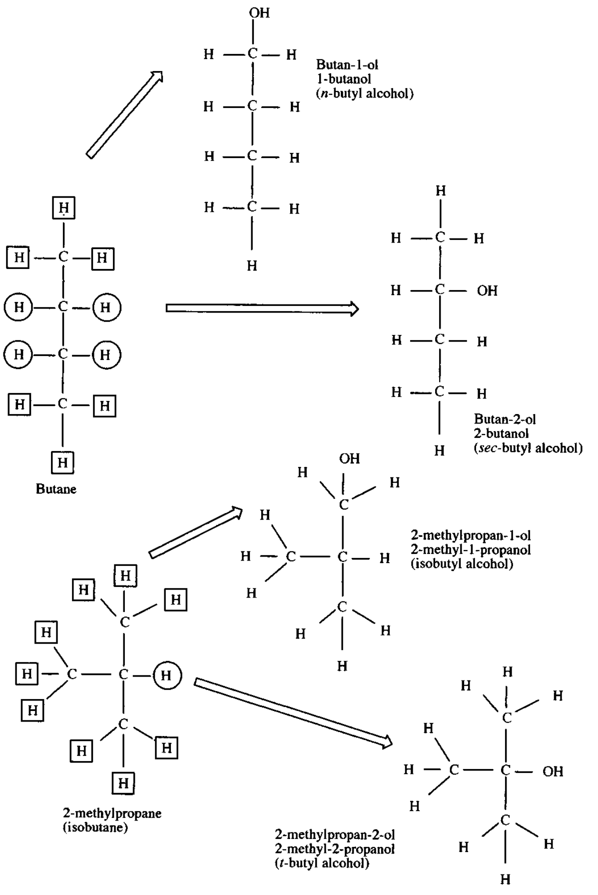


Fig. 1.8

1.4 Physical Properties of Alcohols

Since the hydrocarbon fragment of the molecule is essentially non-polar one might expect properties of alcohols to parallel those of the corresponding hydrocarbon homologous series. This is not the case. The high polarity of the hydroxyl group and its ability to form strong hydrogen bonds results in the physical properties of alcohols being dominated by the functional group of the molecule, Fig. 1.9, at least for the lower members of the series.

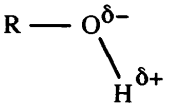


Fig 1.9

Some physical data for the first ten straight-chain members of the aliphatic monohydric alcohols are summarised in Table 1.2. Physical data for the isomers of propanol and butanol are given in Table 1.3.

Name	Formula	m.p./°C	b.p./°C	Density/ g cm^{-3}	Sol. in H_2O/ (g/100g)
Methanol	CH_3OH	- 97.0	64.5	0.793	∞
Ethanol	C_2H_5OH	-115.0	78.3	0.789	∞
Propan-1-ol	C_3H_7OH	-126.0	97.0	0.804	∞
Butan-1-ol	C_4H_9OH	- 90.0	118.0	0.810	7.9
Pentan-1-ol	$C_5H_{11}OH$	- 78.5	138.0	0.817	2.3
Hexan-1-ol	$C_6H_{13}OH$	- 52.0	156.5	0.819	0.6
Heptan-1-ol	$C_7H_{15}OH$	- 34.0	176.0	0.822	0.2
Octan-1-ol	$C_8H_{17}OH$	- 15.0	195.0	0.825	0.05
Nonan-1-ol	$C_9H_{19}OH$	- 6.0	215.0	0.827	-
Decan-1-ol	$C_{10}H_{21}OH$	6.0	228.0	0.829	-

Table 1.2 *Some physical data for alcohols*

Analysis of the data presented in Table 1.2 tells us that alcohols have elevated boiling points for compounds of low relative molecular mass (the b.p. values of methane, ethane and propane are -162 °C, -88.5 °C and -42 °C, respectively). This illustrates the stark contrast in the binding forces within liquid alcohols and the corresponding liquid alkanes. Within alkanes it is the molecular mass and the shape of the molecule which dictate the boiling point (and indeed the m.p. also) as the intermolecular forces are of the weak van der Waals variety. Within alcohols the high polarity of the functional group results in an *associated liquid* with hydrogen bonding strongly influencing the boiling points, Fig. 1.10. The b.p. values show a steady increase as the carbon chain is lengthened. This increase is mainly due to increase in molecular mass with an increase of about 22 °C for every CH_2 added. The m.p. values again show an increase with molecular mass but this is not as regular as the trend shown in b.p. data.

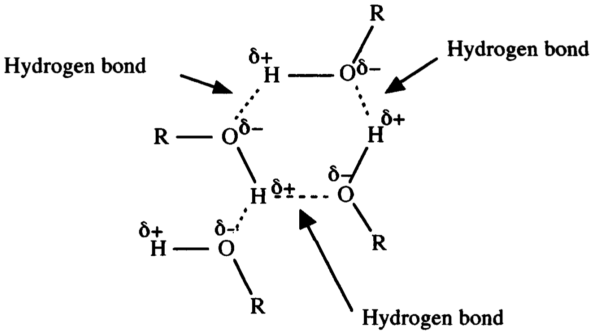


Fig 1.10

The data for the solubilities in water of alcohols show the smaller molecules to be infinitely soluble in water. For the alcohols with carbon number C_1 to C_3 the high polarity of the functional group completely dominates their properties in this respect and they are infinitely miscible with water. However, as the purely hydrocarbon fragment of the molecule increases in size the non-polar nature of this portion of the molecule starts to influence the water solubility. This results in a dramatic reduction in water solubility as we proceed from C_4 to C_9, where only very sparing solubility is noted. It is the difficulty associated with taking the non-polar portion of the molecule into a highly associated solvent such as water (where there is very strong hydrogen bonding) which gives rise to this decrease in solubility.

Name	Formula	m.p./°C	b.p./°C	Density/ g cm^{-3}	Sol. in H_2O/ (g/100 g)
Propan-1-ol (*n*-propyl alcohol)	C_3H_7OH	-126	97	0.804	∞
Propan-2-ol (isopropyl alcohol)	C_3H_7OH	-86	82.5	0.789	∞
Butan-1-ol (*n*-butyl alcohol)	C_4H_9OH	-90	118	0.810	7.9
Butan-2-ol (*s*-butyl alcohol)	C_4H_9OH	-114	99.5	0.806	12.5
2-methylpropan-1-ol (isobutyl alcohol)	C_4H_9OH	-108	108	0.802	10.0
2-methylpropan-2-ol (*t*-butyl alcohol)	C_4H_9OH	25	83.0	0.798	∞

Table 1.3 *Comparative data for some isomeric alcohols*

The data for the isomers of propanol and butanol show a b.p. trend where primary alcohols have higher b.p. values than secondary alcohols, which in turn have higher b.p. values than the tertiary alcohols of the same molecular formula. This trend can be attributed to the lower structural hindrance about the hydroxyl-bearing carbon in 1° alcohols over 2° alcohols, which in turn are less structurally hindered than 3° alcohols. Thus, the efficiency of hydrogen bonding within the alcohols will be better in the case of 1° alcohols. This efficiency will vary, with 1° > 2° > 3°. However, the solubilities in water favour the 3° alcohol over its 2° isomer. The 3° alcohol is more water soluble than its 1° counterparts. This is explained in terms of the dipole moment of the compounds. The hydrocarbon fragment of the molecule is most compact in the case of the tertiary alcohol and the molecule has the greatest dipole moment. However, in the case of the primary alcohol the length of the hydrocarbon fragment causes a lowering of the dipole moment which affects the solubility.

1.5 Preparation of Alcohols

While it is possible to synthesise alcohols by a variety of routes the bulk production of alcohols is dominated by two distinctly different processes. The first of these is the hydration of alkenes. The second involves the fermentation of carbohydrates and is probably the oldest synthetic chemical process carried out by man. In addition, due to the synthetic importance of alcohols, other common routes are subsequently summarised in less detail below. Further information on these reactions can be found in most third level organic chemistry texts.

Hydration of Alkenes

The ready availability of alkenes of C_1 to C_5 from the petrochemical industry, where alkenes are a major product of the cracking of crude oil (see module on Hydrocarbons), plays a large part in the importance of this route to alcohols. In addition, the route also benefits from the ease with which hydration can be achieved and from the ability to select the orientation of hydration by careful choice of reagents and conditions. Three methods of hydration are discussed here in some detail. The first two give addition in accordance with Markovnikov's rule and the third gives opposite orientation of addition (i.e. anti-Markovnikov addition).

Addition of water under acidic conditions

Direct addition of water across the double bond can be achieved by addition of sulphuric acid across the double bond followed by hydrolysis of the alkyl hydrogensulphate with water, Fig. 1.11(a).

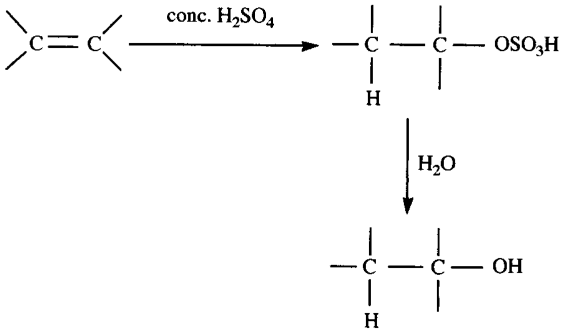


Fig. 1.11(a)

Alternatively, simple addition of water across the double bond under mildly acidic conditions can be achieved in the case of more reactive alkenes, Fig. 1.11(b).

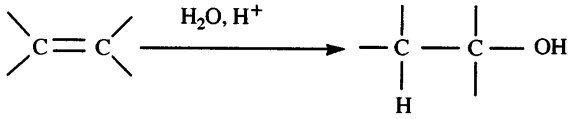


Fig. 1.11(b)

These additions follow Markovnikov's rule, with the alkene carbon which bears the most hydrogens getting the added hydrogen. Hence, the most substituted product is formed. The reason for this is the fact that the mechanism proceeds with addition of a proton to the alkene resulting in the formation of a carbonium ion intermediate. The most stable carbonium ion is formed and this will lead to the most substituted alcohol product, Fig. 1.12.

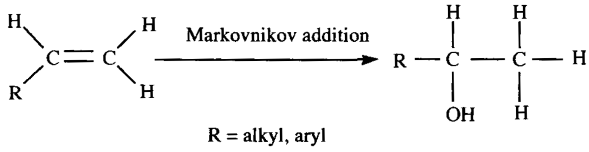


Fig. 1.12

This type of mechanism is called electrophilic addition and is described with the reactions of alkenes in the module on Hydrocarbons. The major difficulty with this method of alcohol production is the possibility of group migration within the intermediate carbonium ion (to form a more stable intermediate). This leads to rearrangements of the skeleton of the molecule. This problem is not discussed further here but can be found under the headings of 'rearrangements, neighbouring group effects' and 'migratory aptitudes' in any good third level organic text.

Oxymercuration-demercuration

This is an excellent technique as the reaction is highly regiospecific, giving the Markovnikov product. (A regiospecific reaction is specific in the location and orientation of reaction, i.e. where and how the reaction takes place. It is not subject to rearrangements and the products are predictable.) In addition, the reaction can be carried out under mild conditions. The problem of rearrangements, which presents a difficulty in the previous method, does not arise and a highly specific *anti*-addition of H_2O across the double bond results (see below). The reaction is carried out in two stages. First, an oxymercuration step where -OH and -HgOAc (OAc = $OOCCH_3$) groups are added across the double bond. The second involves the demercuration step which is achieved by reaction of this intermediate with sodium borohydride, Fig. 1.13.

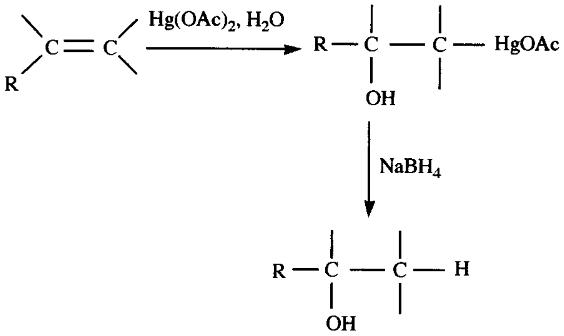


Fig. 1.13

It would appear that a bridged intermediate involving a mercurinium ion is involved, Fig. 1.14.

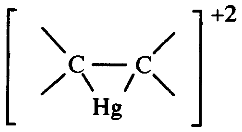


Fig. 1.14

This stabilises the intermediate ion and also ensures anti-addition (i.e. overall the -H adding from above the plane of the alkene and the -OH from below the plane of the alkene or *vice versa*). The mechanism of addition is analogous to the type of mechanism described in the Hydrocarbons module for the addition of bromine to alkenes, i.e. electrophilic addition.

Hydroboration-oxidation

The principal importance of this reaction pathway is that it yields anti-Markovnikov addition of H_2O across the alkene. The alkene is reacted with diborane (B_2H_6) to form an alkyl borane intermediate which is then 'oxidised off' using hydrogen peroxide solution under alkaline conditions, Fig. 1.15.

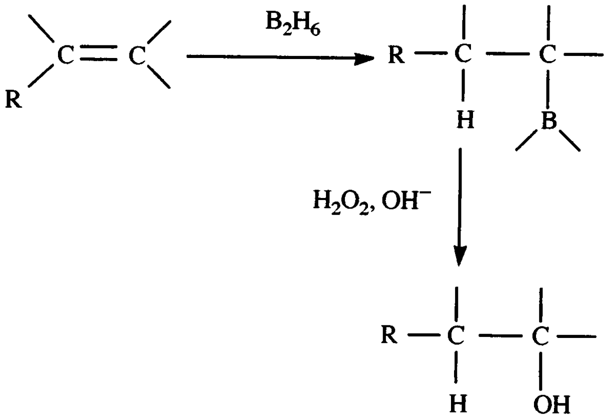
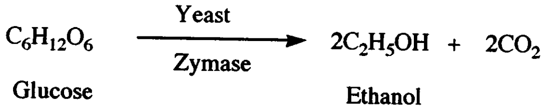


Fig. 1.15

The mechanism here involves initial addition of hydrogen to one of the alkene carbons and boron to the other. The least sterically crowded intermediate is formed and this means that the boron becomes attached to the least substituted carbon of the double bond. When oxidation follows, the boron is replaced by an -OH group, generating the alcohol. This reaction is very regiospecific and is not accompanied by rearrangements.

Fermentation of carbohydrates

Ethanol can be produced by fermentation of grain. Here a sugar is converted by yeast to form alcohol by an anaerobic digestion reaction, Fig. 1.16.



$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow[\text{Zymase}]{\text{Yeast}} \underset{\text{Ethanol}}{2C_2H_5OH} + 2CO_2$$

Fig. 1.16

The fermentation of carbohydrates is probably the oldest synthetic chemical process carried out by man. Details of the industrial preparation of alcohol by fermentation for the alcoholic beverages industry and for the pharmaceutical and healthcare industries are discussed in section 1.6.

Other Important Synthetic Routes to Alcohols

Hydrolysis of alkyl halides

Alcohols can be prepared by hydrolysis of alkyl halides, Fig. 1.17.

$$R{-}X \xrightarrow{OH^- \text{ or } H_2O} R{-}OH$$

Fig. 1.17

However, since one of the most direct methods of making alkyl halides is from the corresponding alcohol and since the alcohols are, in general, more readily available, the method has an obvious limitation. In addition, the mechanism of substitution of the halide -X by -OH varies with the degree of substitution of the alkyl halide and the conditions employed. There can also be competing elimination reactions which lead to alkenes. None of these possibilities will be considered here.

Grignard reagents

Alkyl Grignard reagents are prepared by the reaction of magnesium with alkyl halides. If the Grignard reagent is simply reacted with water the product is the corresponding alkyl alcohol. If methanal (HCHO, formaldehyde) is used the product is the primary alcohol one carbon longer than the alkyl group of the Grignard. When any other aldehyde is used the product is a secondary alcohol and when a ketone is used the product is a tertiary alcohol, Fig. 1.18.

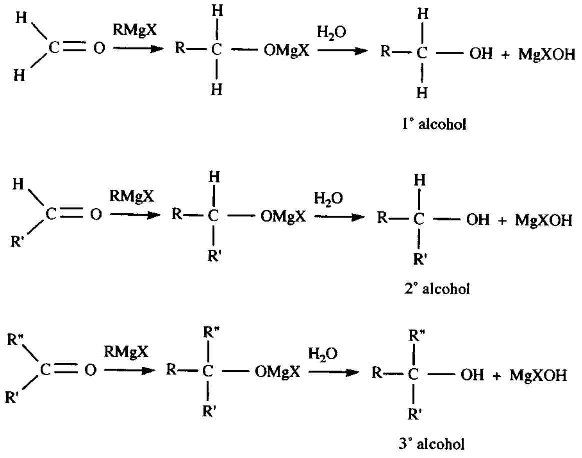


Fig. 1.18

Grignard reagents can also be added to epoxides such as ethylene oxide. In this case the carbon chain of the resulting alcohol is two carbons longer than that of the alkyl of the Grignard, Fig. 1.19.

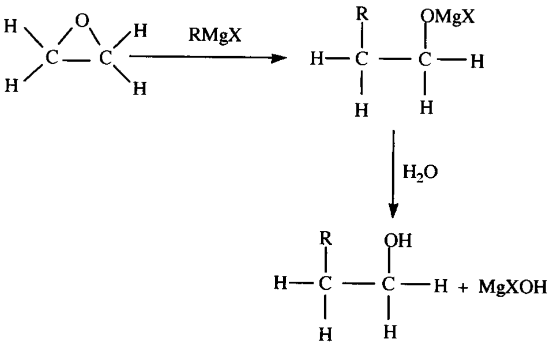


Fig. 1.19

In the reaction of Grignard reagents with esters two moles of Grignard reagent react with one mole of ester generating a tertiary alcohol, Fig. 1.20.

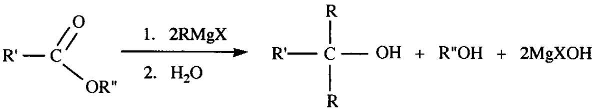


Fig. 1.20

The obvious versatility of this method is in fact its greatest drawback. While it is suitable for small and simple molecules the high reactivity of Grignard reagents results in a lack of specificity in reactions where more complex molecules with many functional groups are being utilised. Despite this problem it is still among the most important synthetic routes to alcohols.

Reduction of the carbonyl group in aldehydes and ketones

Reduction of aldehydes yields a primary alcohol. Reduction of ketones gives a secondary alcohol. These reductions can be carried out by a number of different methods. The elements of hydrogen can be added across the double bond of the carbonyl group by hydrogenation using a platinum, a copper or a nickel catalyst, Fig. 1.21. A simple laboratory experiment based on this reaction is discussed later in this chapter with reactions of alcohols.

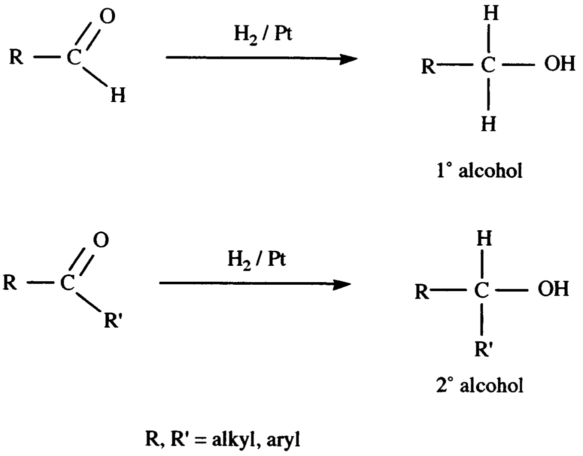


Fig. 1.21

Lithium aluminium hydride ($LiAlH_4$) is a powerful reducing agent. It reacts violently with water and is always used in solution in an ether. It serves as a source of nucleophilic hydride ion which attacks the electron-deficient carbonyl carbon. Hydrolysis of the intermediate with water yields the alcohol, Fig. 1.22. Lithium aluminium hydride ($LiAlH_4$) is an expensive reagent, so the catalytic hydrogenation described above is preferred on an industrial scale.

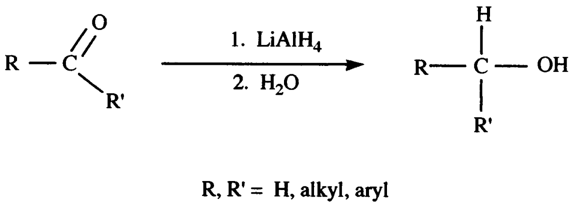


Fig. 1.22

Sodium borohydride versus lithium aluminium hydride as a reducing agent

Sodium borohydride ($NaBH_4$) is recommended in some texts for these reductions. However, its application is restricted to only a limited number of substrates and lithium aluminium hydride is a far stronger reducing agent and much more widely used. It should be noted that great care is needed in the handling of these reagents.

1.6 Social and Applied Information on Alcohols

Methanol (CH_3OH)

This was originally produced by the destructive distillation of wood and as such was called wood alcohol or wood spirit. Methanol also occurs in wood smoke and in trace quantities in new wines where it contributes to the bouquet. The poisonous nature of methanol is indirect in that it is methanal (formaldehyde) and methanoic acid (formic acid) which are formed from methanol in the body due to the action of the enzyme alcohol dehydrogenase that are the major cause of toxicity. Methanal and methanoic acid attack ganglion cells in the retina and blindness can result.

The main uses of methanol are as a denaturant of pure ethanol, i.e. making the ethanol unfit to drink, and as an antifreeze. In addition, it has applications as a motor fuel (see Hydrocarbons module). It is also used in the synthesis of methanal (HCHO).

Ethanol (C_2H_5OH)

Ethanol is the alcohol that is commonly referred to simply as alcohol. Ethanol is a depressant. It may seem to be a stimulant to those who drink it because it actually frees parts of the cortex from inhibitory control. Physiologically it interferes with the action of anti-diuretic hormones in the body, resulting in dehydration of the consumer. It also causes blood vessels to dilate which results in a feeling of warmth and a rosy hue. Ethanol is converted by alcohol dehydrogenase in the body to ethanal (acetaldehyde) which causes hangovers. Because whiskies and wines contain traces of higher alcohols and other compounds, the metabolism of ethanol in the liver to ethanal and on to ethanoic acid (acetic acid) is slowed and a hangover lasts. Because vodka is essentially pure alcohol in water (it is purified by passing it through charcoal) it is broken down much more quickly in the body than other alcoholic beverages.

Ethanol can be produced by fermentation and as such was called grain alcohol. It is a good solvent for both polar and non-polar solutes, e.g. both sodium hydroxide and hexane dissolve in ethanol. As well as an alcoholic beverage ethanol is used as a fuel, as a preservative, in thermometers, and as a raw material for other organic chemicals. Ethanol is also used in aftershave preparations because of its ability to dissolve the oils which provide the aroma and the water which makes up the bulk of the lotions; it also acts as an astringent and an antiseptic.

When ethanol is used with a non-volatile solute it is called a tincture, e.g. tincture of iodine, and when used with a volatile solute it is called a spirit.

Ethane-1,2-diol (Ethylene Glycol), CH_2OHCH_2OH

Ethane-1,2-diol has an -OH group at each end of the molecule and therefore the liquid shows very strong hydrogen bonding. It is miscible with water and is widely used as antifreeze for automobiles. Its other major use is in the production of polyesters as it can undergo an esterification at each end. Combined with a diacid such as terephthalic acid poly(ethylene terephthalate) (Terylene) is formed.

Propane-1,2,3-triol (Glycerol), $CH_2OHCHOHCH_2OH$

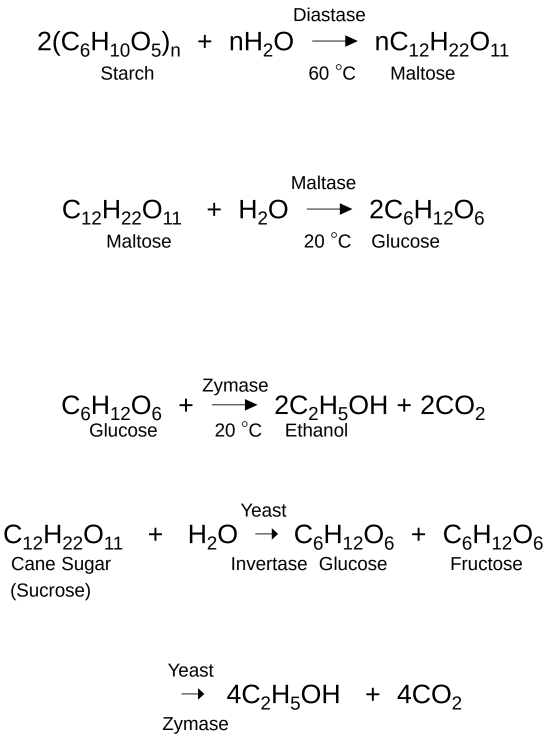
Glycerol with its three -OH groups is highly hydrogen bonded and is a syrupy liquid. It is the alcohol which binds three fatty acids together in the tri-esters of fats (e.g. tristearin, see fats and soaps in the appendix).

The sweetness and smoothness of glycerol make it a desirable component of wines. The fungus *Botrytis cenerea*, which gives rise to ‘noble rot’ in grapes on the vine, damages the skin of the grape and allows evaporation of some of the water out of the grape. This leaves the grapes richer in glycerol and many premium wines of France, Germany and now Australia all have contributions from the ‘noble rot’ .

The Austrian wine scandal of 1985 involved contaminating wines with diethylene glycol, $CH_2OHCH_2OCH_2CH_2OH$. This toxic substance was introduced deliberately to try to enhance the sweetness and smoothness of the wine in order to increase its value. The scandal seems to have originated from a confusion of glycerol with ethylene glycol and then confusing this with diethylene glycol. The latter compound is an industrial solvent. Glycerol is used in the cosmetics industry as a softener and as a smoother (due to its ability to bond to water molecules). It is also used in tooth paste as an anti-caking agent. It is used in cake icing to stop it cracking. Glycerol is used in glues to slow down their drying.

Ethanol for the Alcoholic Beverages Industry

Ethanol can be produced by fermentation of grain, Fig. 1.23. Here a sugar is converted by yeast to form alcohol by an anaerobic respiration reaction.



$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n} + nH_2O \xrightarrow[60\ ^\circ\text{C}]{\text{Diastase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}}$$

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[20\ ^\circ\text{C}]{\text{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

$$\underset{\text{Glucose}}{C_6H_{12}O_6} + \xrightarrow[20\ ^\circ\text{C}]{\text{Zymase}} \underset{\text{Ethanol}}{2C_2H_5OH} + 2CO_2$$

$$\underset{\text{(Sucrose)}}{\underset{\text{Cane Sugar}}{C_{12}H_{22}O_{11}}} + H_2O \xrightarrow[\text{Invertase}]{\text{Yeast}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\xrightarrow[\text{Zymase}]{\text{Yeast}} 4C_2H_5OH + 4CO_2$$

Fig 1.23 *Production of ethanol*

The fermentation of carbohydrates is probably the oldest synthetic chemical process carried out by man. In fact the first enzymes isolated were from yeast. They were called zymase and invertase and the name enzyme was proposed in 1867 by **Wilhelm Kune** (1837-1900).

The sugar yeast mixture after fermentation contains between 10% and 15% alcohol. Higher concentrations of alcohol kill the yeast. Higher concentrations are achieved by distillation and up to 95.6% alcohol, which is an azeotropic mixture, are easily obtained. (An azeotropic mixture is a mixture of two liquids which boil at constant composition, i.e. the composition of the vapour is the same as that of the liquid.) This concentration is called rectified spirit. Still higher concentrations are formed by azeotropic distillation with benzene. This is called absolute alcohol 99.5%.

Commercially, alcohol is liable to a heavy excise duty but it can be sold duty free under licence provided it is denatured, i.e. made unfit to drink. Denatured alcohol is called methylated spirits. There are two forms of methylated spirits, viz. industrial methylated spirits and mineralised methylated spirits.

Industrial methylated spirits has a composition of 95% rectified spirit and 5% methanol. It is often referred to as colourless methylated spirits.

Mineralised methylated spirits is more denatured in that it only contains 90% alcohol (rectified spirit) and 9.5% methanol and small amounts of pyridine, C_5H_5N, and paraffin oil. It is also coloured by a dye called methyl violet to discourage accidental imbibing.

Ethanol Content of Alcoholic Beverages

Alcoholic strength is measured in degrees proof. Strengths of alcohols used to be tested by pouring the alcohol over gunpowder and then igniting it. The weakest alcohol/water mixture which allowed the gunpowder to light was assigned 100° proof. Stronger solutions were over proof and weaker solutions were under proof. Today 100° proof alcohol is a mixture of alcohol and water which at 51 °F (10.5 °C) weighs exactly 12/13 of the weight of the same volume of distilled water and contains 49.3% ethanol and 50.7% water. As a rough guide take the proof as approximately twice the alcohol content by volume.

Beverage	°Proof	% Ethanol(v/v)
Vodka	75° - 100°	37.5% - 50%
Whiskey, Gin, Rum, Brandy	70°	40%
Sherry, Port	35°	17.5%
Wine	20° - 25°	10% - 12%
Beer, Cider	5° - 9°	2% - 4%

Table 1.4 *Alcohol content of common alcoholic beverages*

Beer and Ale Production

These are produced by the brewing process. It is convenient here to divide the process into five stages. The process is summarised in Fig. 1.24.

1. **Malting.** This involves the steeping of barley for up to 72 hours. Germination is allowed to occur and the sprouted grain is called malt. In the germination process, natural enzymes release sugars from the starch present in the grain. The malt is then kiln dried and may be roasted to give a light tan or dark brown colour. The extent of heating affects the nature of the final product. Roasted malt barley is used to make stout.

2. **Mashing.** The malt is then crushed and mashed with water in mash tuns (large mixing vats). The mash now has a porridge-like consistency. The mash is allowed to settle and the liquid portion, called sweet wort, is drawn off into copper kettles. Hot water is drawn through the mash to extract starch, sugars and enzymes released in the malting process. The washing is repeated to ensure all the wort is rinsed out. The solid residue is recovered for use as animal feed.

3. **Cooking**. The wort is mixed with roasted hops and boiled to extract the flavour of the hops. The extracts from the hops give the beer its characteristic taste and aroma. The brew is then transferred to a whirlpool where it is rotated at high speed. This causes the hop residues to settle in the middle and these can be drained off.

4. **Fermentation.** The hot wort is cooled and placed in fermentation tanks. Yeasts (brewers strains) are added to the wort and fermentation

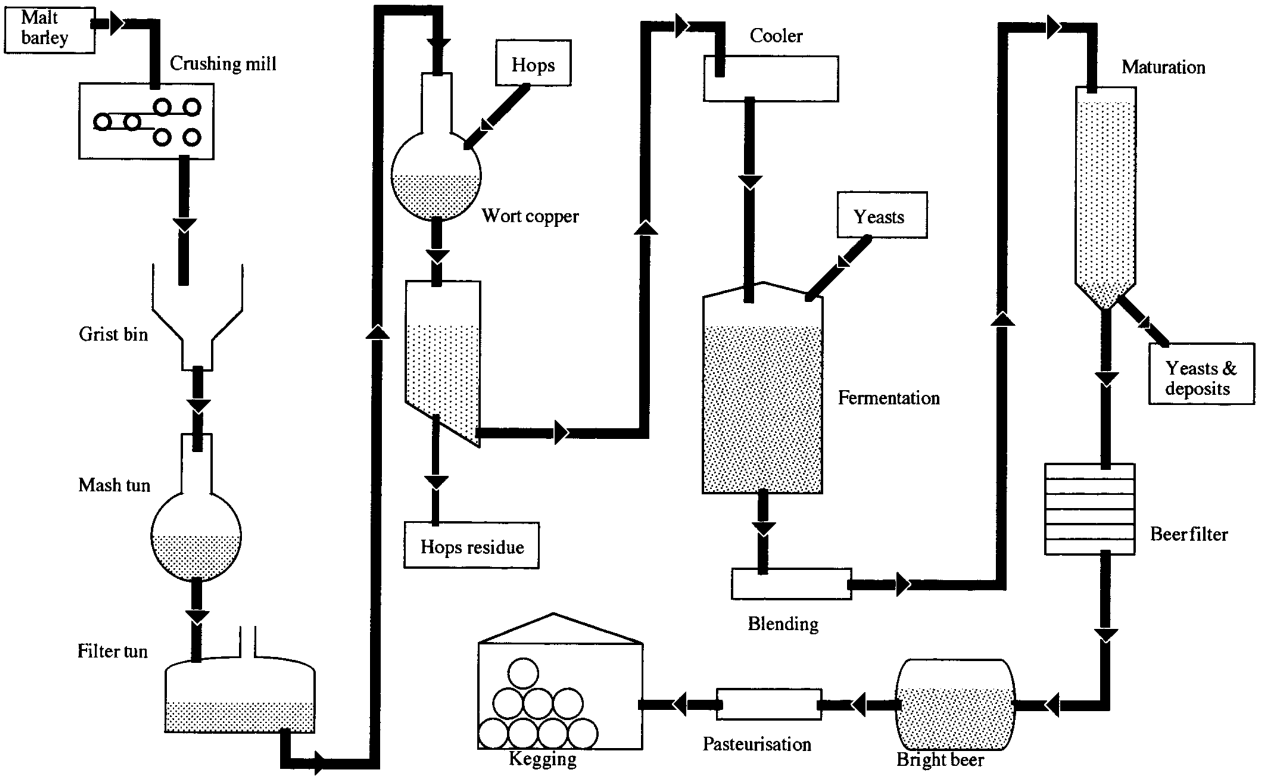


Fig. 1.24

proceeds. Yeast which settles on the bottom is used to make lagers, while top floating yeast is used to make ales.

5. **Maturation.** When fermentation is complete the beer is drawn off and placed in storage vats for up to 3 months while the flavour develops. When mature the remaining yeast cells are removed either by centrifugation or filtration. Carbon dioxide and nitrogen levels are adjusted to the desired levels and the product is filled into kegs. After final quality control the product is ready for distribution.

It is now common to pasteurise beers. This is normally done prior to kegging and before the carbon dioxide and nitrogen levels are adjusted.

The Irish beer market was worth £1.7 billion in 1996. This represented a volume of 480 million litres. Of this, less than 9% was sold through 'off-licence' outlets. Stout, with about 49% of the market, was the major product sold; lager, with about 42% of the market, was second, while ale was third with about 9.5%. Low-alcohol and non-alcoholic lagers and beers accounted for only 0.3% of the market.

While excess consumption of alcohol is to be avoided (see p. 18) beers and ales do contain a range of substances of nutritional benefit. For example, the nutritional content of one pint of stout includes: 200 kcal; 0.18 g protein; 17.4 g alcohol; 25.2 g sugars; 138 mg sodium (salt); 270 mg potassium; 48 mg calcium; 0.3 mg iron; 0.48 mg copper; 0.24 mg riboflavin (vitamin B_2); 2.58 mg niacin (vitamin B_3); 0.06 mg pyridoxine (vitamin B_6); 0.06 mg pantothenic acid; 0.66 mg vitamin B_{12}; 26.4 mg folic acid; 3.0 mg biotin.

Irish Whiskey

The Irish spirit is whiskey while the Scottish one is whisky. There are a number of different aspects to the method of production in the two countries. These are dealt with in the section on Whisk(e)y Manufacture.

The original name for whiskey is the same as the Irish word used today - 'uisce beatha', which means 'water of life'. How the word 'whiskey' originated from this is interesting. During the invasion of Ireland by Henry II in 1170 his soldiers became partial to 'uisce beatha'. They Anglicised the name first to 'uisce', then to 'fuisce', and finally to whiskey. The Scottish word 'whisky' constitutes a further corruption of the name.

It is very difficult to date precisely the origin of whiskey-making in Ireland. It is thought that the art of distillation was brought by monks to Ireland from the Middle East (where the process was being used to isolate perfumes) in about the sixth century AD. The monks developed the pot still from what they had learned. Whiskey was used as a medicine in the Dark Ages. This was a time when stomach problems arising from eating food which had 'gone off' were regular and consumption of alcohol helped cure the patient. Alcohol was administered to soldiers going into battle in the Middle Ages and the practice was still in vogue in the Great War.

The world's first licensed whiskey distillery is sited at Bushmills, Co. Antrim. This dates from 1608. There was a tradition of distilling on this site dating back to 1276.

The people reported to have favoured Irish whiskey included Elizabeth I of England (Sir Walter Raleigh would have been responsible for this introduction). Sir Walter Raleigh himself received (very gratefully!) a 32 gallon cask of the Earl of Cork's home distilled 'uisce beatha' prior to his departure for what is now Guyana. Peter the Great placed it ahead of all other spirits and Dr Johnson wrote favourably of it in his 1760 dictionary.

By the late 1700s there were nearly 2000 stills making whiskey in Ireland and Irish whiskey was transported to all parts of the civilised world. In the late 1700s taxes were introduced which favoured the larger manufacturers and so began the demise of the local small distillery. Further acts in the 1800s regulated the raw materials, the 'upper strength' to which the spirit could be distilled and the minimum maturation time in oak of the whiskey. The whiskey houses of John Jameson & Son (founded in Bow St, Dublin, in 1780) and Sir John Power (founded in St John’s Lane, Dublin, in 1791) were well established and had good reputations even at this time. It was the favoured drink throughout the British Empire and in America in the 19th century. Its only competitor was brandy exported from France. Vine disease in Europe in the middle of the 19th century more or less eliminated this competition and Irish whiskey dominated the market. Irish whiskey was also the preferred drink in England until the introduction of ‘blending’ (see Whisk(e)y manufacture, p. 14) by the Scots in the 19th century gave rise to the forerunners of the modern blended Scotch whisky. It took several court cases and a Parliamentary Commission to finally allow the name ‘whisky’ be used in identifying these spirits.

The demise of the Irish whiskey empires and the rise of the Scottish industry really hinged on happenings in America and poor Irish-British relations following the War of Independence in Ireland. The introduction of Prohibition in the United States of America in 1919 prohibited the manufacture, importation, sale or consumption of alcoholic beverages. Consequently, the bottom fell out of the whiskey industry and it did not look like it would ever return to its former glory. The reputation of Irish whiskey was damaged by ‘bootleggers’ supplying all sorts of illicit spirits in the name of ‘Irish’. The trade war with England which followed the War of Independence resulted in a loss of access to all of the British Empire. Scottish whisky manufacturers moved to fill this particular void. Meanwhile, many small distilleries closed and even the large distilleries rationalised their operations, reducing their stocks of new and maturing spirit. When the Prohibition Laws were finally revoked in 1933, Irish distilleries were not in a position to respond to the revived demand for spirits (the new spirit would have to have been made at least seven years earlier to allow maturation of the whiskey in the casks before bottling).

From then until the mid 1960s the Irish whiskey industry essentially serviced the home market. It made little impact on the world stage. Irish whiskey has always held its strong position in the Irish market for spirits. In 1966 John Jameson & Son, John Power & Son and Cork Distilleries Company merged to form Irish Distillers Ltd and in 1974 Bushmills Distillery joined the Irish Distillers Group. (It is interesting to note that the Tullamore Dew trademark had been acquired by John Power & Son in 1952 when the midland distillery of D. E. Williams Ltd in Tullamore ceased operations in that year. The ‘Dew’ part of this trademark came from the D. E. Williams name.) There followed a renewed launching on the world market of Irish whiskey and it is again gaining a place in this market. Primarily, distilling occurs at two sites in Ireland at present: Bushmills, Co. Antrim in Northern Ireland which produces Bushmills, Black Bush and Bushmills Malt (the only pure malt produced by Irish Distillers) and Midleton, Co. Cork, the larger plant. Currently, 12 - 13 million litres of whiskey is produced in Ireland each year. Of this approximately 60% is for export.

Visitors' centres are open to the public at the Jameson Heritage Centre, Midleton, Co. Cork, where the world's largest pot still is on display, at Bushmills, Co. Antrim, the world’s oldest distillery and at the Irish Whiskey Corner Museum, Dublin. Excellent slide presentations covering the history of whiskey manufacture in Ireland and guided tours are available at these centres as well as an opportunity to taste the product.

Whisk(e)y and Related Spirits

The different types of whisk(e)y are:

Scotch	distilled from barley
Irish	distilled from a mixture of five different grains including barley
American	distilled from either rye or corn (Bourbon originates in Kentucky)
Canadian	distilled from a blend of cereal grains
Japanese	distilled from a blend of grains and a little rice (neither wheat nor rye is used)

Whiskey and Whisky Production

The basic principles involved in whiskey and whisky production are similar in that the raw materials and the general process are controlled by legislation. However, subtle differences in the process give rise to differing products.

Firstly, in the malting process described below the germination of the barley is stopped by drying the malt by heating. In Ireland this is done using hot air produced by a closed kiln. This clean drying process, together with the mixing of malted and unmalted barley (different mixtures for different brands) before the start of the process, gives Irish whiskey a clean barley taste. In Scotland an open peat fire is used to stop the malting process. The latter imparts a peaty, smoky taste to the whisky and indeed the nature of this peaty-smokiness can be used to differentiate whiskies from different locations in Scotland. Secondly, Irish whiskey is distilled three times from copper pot stills whereas most other whisk(e)y-type spirits are distilled no more than twice.
Malt whisk(e)y is made using large quantities of malted barley. Other types of whisk(e)y use less malted barley.

Whisk(e)y manufacture

After barley is harvested selected barley is purchased by the distillery. It is dried (to prevent germination) and stored as dormant grain. The manufacturing process may be considered to consist of seven stages, see Fig.1.25.

1. **Steeping.** Water is added to allow the grain to germinate.

2. **Malting.** The grain is allowed to start to germinate under controlled conditions. It is turned regularly to prevent overheating. The germination releases certain natural enzymes and results in a better release of the starch and sugars necessary for the fermentation process. The dried malt can be stored at this stage for subsequent use.

3. **Milling.** The malt (and added unmalted barley if used) is ground to what is called ‘grist’.

4. **Mashing.** The grist is placed in large vessels called ‘mash tuns’ where boiling water is added and the mixture agitated for several hours to extract the starch, sugars and natural enzymes present. The liquid, now known as ‘wort’, is removed and the spent grain, known as ‘distillers dark grain’, is recovered, dried and sold as a high quality animal feed (this represents a good use of a waste product).

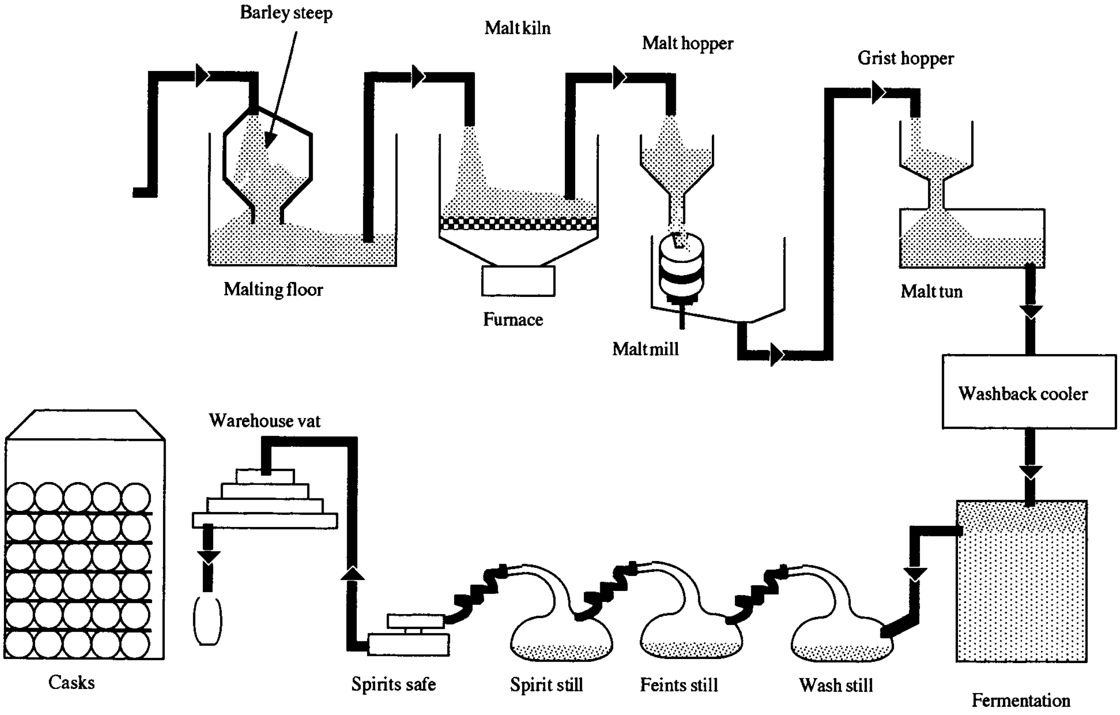


Fig. 1.25

5. **Fermentation.** The wort is cooled to 27 °C and yeasts (distillers' strains) added. After about 60 hours the wash contains about 9% alcohol and is ready to be sent to the still for distillation.

6. **Distillation.** The wash still (the first still) produces a distillate known as 'feints' which goes to the feints still (the second still). The distillate from here is called 'spirits' and goes to the spirits still (the third still) for the third distillation. The exact fractions which are drawn off in each of these distillations depend on the ultimate destiny of the final distillate (i.e. which whiskey from the product range it will become or contribute to after maturation). While a three-pot distillation is carried out in the manufacture of Irish whiskey, in whisky (Scotch) production only two distillations are carried out using pot stills - a wash still and a spirit still.

7. **Maturation.** The new spirit which has a very high alcohol content is diluted to an appropriate concentration prior to filling it into oak casks. Here it rests under controlled conditions for a minimum of three years by law but in practice more than five years, over which time the colourless spirit becomes whisk(e)y. Premium brands are allowed mature for longer periods. The whisk(e)y is then bottled. The main method of analysis is still human taste. A panel of tasters assess the quality of the product. Techniques such as gas chromatography have a role but as a fine whisk(e)y is estimated to have as many as seven thousand different compounds present the usefulness of the technique is limited.

The oak casks used are former sherry, rum or American bourbon barrels. Different types of previous occupier give rise to different final products. It is preferred that the casks have been used once before (bourbon barrels are used for bourbon maturation only once) as this previous use will have removed the more strongly woody flavours and the casks will have been seasoned by the bourbon or sherry. The casks are not used for whisk(e)y maturation on more than three occasions. The maturation process involves the exchange of compounds from the wood to the distillate and the exchange of compounds from the distillate to the wood and indeed the warehouse atmosphere.

It is slight variations in the mixture of raw materials (i.e. malt and unmalted barley), taking slightly different distillate fractions from the pot stills, maturation in barrels of different previous occupiers and different periods of maturation that all contribute to the different characteristics of different whiskies. Tradition plays a major role here and it is the different methodologies developed by different distillers in different distilleries over generations which have led to the diversity of whiskies available.

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Single malt whisk(e)y

Single malt is the produce of one distillery. It is normally matured for eight to fifteen years (even though the legal requirement is just three years). This allows time for the flavours and character of the spirit to become rounded and pronounced. It is normally a mixture of whiskies from different casks, where whiskies of different ages and proofs are combined to give a consistent product. Differing distillations will inevitably have slightly different compositions. Dilution may also be part of this process as cask whisk(e)y may have as high an alcohol concentration as 60% (by volume), while the marketed product tends to vary in the 40 - 43% (by volume) range. The age assigned to a single malt will be the age of the youngest distillation present in the bottle.

Single-cask malts are a sub-group of single malt whiskies. Here the contents of the bottle come from a single distillation, bottled straight from the cask with no vatting (see below) with other distillery produce. These are very much premium whiskies and more expensive.

Vatted malt whisk(e)y

In contrast to single malt whisk(e)y these whiskies are a vatted mixture of malt whiskies from many distilleries. They are the original blended whiskies. Many Scottish distilleries do not bottle their own product but rather sell it on to large distilleries who bottle blended malt whisky. A vatted malt will contain a very large mixture of malt whiskies. This protects the producer from product changes should one of their suppliers, for any reason, fail to deliver its quota of malt whisky. The words ‘vatted malt’ rarely appear on the label. However, they are generally recognised by the absence of the word ‘single’ from the label.

Grain whisk(e)y

Grain whisk(e)y differs from malt whisk(e)y in that it uses less malted barley. Maize, unmalted barley or other cereals (such as wheat) are used instead. The other main differences are in the distillation procedure where patented Coffey stills are used. Here glass column stills which can run continuously replace the batch run pot stills. The separation is more chemically precise and produces a very pure alcohol. The pot still is better for producing ‘flavoured whisk(e)y’ and leads to a more valuable product. Grain whisk(e)y matures faster than the pot stilled spirit and is very reliable in terms of quality consistency. It is mostly used for blending and is ready for this purpose after as little as three years’ (the minimum by law) maturation.

Blended whisk(e)y

Blended whisk(e)y is a mixture of different batches of mature malt whisk(e)y and grain whisk(e)y designed to produce a product with particular characteristics. This is really the mainstream of whisk(e)y production and the real volume market. Caramel is often used to enhance the colour of a blended whisk(e)y. The process was developed mainly to stretch malt whisk(e)y stocks and to ‘dilute’ the strong flavours of Scotch malt whiskies for the English and overseas markets during the 19th century. At the time there was much debate and political wrangling over allowing such mixtures be called whisky (see p. 13).

Wines

Vines were cultivated many thousands of years BC and are mentioned many times in the Old Testament. Wine was made in ancient Egypt and the ancient Greeks were exporters of wine. Through the Middle Ages the art of wine-making was kept alive in monasteries. Certification or classification of wines in the Bordeaux region dates from 1725. In ascending rank are vin de tables, vin de pays, vin delimité de qualité supérieure (VDQS) and appellation d'origine contrôlée (AOC or AC). Some regions have a premier cru rank above this and the Burgundy region offers an even higher grand cru classification. In Germany the ascending order is Kabinett, Spatlese, Auslese, Beerenauslese and Trokenberenauslese.

Wine is made by the process of fermentation using yeast and ripe grapes as the source of sugar. The fermentation is allowed to continue until all the sugar in the grape juice has been converted into alcohol by the yeast. White wine is fermented from green grapes and red wine from black grapes. Rosé wines are left in contact with the black grapes only until a light red colour is imparted to the wine and then the grape skins are removed. Red wines contain tannin which over time converts into a sediment which can be separated by decanting before the wine is used. The more tannin present the drier the wine.

Sparkling wines like champagne are bottled before fermentation is complete and the carbon dioxide produced bubbles out when the cork is drawn.

Fortified wines, such as port from Portugal, sherry from Spain and madeira from the Portuguese-owned island off the coast of Morocco, consist of a wine fortified, as the name suggests, with a distilled spirit such as brandy. This process originated as a method of preserving wines for transport to colonial outposts.

Certain types of wine are considered to be complementary to certain foods. These are:

Champagne	Caviar
Dry white wine	Hors d’oeuvres, fish, shellfish, light fowl
Bordeaux-type reds	Roast fowl and lighter roast meats
Burgundy-type reds	Rare meats and game
Sweet white wine, or champagne	Desserts
Red wine or port	Cheese

Brandy

This is produced by the distillation of grape wine. The distillation increases the alcohol content. The brandy is left to mature in wooden casks. When made the brandy is colourless but it absorbs some colour from the casks and may be further coloured by the addition of caramel. Cognac is probably the most famous of brandies and is made by distilling white wine. Kirsch is made by distilling the fermented juice of the black morello cherry. Slivovitz is a dry colourless brandy made from plums. Metaxa is a Greek brandy.

Gin

This is prepared from grain alcohol which has been purified by fractional distillation. It is then mixed with juniper berries and distilled once more. The name comes from either the French *genievre* or the Dutch *juniver* which both mean juniper. The two main types of gin are American/London dry gin or the Dutch gin also called schnapps.

Vodka

This is produced by distilling wheat mash and is the national drink of Russia. It is usually sold in Ireland as 75° to 100° proof. It is colourless and odourless and is often used in cocktails. It is essentially pure alcohol in water.

Rum

This is distilled from fermented cane sugar products, usually molasses. Rum may be either white or darkened by the addition of caramel or storing in wooden casks. Its characteristic flavour is derived from the organic ester, ethyl butanoate.

Sake

This is a fermented beer made from rice and is native to Japan. The rice, called *koji,* is mixed and kneaded with a cultivated mould and water, then heated and placed in large vats for fermenting. Yeast is sometimes added to aid the fermentation.

Poteen (Poitĺn)

This is the name given to the illicit spirit produced in Ireland. It is somewhat like vodka in that it is colourless and is not matured. It is produced usually by fermentation of grain or potatoes. It is an illegal spirit - it is not produced under the conditions directed by the spirits laws nor is government excise duty paid on it. Furthermore, the crude distillation and general lack of quality control create the possibility of the product being contaminated with poisonous alcohols such as amyl alcohol. In addition, the alcohol content can be very high, creating a further risk for the would-be consumer.

Alcohol Production from Waste from the Milk Processing Industry

Carbery Milk Products Ltd, Ballineen, Co. Cork, was set up by Express Dairies of London and a number of local co-operative creameries in 1966. Cheese, milk powder and whey powder production started in 1968.

Whey is produced in large quantities at the plant. Whey contains lactose, a milk sugar, which can be fermented by certain yeast strains to produce ethanol. It is more difficult to ferment than sucrose and only a few yeast strains are suitable.

In 1977 Carbery Milk Products Ltd decided to go into alcohol production for a number of reasons.

- The alcohol produced is a more valuable product than whey powder and it has a stable market.
- The group to which Carbery belongs has a need for reliable supplies of potable alcohol.
- The new technologies being developed had licensing potential.
- The drying equipment used to dry whey would be released for use to produce milk powder, avoiding the installation of another drier at that time.

The Process at Carbery Milk

The filtrate from the whey protein plant’s ultra filtration unit is cooled to 30 °C, the pH is adjusted and the filtrate is fermented in 170 000 litre stainless steel vats using special strains of yeast. The alcohol is isolated using a series of column stills. 96% alcohol is produced. Approximately 50% of the alcohol produced goes to the cream liqueurs industry (and so is subject to excise duty). The remainder is sold to various sectors of the chemical industry, including pharmaceutical, health care, cosmetics, agrichemicals, etc.

The carbon dioxide produced in the fermentation is sold into the soft drinks industry.

It is an interesting example of how technology has been used to convert a waste product, or at the very most a low value material, to a valuable product.

Dangers of Alcohol Consumption

It should be remembered that pure ethanol is poisonous and so should never be consumed. Furthermore, over-consumption of alcohol in any form should be avoided. The recommended maximum weekly consumption of alcohol is 14 units for women and 21 units for men. (A unit is approximately equivalent to a half-pint of beer, a glass of wine or two thirds of a small measure of spirits.)

1.7 Reactions of Aliphatic Alcohols

The chemistry of alcohols, R-OH, is mainly dictated by the -OH functional group. The reactions invariably involve cleavage of the R-OH bond or the RO-H bond. Most reactions can be classified into one of two categories. The first category involves substitution reactions where either the -OH or the -H is simply replaced or substituted by another monovalent element or group. The second category involves elimination reactions where a small molecule (usually H_2O) is eliminated and a double bond generated. The effects of the alkyl group, R, on the reactivity are much more subtle. These effects are in general directly related to structural variations in the alkyl group, being most notable when comparing reactions of primary, secondary or tertiary alcohols. These differences will be referred to as they arise. They will not be dealt with in detail.

Reactions Involving Cleavage of the R-OH Bond

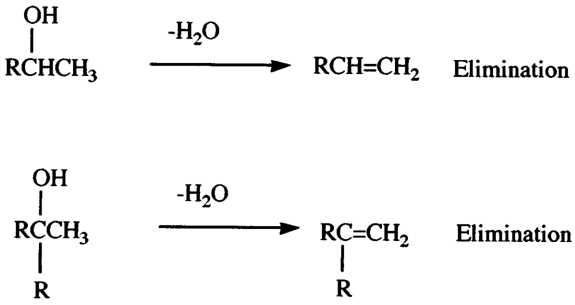
Substitution of the -OH group by a halide

The simplest possible reaction here is substitution of the -OH by the halogen -X by use of halide ion as a nucleophile, Fig. 1.26.

$$\mathrm{RCH_2OH} \xrightarrow{\mathrm{Cl^-}} \mathrm{RCH_2Cl} \qquad \textbf{Substitution}$$

Fig. 1.26

However, the possibility of rearrangement of the alkyl group -R is very real as carbonium ion intermediates are likely. Carbonium ions are particularly prone to rearrangement to more stable ions. In the case of tertiary alcohols (and to a slightly lesser extent secondary alcohols) there is also the possibility of competing elimination reactions and alkenes are very likely to appear in the product mixture, Fig. 1.27.



$$\mathrm{R\overset{OH}{C}HCH_3} \xrightarrow{\mathrm{-H_2O}} \mathrm{RCH{=}CH_2} \qquad \textbf{Elimination}$$

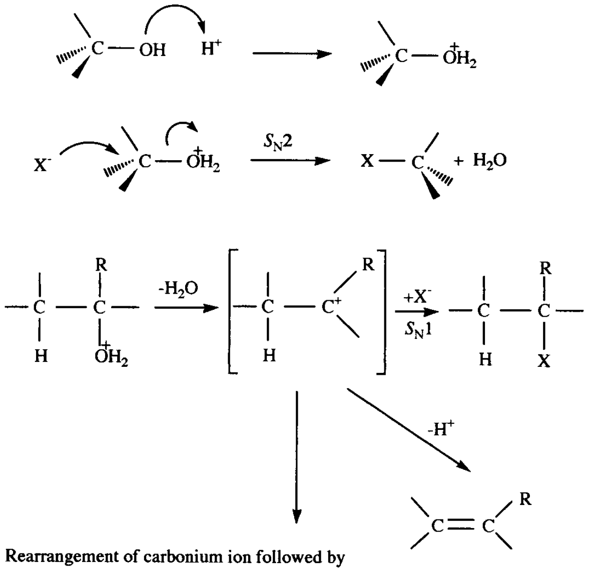
$$\mathrm{R\overset{OH}{\underset{R}{C}}CH_3} \xrightarrow{\mathrm{-H_2O}} \mathrm{R\underset{R}{C}{=}CH_2} \qquad \textbf{Elimination}$$

Fig. 1.27

Mechanism for the reaction of alcohols with hydrogen halides

The reaction of an alcohol with hydrogen halides is likely to proceed via a mechanism where the -OH group of the alcohol is first protonated, thus making it a better leaving group which can then either undergo S_N2 substitution, giving the corresponding alkyl halide, or elimination of H^+ to yield an alkene, Fig.1.28. Alternatively, and more likely in the case of secondary and tertiary alcohols, the protonated alcohol can undergo disintegration to form a carbonium ion followed by nucleophilic attack by a halide ion in an S_N1 reaction, Fig. 1.28.

There is also the possibility of the carbonium ion undergoing a rearrangement to a more stable carbocation which can be followed by either attack of a halide to yield the alkyl halide or elimination of H^+ to give an alkene, Fig. 1.28.

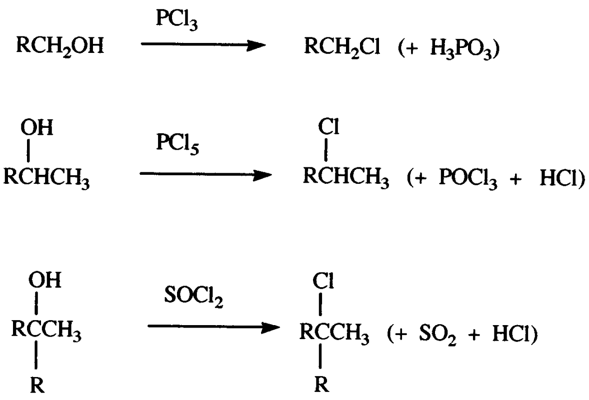


Rearrangement of carbonium ion followed by either attack of a halide ion to give a different alkyl halide or elimination of H^+ to yield an alkene.

Fig. 1.28

The competition between these possible outcomes of this reaction depends greatly on the nature of the alcohol. Tertiary alcohols form carbonium ions more readily than secondary alcohols which in turn form more stable carbonium ions than primary alcohols. The possibility of rearrangement depends on the availability of a neighbouring group which is available to migrate to generate a more stable (more substituted) carbonium ion. Thus, the products will depend very much on the stability of the intermediates formed.

However, this conversion of alcohol to alkyl halide can be reliably carried out using other reagents. Phosphorus(III) chloride, PCl_3, phosphorus(V) chloride, PCl_5, or thionyl chloride, $SOCl_2$, will all yield the alkyl chloride without rearrangement, Fig. 1.29.



$$RCH_2OH \xrightarrow{PCl_3} RCH_2Cl \ (+ \ H_3PO_3)$$

$$R\overset{OH}{\overset{|}{C}}HCH_3 \xrightarrow{PCl_5} R\overset{Cl}{\overset{|}{C}}HCH_3 \ (+ \ POCl_3 \ + \ HCl)$$

$$R\underset{\underset{R}{|}}{\overset{\overset{OH}{|}}{C}}CH_3 \xrightarrow{SOCl_2} R\underset{\underset{R}{|}}{\overset{\overset{Cl}{|}}{C}}CH_3 \ (+ \ SO_2 \ + \ HCl)$$

Fig. 1.29

The mechanism of these reactions is not discussed here but it is likely to have a ringed intermediate as the structure of the alcohol precursor is preserved in the alkyl halide, Fig. 1.30. The driving force for these reactions is the high affinity of phosphorus and sulphur to become bonded to oxygen.

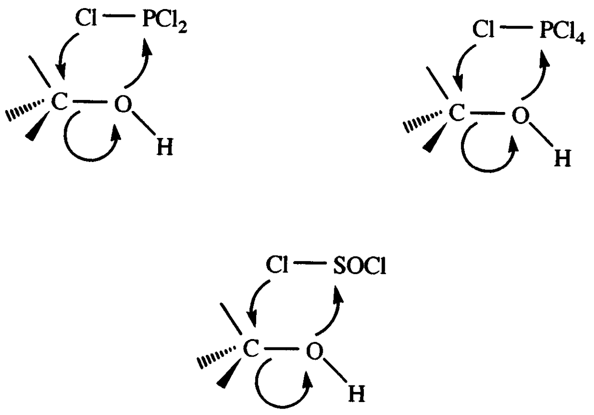


Fig. 1.30

Dehydration

The elements of water can be eliminated using the strongly dehydrating conditions of concentrated sulphuric acid and a temperature of 170 °C, or aluminium oxide and a temperature of the order of 250 °C, Fig. 1.31.

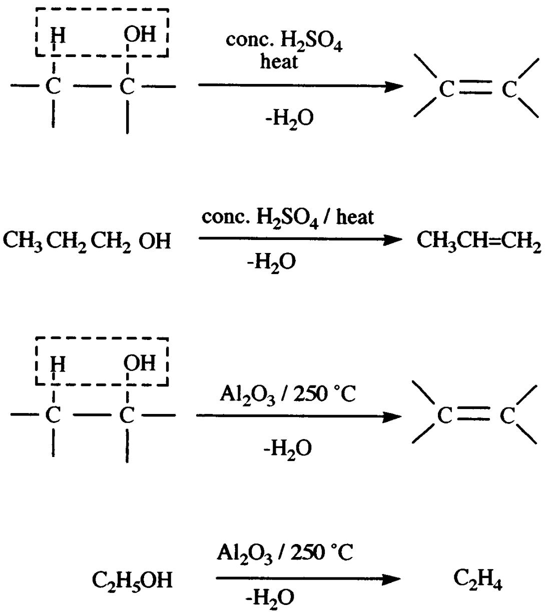


Fig. 1.31

The accepted mechanism for the acid-catalysed dehydration of alcohols involves the protonation of the -OH group followed by elimination of H_2O to give a carbonium ion. This is possible as H_2O is a good leaving group. The carbonium ion then loses H^+ to form an alkene, Fig. 1.32.

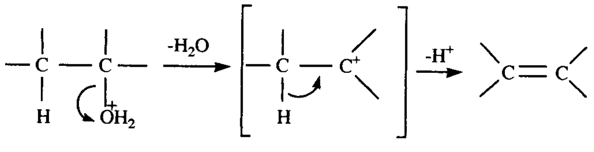


Fig. 1.32

The loss of H^+ is such as to favour the formation of the most stable alkene (i.e. most substituted and with the most conjugation possible with other double bonds). The usual problems of rearrangement associated with reactions involving carbonium ion intermediates are again in evidence here.

Experiment 1.1

Elimination of H_2O From Ethanol to Produce Ethene

Ethene is conveniently prepared by the dehydration of ethanol using hot aluminium oxide, Fig. 1.33.

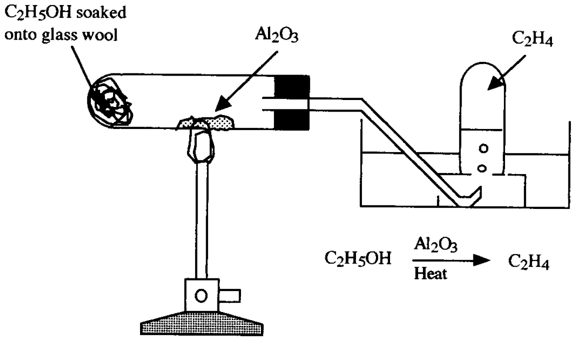


Fig. 1.33

The standard tests for alkenes can then be carried out on test-tubes of the collected gas. These include the following.

1. Ethene is a colourless gas with a sweetish odour.

2. Combustion: ethene burns with a slightly luminous flame. Then test for CO_2 with limewater.

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$

3. Bromination: ethene decolourises a solution of bromine water.

$$C_2H_4 + Br_2H_2O \rightarrow \underset{\text{2-bromoethanol}}{CH_2OHCH_2Br}$$

The contrasting products of the reaction of bromine and bromine water with alkenes has been discussed in the Hydrocarbons module.

4. Reaction with acidified potassium manganate(VII) (potassium permanganate): the purple solution is decolourised.

$$C_2H_4 \xrightarrow[H_2SO_4]{KMnO_4} CH_2OHCH_2OH$$

ethane-1,2-diol
(ethylene glycol)

Notes on procedure

1. The reaction is carried out at around 250 °C and consequently the delivery tube must be removed from the trough before the apparatus is allowed to cool, otherwise a suck-back of cold water will occur and the test-tube may break.

2. Discard the first few tubes of gas collected. They contain mainly air displaced from the system.

3. The purpose of the glass wool is merely to keep the ethanol at the end of the test-tube. Care should be taken with the use of glass wool since it may irritate sensitive skins. Minimise handling of it and avoid inhalation.

Reactions Involving Cleavage of the RO-H Bond

Reactions with metals and strong bases

The weakly acidic nature of the alcoholic hydrogen is seen by the reaction of alcohols with electropositive metals or strong bases, Fig. 1.34.

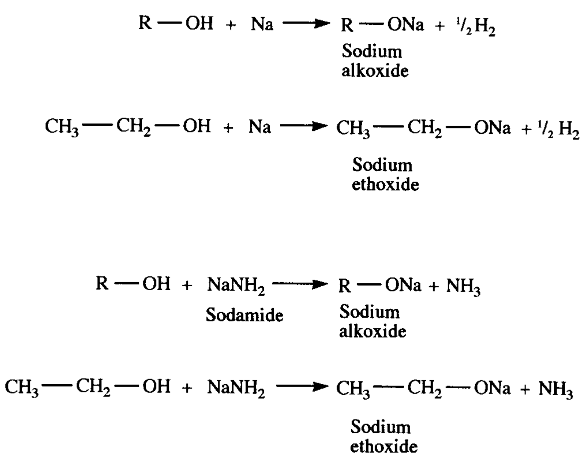


Fig. 1.34

It should be stressed that alcohols are more weakly acidic than water. However, they are more strongly acidic than terminal alkynes (acetylides) or ammonia. Thus, an acetylide ion, $RC{\equiv}C^-$ (which is the conjugate base of $RC{\equiv}CH$), or the conjugate base of ammonia, NH^-_2, will abstract the hydrogen from the -OH group of an alcohol.

NB Care is needed if these reactions are to be demonstrated.

Esterification

Here an alcohol undergoes a condensation reaction with an acid eliminating the elements of water and forming an ester, Fig. 1.35. The reaction is catalysed by small quantities of concentrated sulphuric acid or dry hydrogen chloride gas in cases where one of the reactants might undergo a side reaction with concentrated sulphuric acid, i.e. with methanoic acid or secondary or tertiary alcohols.

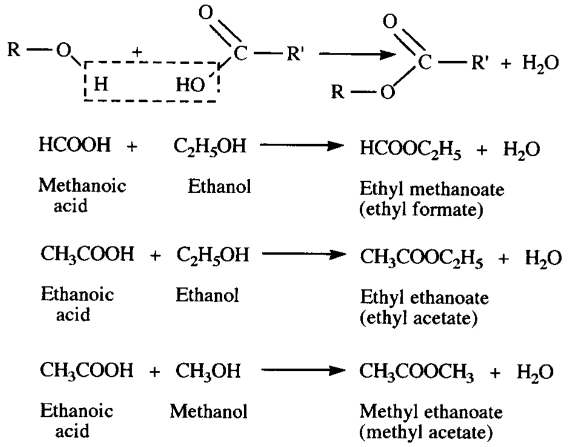


Fig. 1.35

The names of the esters are derived from the parent alcohol and carboxylic acid.

The mechanism of this reaction involves 100% retention of the alcoholic oxygen in the ester formed (i.e. the H_2O is formed from the H of the alcohol and the OH from the carboxylic acid). This is shown by using ^{17}O - labelled alcohol in the preparation of an ester. All of the ^{17}O is retained in the ester produced and none in the water, Fig.1.36. The mechanism for this reaction is discussed later with the reactions of carboxylic acids.

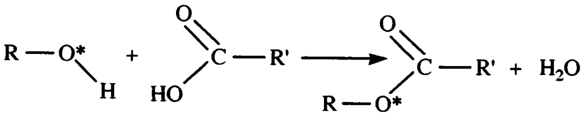


Fig. 1.36

Where the acid is a carboxylic acid the ester formed usually has a pleasant fruity odour. Many natural fruit fragrances are in fact cocktails of esters. Some common esters which are readily preparable and which have distinctive odours are listed in Table 1.5.

Ester	Smell/taste	Natural occurrence
$C_2H_5COOCH_3$ methyl propanoate	rum/blackcurrant	California orange
$C_3H_7COOCH_3$ methyl butanoate	apple/banana	wood oil
$C_6H_{13}COOCH_3$ methyl heptanoate	orris/currant	pineapple Florida orange
$C_6H_4(OH)COOCH_3$ methyl salicylate	wintergreen	wintergreen birch
$C_3H_7COOC_2H_5$ ethyl butanoate	rum/pineapple	strawberry juice
$C_5H_{11}COOC_2H_5$ ethyl hexanoate	pineapple	pineapple

Table 1.5 *Some distinctive naturally-occurring esters*

Sulphonic acid esters

It is not uncommon in organic synthesis to form esters of alcohols using sulphonyl chlorides such as para-toluenesulphonyl chloride, Fig. 1.37. The resulting ester has a very good leaving group in the sulphonate ion which has a low basicity. The choice of the para-toluenesulphonate ester rests in its ease of identification by ^{1}H n.m.r.

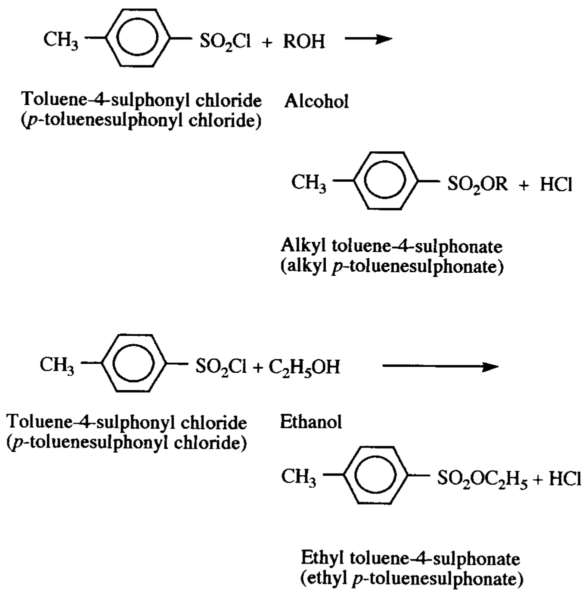


Fig. 1.37

Oxidation of Aliphatic Alcohols

The susceptibility of alcohols to oxidation and their response to oxidising reaction conditions is directly influenced by the number of hydrogens present on the hydroxyl-bearing carbon. Primary alcohols have at least two hydrogens on the hydroxyl-bearing carbon and are oxidised to aldehydes which in turn are very readily oxidised to carboxylic acids, Fig. 1.38.

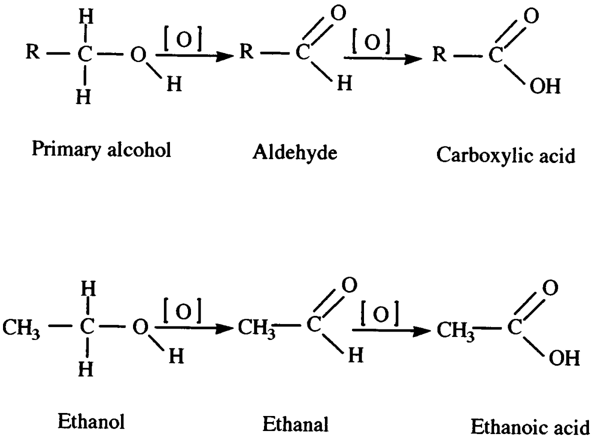


Fig. 1.38

Secondary alcohols have one hydrogen on the hydroxyl-bearing carbon and are oxidised to ketones which are not readily oxidised further, Fig. 1.39.

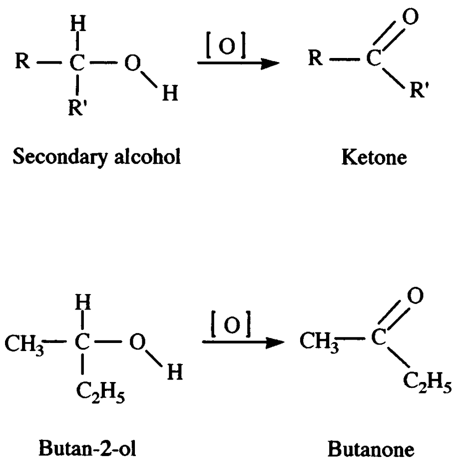


Fig. 1.39

The oxidations outlined in Fig. 1.38 and Fig. 1.39 can be achieved using reagents such as permanganate, chromate or dichromate ions and are dealt with in more detail in later chapters where the preparation of aldehydes, ketones and carboxylic acids are considered. The oxidations as far as the aldehyde or ketone can also be achieved by catalytic dehydrogenation over hot platinum or copper as catalyst. An interesting laboratory demonstration of this process is described in Chapter 2 with the preparation of aldehydes.

Tertiary alcohols have no hydrogen on the hydroxyl-bearing carbon and so cannot be oxidised in the same way as primary and secondary alcohols. However, when they react with permanganate, chromate or dichromate ions under hot acidic conditions they first undergo elimination reactions to form alkenes which are then oxidised. The oxidation of alkenes by permanganate ion is treated in the module on Hydrocarbons.

The oxidation of primary and secondary alcohols using chromate ions is believed to proceed by initial formation of a chromate ester.

Experiment 1.2
Properties of Alcohols

Small scale reactions can be carried out in a test-tube to illustrate the properties of alcohols. With the exception of the reaction of sodium with alcohols these tests are suitable for students. (If this test is carried out with ethanol, **absolute ethanol** should be used and not 95% ethanol.) Any of the lower alcohols will suffice to carry out these tests.

Tests on ethanol

1. **Solubility in water**
   A few cm^3 of water is placed in a test-tube and ethanol added dropwise. The two liquids are miscible regardless of which liquid is in excess.

2. **Combustion**
   Ethanol burns with a clean flame. The carbon dioxide produced can be tested with lime water.

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

3. **Reaction with sodium**
   When a very small piece of sodium is placed in absolute ethanol hydrogen gas is evolved. Note that 95% ethanol should not be used in this reaction.

$$C_2H_5OH + Na \rightarrow \underset{\text{Sodium ethoxide}}{C_2H_5ONa} + {}^1\!/_2H_2$$

4. **Tests with litmus paper**
   No colour change is observed when ethanol is tested with blue or red litmus.

5. **Test with sodium hydrogencarbonate**
   When a spatula tip of sodium hydrogencarbonate is placed in absolute ethanol no reaction is observed.

6. **Esterification**
   A few cm^3 of ethanoic acid and a few cm^3 of ethanol are treated with a few drops of concentrated sulphuric acid and the mixture heated gently for 1-2 minutes. The mixture is then poured into a beaker of cold water. The fruity odour of the ester is detected. (A hot water bath is suitable for the heating.)

$$CH_3COOH + C_2H_5OH \xrightarrow{H_2SO_4} \underset{\text{Ethyl ethanoate}}{CH_3COOC_2H_5} + H_2O$$

   Repeat this reaction with appropriate combinations of acids and alcohols to give the esters listed in Table 1.5, p. 22.

CHAPTER 2

ALDEHYDES AND KETONES

2.1 Introduction

Aldehydes and ketones are characterised by the presence of a carbonyl group, $>$C=O. Aldehydes are compounds of the general formula RCHO, where R is an alkyl, substituted alkyl, alkenyl or aryl group. All aldehydes have a hydrogen on the carbonyl carbon, Fig. 2.1. Ketones on the other hand have carbon atoms attached to the carbon of the carbonyl group. These carbon atoms can be part of an alkyl, substituted alkyl or aryl group giving ketones a general formula $RR'CO$, Fig. 2.1.

R = H, alkyl or aryl

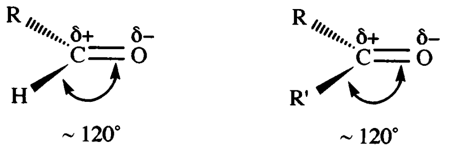
R, R' = alkyl or aryl

Aldehyde

Ketone

Fig. 2.1

The structure of the carbonyl group of aldehydes and ketones is the same, with a trigonal planar arrangement of atoms about the carbonyl carbon. The bond angles are about 120°, Fig. 2.2. The high difference in electronegativity between carbon and oxygen results in significant polarity across the carbonyl group, Fig. 2.2.



R = H, alkyl or aryl

R, R' = alkyl or aryl

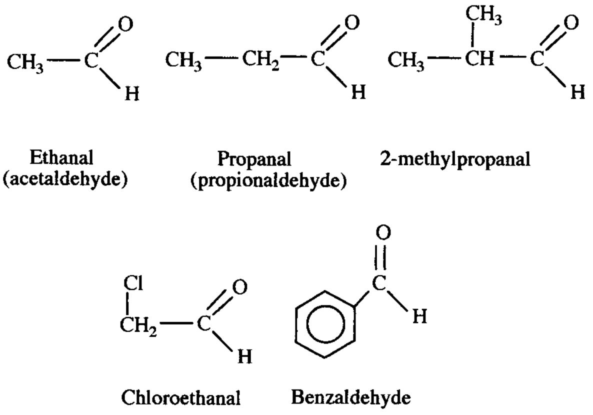
Aldehydes

Ketones

Fig. 2.2

The presence of the carbonyl group dictates the main chemical and physical characteristics of aldehydes and ketones. The uncrowded nature of the carbonyl carbon combined with the polarity of the carbonyl group have a major influence on the chemistry of aldehydes and ketones.

The R group(s) attached to the carbonyl group may be alkyl groups which are straight-chain or branched, or they may be ring in nature. They may contain multiple bonds, a halogen or indeed an aromatic group, Fig. 2.3 and Fig. 2.4.



Ethanal (acetaldehyde)

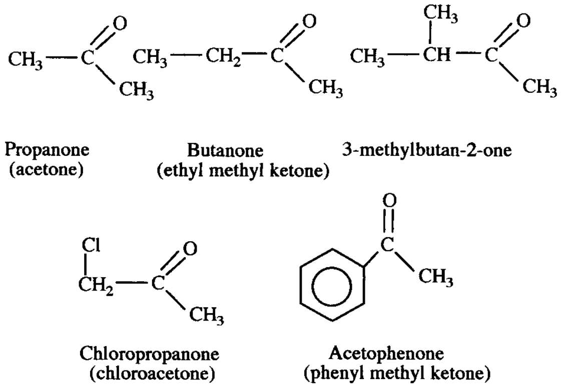
Propanal (propionaldehyde)

2-methylpropanal

Chloroethanal

Benzaldehyde

Fig. 2.3



Propanone (acetone)

Butanone (ethyl methyl ketone)

3-methylbutan-2-one

Chloropropanone (chloroacetone)

Acetophenone (phenyl methyl ketone)

Fig. 2.4

While much of the chemistry of aldehydes and ketones is similar, there are some differences in their reactions. These are consistent with, and can be explained by, consideration of their structural differences. Because of the similarities in the chemistries of aldehydes and ketones their chemistry will be treated together and the differences will be referred to and explained as they arise in the material treated below.

2.2 Naming of Aliphatic Aldehydes

Nomenclature of the Aliphatic Aldehydes

Saturated aliphatic aldehydes form a homologous series of the general formula $C_nH_{2n+1}CHO$ ($n \geq 0$). Aldehydes can be viewed essentially as alkanes where two of the hydrogen atoms of a terminal carbon have been replaced by a doubly-bonded oxygen, forming a carbonyl group, C=O, and hence the aldehyde functional group, -CHO. Their names are derived from that of the parent alkane, with an 'al' replacing the final 'e' to signify the presence of the aldehydic functional group. Thus, the name of the aldehyde derived from methane is methanal, the aldehyde derived from ethane is ethanal, etc. Since the aldehyde group has to occur on a terminal carbon of the carbon chain or side chain (the -CHO group has a valency of 1 hence it cannot occur internally in a chain) there is no need to include a number as part of the name. However, numbers will occur in the name to indicate the location of other groups attached to the basic skeleton of the molecule. The names of the first ten members of the saturated aliphatic aldehydes are given in Table 2.1. Isomerism in aldehydes up to C_4 is considered below.

It is worth stressing to students that the 'C' of the CHO functional group is not numbered in the naming of aldehydes, e.g. $CH_3CHClCH_2CH_2CHO$ is 4-chloropentanal and not 4-chloropentan-1-al.

IUPAC Name	**Common Name**	**Formula**
Methanal	Formaldehyde	$HCHO$
Ethanal	Acetaldehyde	CH_3CHO
Propanal	Propionaldehyde	C_2H_5CHO
Butanal	Butyraldehyde	C_3H_7CHO*
Pentanal		C_4H_9CHO*
Hexanal		$C_5H_{11}CHO$*
Heptanal		$C_6H_{13}CHO$*
Octanal		$C_7H_{15}CHO$*
Nonanal		$C_8H_{17}CHO$*
Decanal		$C_9H_{19}CHO$*

Table 2.1 *Names of aldehydes*
(*More than one structurally isomeric aldehyde exists for this formula.)

Structure and Nomenclature of Aldehydes - Building Up the Aliphatic Aldehydes (C_1 - C_4)

When considering isomerism in aldehydes it is convenient to view aldehydes in terms of alkanes where two of the hydrogens on a terminal carbon have been replaced by a doubly-bonded oxygen atom. Thus, methanal has only one possible isomeric structure as all of the hydrogens in methane are identical. Similarly, ethanal has only one isomer as all six hydrogens in ethane occupy identical environments, Fig. 2.5.

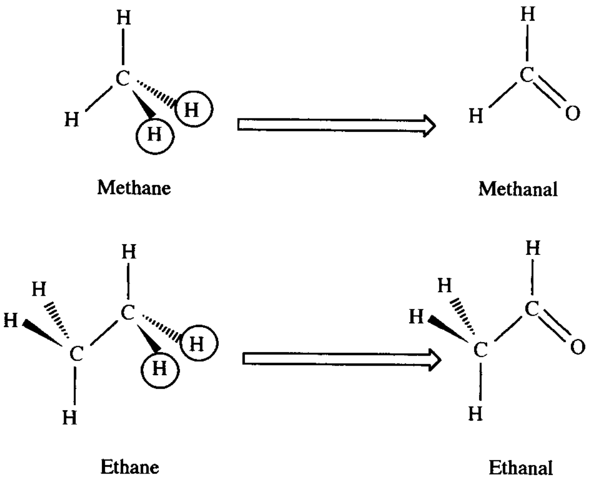


Fig. 2.5

Propane has only one isomer and has hydrogens in two distinct environments. One of these environments has hydrogens on a carbon which is ‘internal’ (i.e. it is bonded to two other carbon atoms). The second has hydrogens on terminal carbons in identical environments and so only one isomer of propanal exists. Only replacement of hydrogens on the terminal carbon can give rise to an aldehyde. This aldehyde is propanal, Fig. 2.6.

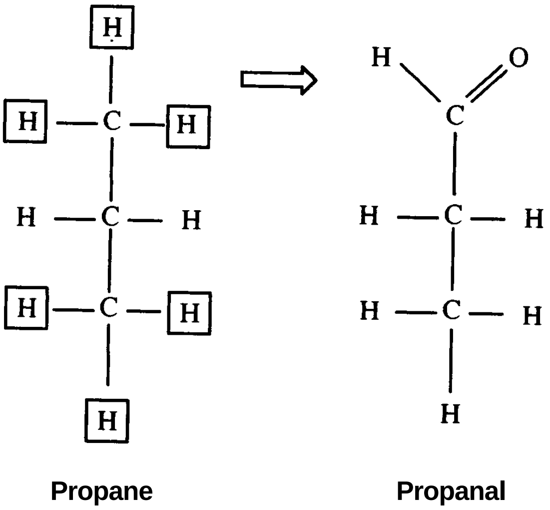


Fig. 2.6

Butane has two isomers, butane (*n*-butane) and 2-methylpropane (isobutane). Each has one unique environment with hydrogens on a terminal carbon atom of the skeleton of the molecule. This gives rise to two isomers of the formula C_3H_7CHO. Their names are butanal and 2-methylpropanal (isobutanal), Fig. 2.7.

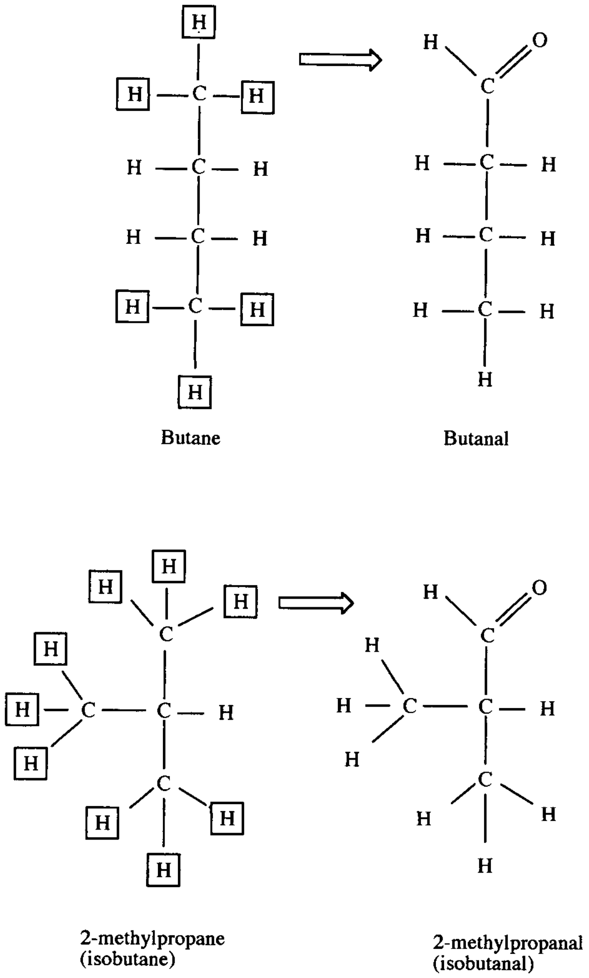


Fig. 2.7

2.3 Naming of Aliphatic Ketones

Nomenclature of the Aliphatic Ketones

Saturated aliphatic ketones are compounds of the general formula $R\text{-}CO\text{-}R^{I}$ (where R, R^{I} = alkyl groups). They can be viewed as alkanes where two of the hydrogen atoms of an internal carbon have been replaced by a doubly-bonded oxygen, forming a carbonyl group, C=O, giving ketones the form $RCOR^{I}$. It is important to note that by necessity the series starts with the C_3 member as the carbonyl carbon has to be flanked on either side by carbon atoms. Their names are derived from that of the parent alkane, with ‘one’ replacing the final ‘e’ to signify the presence of the ketonic functional group.

Thus, the name of the ketone derived from propane is propanone, the ketone derived from butane is butanone, etc. Since the ketone group has to occur internally within a carbon chain or side chain it is often necessary to include a number as part of the name so as to give the precise location of the ketone function. In addition, other numbers will occur in the name to indicate the location of other groups attached to the basic skeleton of the molecule. The names of the homologues to C_{10} of the aliphatic ketones are given in Table 2.2. Isomerism in ketones up to C_5 is considered below.

IUPAC Name	**Common Name**	**Formula**
Propanone	Acetone	C_3H_6O
Butanone	Ethyl methyl ketone	C_4H_8O
Pentanone		$C_5H_{10}O$*
Hexanone		$C_6H_{12}O$*
Heptanone		$C_7H_{14}O$*
Octanone		$C_8H_{16}O$*
Nonanone		$C_9H_{18}O$*
Decanone		$C_{10}H_{20}O$*

Table 2.2 *Names of ketones (*More than one structurally isomeric ketone exists for this formula.)*

Structure of the Aliphatic Ketones - Building Up the Aliphatic Ketones (C_3 - C_5)

When building up the ketones, it is important to consider isomerism. It is convenient to view ketones as derived from alkanes by the replacement of two of the hydrogens on an internal carbon by a doubly-bonded oxygen atom. Thus, propanone has only one isomer, since propane, the parent alkane, has only one internal carbon atom bearing two hydrogen atoms, Fig. 2.8.

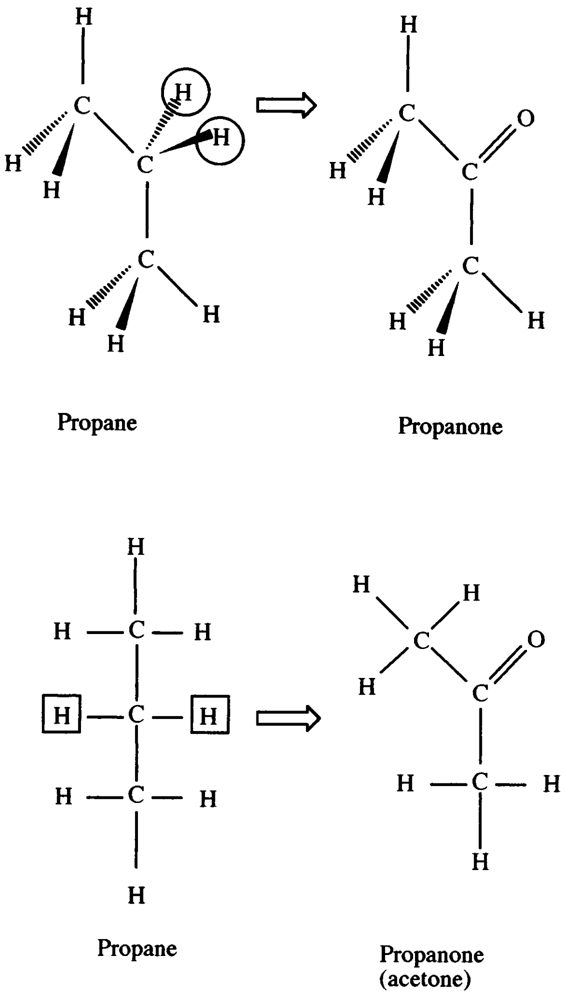


Fig. 2.8

Butane has two isomers, butane (*n*-butane) and 2-methylpropane (isobutane). All four internal hydrogens in butane have identical environments and so only one ketone isomer, namely butanone (ethyl methyl ketone), can be generated. The second isomer, 2-methylpropane (isobutane), has only one internal hydrogen so no ketone can be derived from this structure since two hydrogens have to be replaced by a doubly-bonded oxygen, Fig. 2.9.

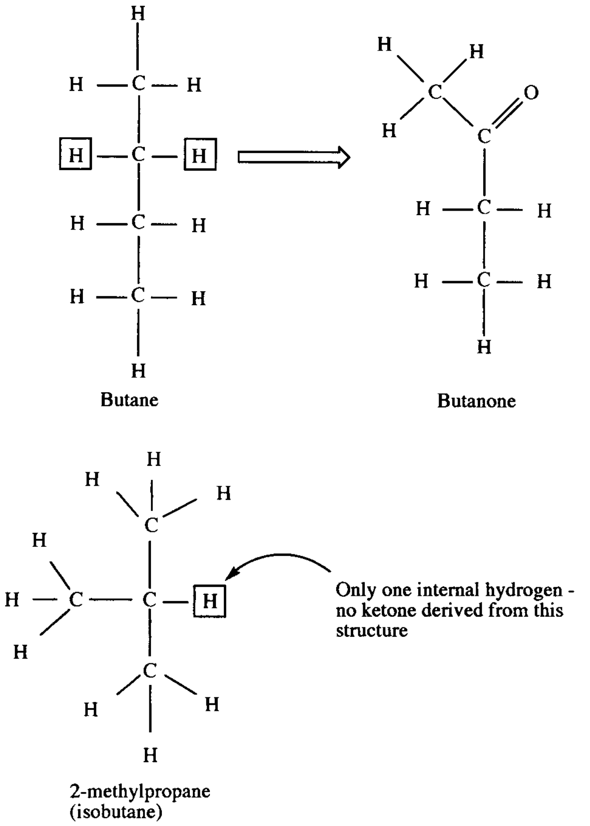


Fig. 2.9

There are three isomers of pentane. Pentane (*n*-pentane) has two distinct internal carbon environments, each with two hydrogens available for replacement (see Fig. 2.10). Thus, two ketone isomers can be derived from this structure. These are pentan-2-one and pentan-3-one, Fig. 2.10. The second isomer of pentane is 2-methylbutane and has only one internal carbon which bears two hydrogen atoms. This can generate the ketone 3-methylbutan-2-one, Fig. 2.10. The third isomer of pentane is 2,2-dimethylpropane and it has no internal carbon bearing two hydrogens and no ketone can be derived from this structure, Fig. 2.10.

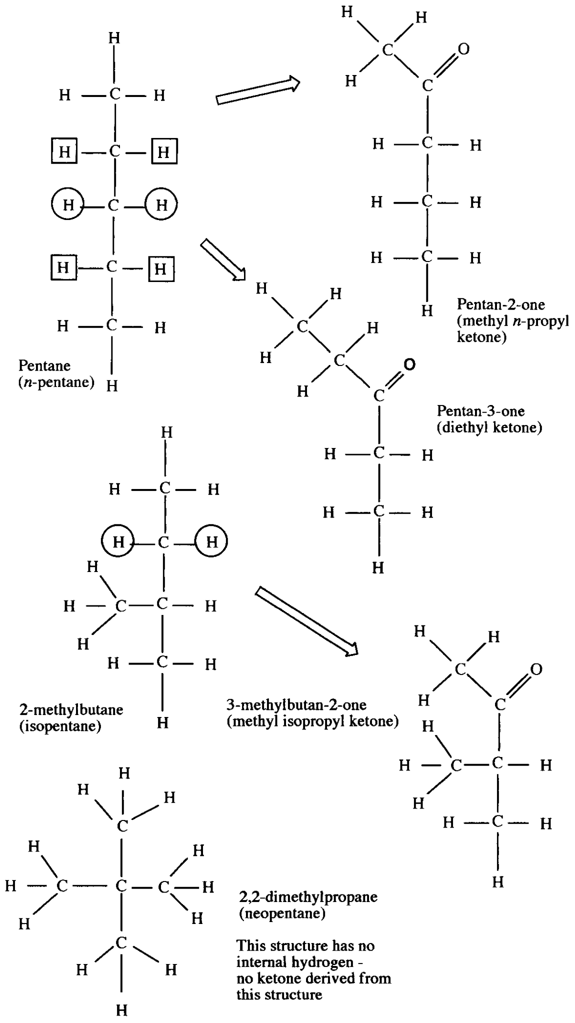


Fig. 2.10

2.4 Physical Properties of Aldehydes and Ketones

Though the hydrocarbon fragment of the molecule is essentially non-polar, the polarity of the carbonyl group causes aldehydes and ketones to become polar. Consequently, they have elevated melting and boiling points when compared with alkanes of similar molecular mass. Since all of the hydrogen atoms are bonded to carbon in aldehydes and ketones they do not share the high polarity of the hydroxyl group in alcohols. Neither do they share alcohol's ability to form strong hydrogen bonds. The melting and boiling points of the lower aldehydes and ketones are summarised in Table 2.3 and some comparative data for compounds of similar molecular mass are summarised in Table 2.4.

Name	Formula	m.p./°C	b.p./°C	Sol. in H_2O/(g/100 g)
Methanal	HCHO	- 92	-21	v. sol.
Ethanal	CH_3CHO	-121	21	∞
Propanal	C_2H_5CHO	- 81	47	16
Butanal	C_3H_7CHO	- 99	76	7
Pentanal	C_4H_9CHO	- 91	103	s. sol.
Propanone	CH_3COCH_3	- 94	56	∞
Butanone	$CH_3COC_2H_5$	- 86	80	26
Pentan-2-one	$CH_3COC_3H_7$	- 78	102	6.3
Pentan-3-one	$C_2H_5COC_2H_5$	- 41	101	5
3-methylbutan-2-one	$(CH_3)_2CHCOCH_3$	- 92	95	s. sol.

Table 2.3 *Physical properties of aldehydes and ketones*

Name (M_r)	Formula	m.p./°C	b.p./°C	Sol. in H_2O/(g/100 g)
Propan-1-ol(60)	C_3H_7OH	-126	97	∞
Propanal(58)	C_2H_5CHO	- 81	47	16
Propanone(58)	CH_3COCH_3	- 94	56	∞
Butane(58)	C_4H_{10}	-138	0	insol.

Table 2.4 *Physical properties of some compounds of similar relative molecular mass*

The polarity of aldehydes and ketones is sufficient to make the first members of the series essentially infinitely soluble in water. However, this solubility falls with increasing carbon number and only slight solubility is observed when one advances above C_5 compounds. They are, however, soluble in all of the common organic solvents. As stated in the chemistry syllabus, only a 'qualitative knowledge' of solubility is required by students.

2.5 Preparation of Aldehydes

Since aldehydes are 'sandwiched' between alcohols and carboxylic acids, it is not surprising that two of the most common synthetic routes to aldehydes involve use of these compounds or their close relatives.

The controlled oxidation of primary alcohols gives the corresponding aldehyde. Prevention of 'over oxidation' is a major consideration here as it yields the carboxylic acid.

In general, the reduction of carboxylic acids is difficult and requires very extreme conditions. Lithium aluminium hydride, $LiAlH_4$, will reduce carboxylic acids. However, it is difficult to stop the reduction at the aldehyde stage. An alternative route is to convert the carboxylic acid to the acid chloride by reaction of the acid with thionyl chloride ($SOCl_2$) or any other suitable reagent. The acid chloride is more readily reduced to the aldehyde and this can be done under less extreme conditions. In the case of aromatic aldehydes the corresponding methylbenzene compound can serve as a suitable precursor.

NB Lithium aluminium hydride and thionyl chloride are hazardous.

Lithium aluminium hydride is a flammable solid. It reacts violently with water and is harmful if swallowed. It decomposes into aluminium oxide and flammable/explosive hydrogen gas. Contact with ethyl acetate, acetonitrile or their vapours results in a violent explosive reaction. Addition to solvents such as ether, THF, etc. when peroxides are present has resulted in explosions. Handling: store in a cool dry place; keep tightly closed; contact with water may cause fire; open under argon.

Thionyl chloride is harmful if swallowed, inhaled or absorbed through the skin. It causes burns, is toxic, corrosive and lachrymatory. Water may cause a violent reaction. If decomposed, toxic fumes of hydrogen chloride and SO_x are produced. Store under nitrogen. Use only in a fume hood. Do not breathe vapour.

Oxidation of Primary Alcohols

The oxidation of primary alcohols gives the corresponding aldehyde, Fig. 2.11.

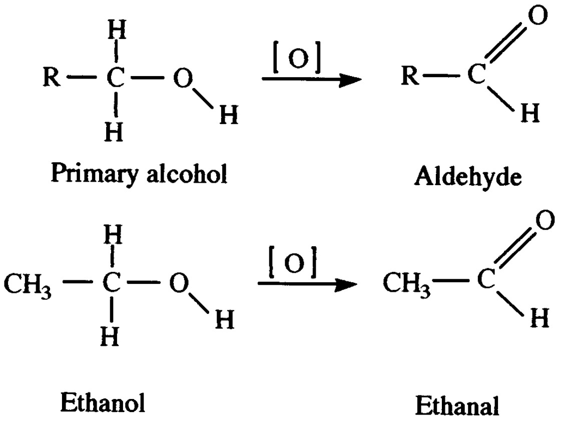


Fig. 2.11

This oxidation, though simple in principle, suffers from the fact that the aldehyde is very readily oxidised to the carboxylic acid, Fig. 2.12.

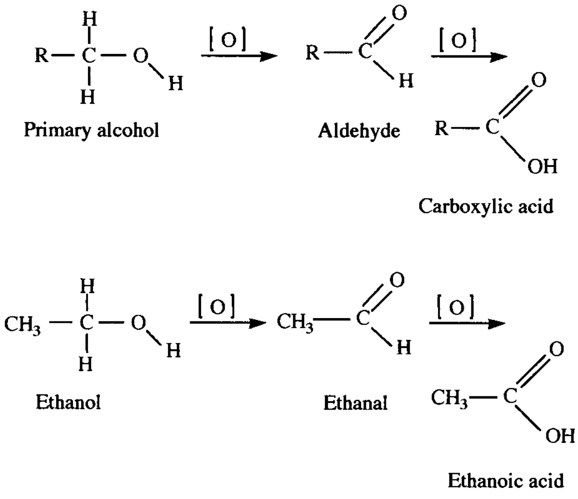


Fig. 2.12

The oxidation described in Fig. 2.12 can be achieved using acidified solutions of chromate or dichromate ions (see practical notes below). However, these conditions can give poor yields of the desired product even when all reasonable experimental precautions are applied (e.g. having less than the stoichiometric amount of oxidising agent, removal of the product as it is produced, etc. - see practical notes). Pyridinium chlorochromate ($C_5H_5NHCl.CrO_3$) is often used as an alternative reagent to oxidise primary alcohols. This reagent is much milder; the process is more easily controlled and gives good yields of aldehyde.

Though often useful in the laboratory, these reagents are expensive, and the heavy metals they contain give rise to disposal problems, so they are less suitable for bulk manufacture. On a large scale, primary alcohols can be converted into aldehydes by use of copper, silver or platinum catalysts at temperatures of 300 - 600 °C in the vapour phase. If air is present oxidation occurs, but in the absence of air the alcohol can eliminate hydrogen directly (dehydrogenation). (See Fig. 2.13.)

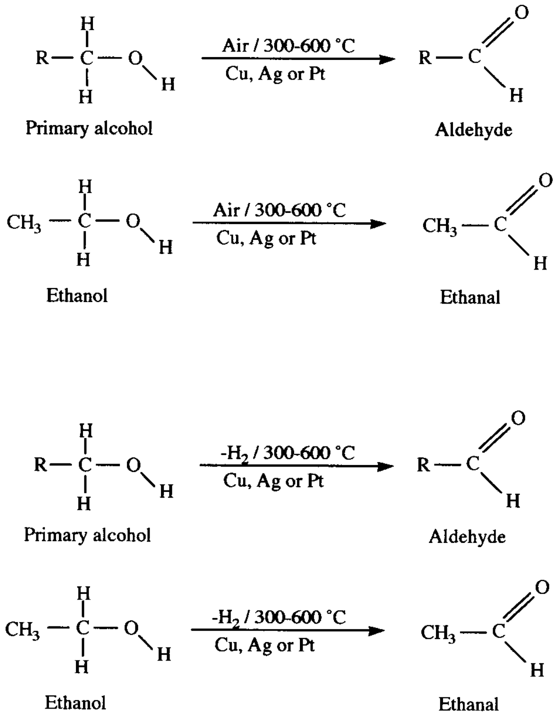


Fig. 2.13 *Air oxidation and dehydrogenation*

Experiment 2.1

Catalytic Dehydrogenation of Ethanol

When a piece of platinum wire is heated over a Bunsen flame and then placed over a small quantity of ethanol (c. 20 cm^3) which has been warmed on a hot plate, Fig. 2.14, the following observations are made.

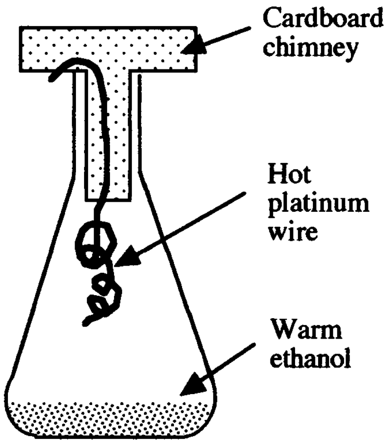


Fig 2.14

The platinum wire glows. This is followed by a brief ‘flash’ or ‘pop’ and the complete cycle repeats. This can go on for some time. The distinctive irritating odour of ethanal may also be detected.

These observations are explained as follows. The ethanol undergoes catalytic dehydrogenation on the hot platinum, generating ethanal and hydrogen gas. The hydrogen (and the ethanal) ignite when mixed with air over the hot catalyst. This causes the flash/pop.

A piece of heavy copper wire can be used instead of platinum. The cardboard chimney helps create a ‘draught’ of alcohol vapour over the hot wire catalyst. However, the cardboard sometimes ignites. The experiment can also be done without the cardboard.

The other synthetic methods of preparing aldehydes mentioned above are not detailed here.

Experiment 2.2

Preparation and Properties of Ethanal

Ethanal can be prepared in the laboratory by the oxidation of ethanol using sodium dichromate and sulphuric acid. Ethanal, like aldehydes in general, is very susceptible to oxidation to the carboxylic acid.

As a consequence of this, the quantity of oxidant is kept to the minimum and the reaction procedure is designed so that the ethanal is removed by distillation as it is produced. A suitable arrangement of apparatus is illustrated in Fig. 2.15.

$$3C_2H_5OH + Na_2Cr_2O_7 + 4H_2SO_4 \longrightarrow 3CH_3CHO + Cr_2(SO_4)_3 + Na_2SO_4 + 7H_2O$$

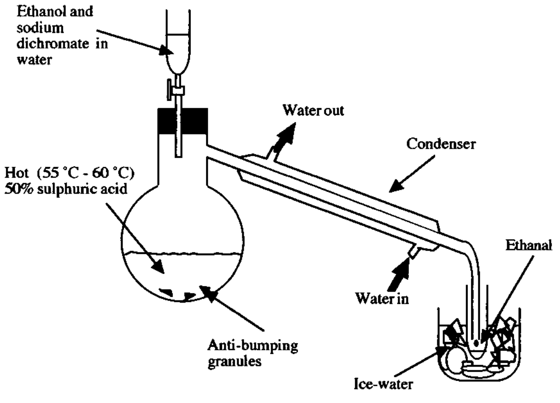


Fig. 2.15

Ethanal is a colourless liquid which is very volatile (b.p. 21 °C) with an irritating odour.

The ionic equation for the above reaction is:

$$3C_2H_5OH + Cr_2O_7^{2-} + 8H^+ \rightarrow 3CH_3CHO + 2Cr^{3+} + 7H_2O$$

Notes on preparation

1. The amount of oxidising agent is controlled/limited in this reaction to that amount (or slightly less than that amount) which would be exactly required to oxidise the alcohol as far as the aldehyde only. This is done in an attempt to increase the likelihood of producing the desired product, as excess oxidising agent would greatly increase the chances of ‘over oxidation’ to produce the carboxylic acid. In a further attempt to produce the desired product, the aldehyde is distilled off as it is produced, thus limiting the chances of it being further oxidised. Yields should always be calculated based on the amount of whichever reagent limits the maximum yield. This reagent is termed the limiting reagent.

2. The purpose of the water in the dropping funnel is not only to dilute the alcohol (thus making the reaction less vigorous), but, more importantly, to act as solvent to the oxidising agent since sodium dichromate is not soluble in alcohol. The oxidant is added from the dropping funnel with the alcohol so as to limit the amount of oxidant available at any time and so help decrease the likelihood of ‘over oxidation’.

3. The reaction vessel is heated to about 50 - 60 °C before the addition is made and the heating suspended when the addition of the reagents is started. The reaction is exothermic and addition of the reagents should be at a rate which will give a steady but not too vigorous reaction. The initial temperature is kept in this region as ethanol boils at 78 °C and it would simply distil over if the temperature in the reaction vessel were to get too high.

4. Ethanal, which has a boiling point of 21 °C, is very volatile, so the receiving vessel should be cooled in an ice-water bath, or, better, an ice-salt bath which can reduce the temperature to -15 °C. If a two-necked flask is available a thermometer can be inserted to monitor the boiling range of the product as it distils off.

5. When the addition is started and reaction occurs the colour of the mixture in the reaction vessel changes from colourless (sulphuric acid solution) to green as Cr^{3+} ions are generated. The oxidising agents used are Cr(VI) salts and these have a yellow (chromate, CrO_4^{2-}) or orange (dichromate, $Cr_2O_7^{2-}$) colour.

6. The purpose of the boiling chips (anti-bumping granules, pumice stones or pieces of porcelain) is to prevent bumping of the mixture.

7. Note that from the point of view of oxidation numbers the conversion of an alcohol to an aldehyde is a two-electron loss process and each Cr(VI) ion in the oxidising agent can gain three electrons, so the ratio of alcohol to Cr(VI) reacting is 3:2.

Tests on the collected ethanal

1. **Combustion**
   Ethanal burns with a clean (non-smoky) flame.

$$2CH_3CHO + 5O_2 \rightarrow 4CO_2 + 4H_2O$$

2. **Reaction with 2,4-dinitrophenylhydrazine**
   An orange-yellow precipitate of the 2,4-dinitrophenylhydrazone results. This test is taken as confirming the presence of the carbonyl group of an aldehyde or ketone.

$$CH_3CHO + (NO_2)_2C_6H_3NHNH_2 \rightarrow CH_3CHNNHC_6H_3(NO_2)_2 + H_2O$$

3. **Tests to distinguish aldehydes from ketones**
   Because aldehydes are readily oxidised to the corresponding carboxylic acids, while ketones are not as easily oxidised, reactions involving mild oxidation are used to differentiate between aldehydes and ketones.

   a) **Fehling's test**
   This uses a mixture of two solutions, Fehling's solutions 1 and 2. The blue solution contains copper sulphate and the colourless solution contains soldium hydroxide with some tartrate salt added (to keep the copper(II) ions in solution when the two solutions are mixed). Equal volumes of Fehling's solutions 1 and 2 are added to the aldehyde and the mixture heated gently (a hot water bath is suitable). A brick-red precipitate of copper(I) oxide results as the aldehyde is oxidised and copper(II) ions are reduced to copper(I).

$$CH_3CHO + 2Cu(OH)_2 \rightarrow CH_3COOH + Cu_2O + 2H_2O$$

   b) **Tollens' test (silver mirror test)**
   This uses an ammoniacal solution of silver nitrate. The aldehyde is mixed with a small amount of the Tollens' reagent in a clean test-tube and the mixture heated gently. A silver mirror is formed on the inside of the test-tube. In this test the aldehyde is again oxidised, but here the silver(I) ions are reduced to silver(0).

$$CH_3CHO + Ag_2O \rightarrow CH_3COOH + 2Ag$$

Preparation of 2,4-dinitrophenylhydrazine Solution

To a dry flask add 2,4-dinitrophenylhydrazine (4 g) and methanol or ethanol (100 cm^3). Slowly add concentrated sulphuric acid (5 cm^3) and warm the mixture until a clear solution is produced. This solution can be stored for long periods.

Tollens' Reagent

To aqueous silver nitrate (5 cm^3) add a few drops of dilute sodium hydroxide solution. Then add just sufficient dilute aqueous ammonia to redissolve the precipitate of silver oxide. For safety reasons Tollens' reagent should be made in small quantities as required. It should not be stored as it may produce explosive residues; it should be disposed of immediately after use.

2.6 Preparation of Ketones

Probably the most common route to aliphatic ketones is the oxidation of secondary alcohols. Reaction of organocadmium compounds (Grignard-type compounds) with acid chlorides is also a useful route to ketones. Aromatic ketones can be synthesised using reactions specific to aromatic systems such as the Friedel-Crafts reaction.

Oxidation of Secondary Alcohols

Any of the oxidising reagents described above for the synthesis of aldehydes can also be employed in the synthesis of ketones with the added advantage that the ketone is not nearly as likely to be oxidised as its aldehyde relation. Chromate or dichromate ion can be used under acidic conditions to effect the reactions described in Fig. 2.16.

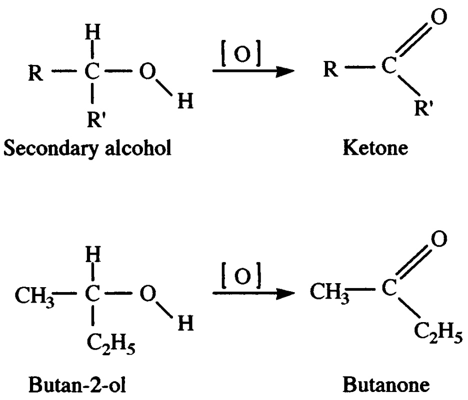


Fig. 2.16

The large-scale conversion of secondary alcohols to ketones can be carried out either by controlled catalytic air oxidation of the alcohol or catalytic dehydrogenation, Fig. 2.17.

These conditions are preferred industrially as they are cheaper and, because they do not use heavy metal salts as oxidising agents, the problem of heavy metal wastes is avoided.

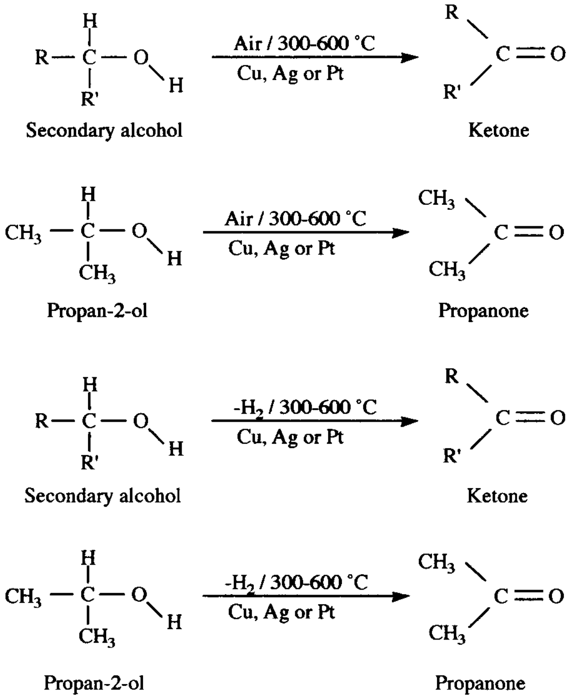


Fig 2.17 *Air oxidation and dehydrogenation*

The other synthetic routes to ketones mentioned above are not discussed further here.

Experiment 2.3

Preparation and Properties of Propanone

Propanone can be prepared by the oxidation of propan-2-ol (2-propanol, isopropyl alcohol) using sodium dichromate and sulphuric acid. Propanone, unlike aldehydes, is not very susceptible to oxidation. It is, however, reasonably volatile with a boiling point of 56 °C and is best collected as it is produced, as in the preparation of ethanal. The efficient cooling of the collection vessel is not as critical as in the preparation of ethanal but is none the less worthwhile. The quantity of oxidising agent is not as critical here as the product is not as susceptible to oxidation as the aldehydes. A suitable arrangement of apparatus is illustrated in Fig. 2.18. The common name for propanone is acetone.

$$3C_3H_7OH + Na_2Cr_2O_7 + 4H_2SO_4 \longrightarrow 3CH_3COCH_3 + Cr_2(SO_4)_3 + Na_2SO_4 + 7H_2O$$

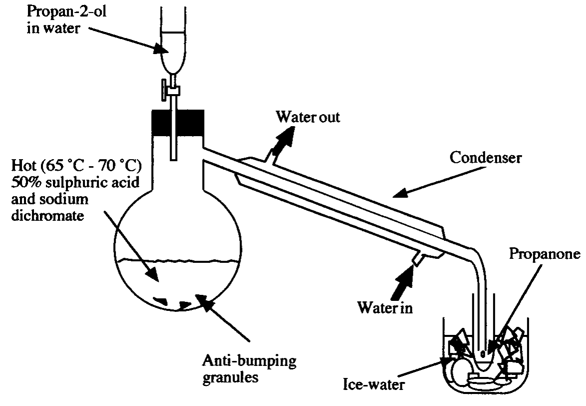


Fig 2.18

Notes on preparation

1. The amount of oxidising agent does not have to be controlled in this reaction. The problem of ‘over oxidation’ is not major as ketones are much more difficult to oxidise than aldehydes. Hence the oxidising agent is placed in the reaction vessel in this reaction, rather than added from the dropping funnel. Yields should always be calculated based on the amount of whichever reagent limits the maximum yield.

2. The purpose of the water in the dropping funnel is to dilute the alcohol. It allows the alcohol to be added in smaller quantities, which are of low concentration, thus making the reaction less vigorous.

3. The reaction vessel is heated to about 70 - 80 °C before the addition is made and the heating suspended when the addition of the reagents is started. The reaction is exothermic and addition of the reagents should be at a rate which will give a steady but not too vigorous reaction. The initial temperature is kept in this region as the propan-2-ol would distil over if the temperature in the reaction vessel were to get too high (b.p. of propan-2-ol is 97 °C).

4. The need for the receiving vessel to be efficiently cooled is not as great here as in the case of the preparation of ethanal since the boiling point of propanone is 56 °C. Cooling is still worthwhile to prevent escape of the volatile product and can be achieved using an ice-water bath. If a two-necked flask is available a thermometer can be used to monitor the temperature at which the product distils off.

5. When the addition is started and reaction occurs the colour of the mixture in the reaction vessel changes from the orange Cr(VI) salt to green as Cr^{3+} ions are generated.

6. The purpose of the boiling chips is to prevent bumping of the reaction mixture.

7. Note that from the point of view of oxidation numbers the conversion of an alcohol to a ketone is a two-electron loss process and each Cr(VI) in the oxidising agent can gain three electrons, so the ratio of alcohol to Cr(VI), reacting is 3:2.

Tests on the collected propanone

1. **Physical properties**

   Propanone is a colourless liquid. It is fairly volatile and has a pleasant odour.

2. **Combustion**

   Propanone burns with a clean (non-smoky) flame

   $$CH_3COCH_3 + 4O_2 \rightarrow 3CO_2 + 3H_2O$$

3. **Reaction with acidified 2,4-dinitrophenylhydrazine**

   An orange-yellow precipitate of the 2,4-dinitrophenylhydrazone results. This result is normally taken as indicative of the presence of the carbonyl group of an aldehyde or ketone.

   $$CH_3COCH_3 + (NO_2)_2C_6H_3NHNH_2 \rightarrow (CH_3)_2CNNHC_6H_3(NO_2)_2 + H_2O$$

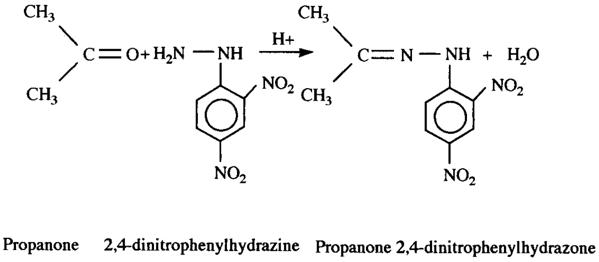


Fig. 2.19

4. Tests to distinguish aldehydes from ketones

Because aldehydes are readily oxidised to the corresponding carboxylic acids while ketones are not as easily oxidised, reactions involving mild oxidation are used to differentiate between aldehydes and ketones.

(a) Fehling's test

This uses a mixture of two solutions, Fehling's solutions 1 and 2. The blue solution contains copper sulphate and the colourless solution contains sodium hydroxide solution with some tartrate salt added (to keep the copper(II) ions in solution when the two solutions are mixed). Equal volumes of Fehling's solutions 1 and 2 are added to the ketone and the mixture heated gently. No reaction occurs.

$$CH_3COCH_3 + Cu(OH)_2 \rightarrow \text{NO REACTION}$$

(b) Tollens' test (silver mirror test)

This uses an ammoniacal solution of silver nitrate. The ketone is mixed with a small amount of the Tollens' reagent and the mixture heated gently. No reaction occurs.

$$CH_3COCH_3 + Ag_2O \rightarrow \text{NO REACTION}$$

2.7 Social and Applied Information on Aldehydes and Ketones

Aldehydes

Methanal (formaldehyde), HCHO

Methanal is a pungent, colourless gas. It is soluble in water. In laboratories it is most commonly found as a 40% solution in water (formalin). It is used as a sterilising agent in biology. Solutions of concentration of about 10% methanal are sufficient for this purpose. Biological specimens can be preserved in methanal. It is used to kill anthrax spores in wool and in the treatment of hides. It is also present in wood smoke and is one of the agents in wood smoke which is responsible for the preservation of the food.

Methanol is metabolised to methanal. The enzyme which does this is present in significant quantities in the retina of the eye. The methanal produced couples with retinal proteins, removing them from active participation in vision. It also inhibits oxygenation of the retina. Low doses can result in blindness.

Methanal is used in the manufacture of 'bakelite'.

Ethanal (acetaldehyde), CH_3CHO

Ethanal is a pungent, colourless liquid, b.p. 21 °C. It is metabolite of ethanol (see ethanol, section 1.7).

Benzaldehyde, C_6H_5CHO

Benzaldehyde is a colourless liquid. It smells of bitter almonds. The smell associated with cherries and almonds is due principally to benzaldehyde. Hydrogen cyanide also has an almond odour and is also present. The Romans and Egyptians extracted this poison by grinding peach kernels.

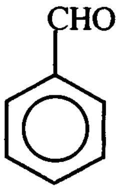


Fig. 2.20 *Benzaldehyde*

Almond oil is used in the beauty therapy industry in warm face masks as an emollient (these have a softening effect on skin).

Vanillin, $C_8H_8O_3$

Vanillin is the essential component of oil of vanilla. Oil of vanilla is produced from the dried fermented seed pods of the vanilla orchid and originates mainly from Madagascar, Mexico and Tahiti. Vanillin is used widely in the perfume and confectionery industries. It is detectable in very low concentrations. Vanillin is leached out of European oak barrels in the ageing process of wines.

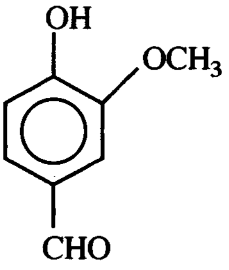


Fig 2.21 Vanillin

Cinnamaldehyde, C6H5CHCHCHO

Cinnamaldehyde occurs in oil of cinnamon. It can be isolated by steam distillation of the bark of the cinnamon tree. Cinnamon sticks are the dried inner bark from the cinnamon tree and cinnamon powder is this bark ground up.

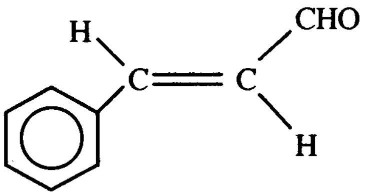


Fig 2.22 Cinnamaldehyde

Acrolein, CH2CHCHO

Acrolein is a volatile aldehyde with an acrid odour. It contributes to the smell of meat being cooked on a barbecue. It results from a glycerol molecule losing two molecules of water. It also contributes to the smell associated with caramel prepared by the heating of sucrose.

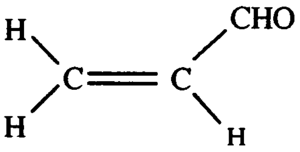


Fig. 2.23 Acrolein

Ketones

Propanone (acetone), CH_3COCH_3

Acetone is a widely used solvent. It is used in many lacquers and paints. In the cosmetics industry it is used in nail varnish removers; usually an oil such as lanolin or castor oil is added to reduce the degreasing effect of the solvent.

Butanone (ethyl methyl ketone), $CH_3COCH_2CH_3$

Butanone is used in the pharmaceuticals industry in the extraction of antibiotics.

Butanedione (diacetyl), $CH_3COCOCH_3$

Butanedione is a diketone with a cheese-like smell. It is the compound which gives butter its characteristic flavour. It is also the odour associated with body odour or sweat. Fresh sweat is almost odourless. The action of bacteria on sweat produces butanedione and other pungent compounds.

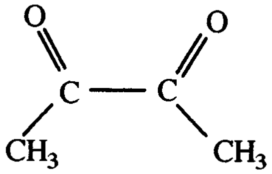


Fig. 2.24 Butanedione

Carvone, $C_{10}H_{14}O$

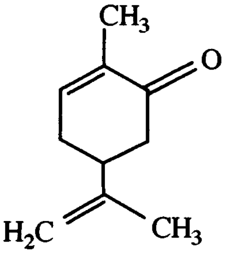


Fig. 2.25 Carvone

Carvone is the main component of oil of spearmint. It is the traditional flavouring for chewing gum. It belongs to the family of essential oils known as terpenes as it is derived from two 2-methylbut-1-ene (isoprene) units.

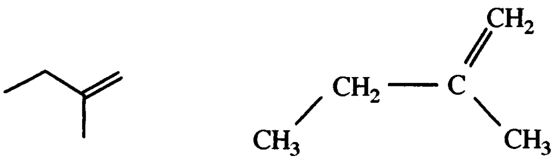


Fig. 2.26 2-methylbut-1-ene (isoprene)

2.8 Reactions of Aliphatic Aldehydes and Ketones

The chemistry of aldehydes, RCHO, and ketones, RCOR^{I}, is mainly dictated by the carbonyl, C=O, functional group. Two features of the functional group contribute to the understanding and predicting of the chemical behaviour of these series of compounds. The first is that the polarity of the carbonyl group and its low level of steric crowding makes it a prime target for nucleophilic attack. Nucleophilic attack involves an electron-rich species (normally with a lone pair of electrons) attacking an electron-poor atom (one which is attached to a more electronegative element). Thus, the carbonyl carbon is the centre of reaction, Fig. 2.27.

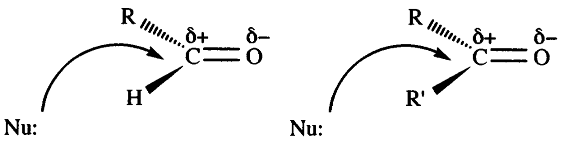
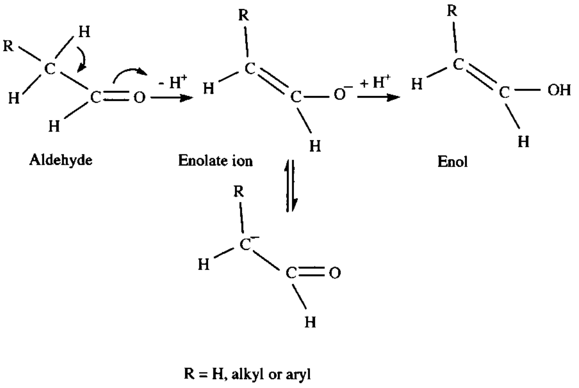


Fig. 2.27

The second relates to tautomerism (rearrangement) of the aldehyde or ketone to form an enol and the slight acidity of the hydrogens on a carbon α to a carbonyl group, Fig. 2.28(a) and 2.28(b). This results in reactions at the carbon α- to the carbonyl of the aldehyde or ketone. This allows a variety of useful alkylation and condensation reactions.



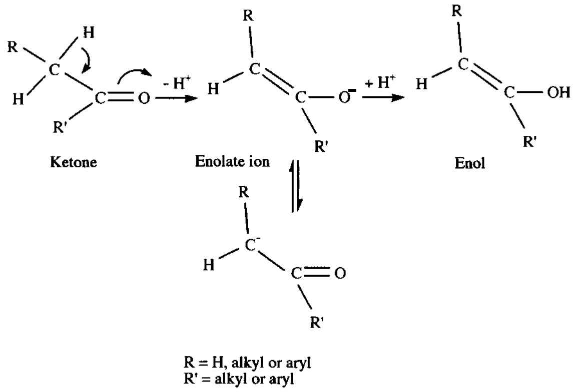
Aldehyde

Enolate ion

Enol

R = H, alkyl or aryl

Fig. 2.28(a)



Ketone

Enolate ion

Enol

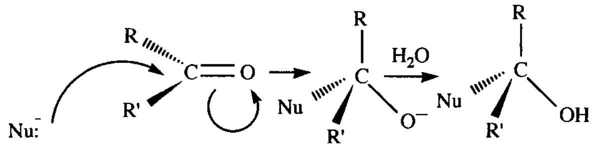
R = H, alkyl or aryl
R' = alkyl or aryl

Fig. 2.28(b)

There are some differences in the reactions of aldehydes and ketones. These arise mainly from the ability of aldehydes to undergo mild oxidation (as there is a hydrogen on the carbonyl carbon). These reactions will be treated separately under the heading 'Oxidation of Aldehydes and Ketones', p. 40.

Reactions Involving Nucleophilic Attack on the Carbonyl Group

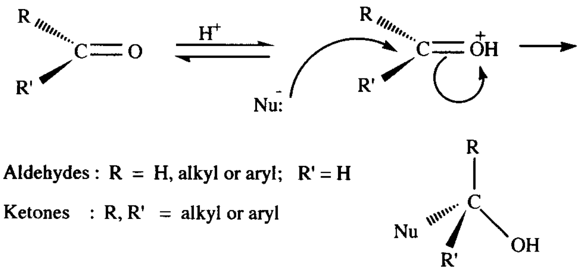
Reactions of aldehydes and ketones involving attack of a nucleophile on the carbonyl group are extensive and form the basis of much of the chemistry of aldehydes and ketones. Indeed, nucleophilic reactions can be considered the typical reactions of aldehydes and ketones. The polarity and the openness of the carbonyl group make it an ideal site for nucleophilic attack. The basic mechanism is outlined in Fig. 2.29(a). The process can be catalysed by acids and the acid-catalysed mechanism is outlined in Fig. 2.29(b).



Aldehydes : R = H, alkyl or aryl; R' = H

Ketones : R, R' = alkyl or aryl

Fig. 2.29(a)



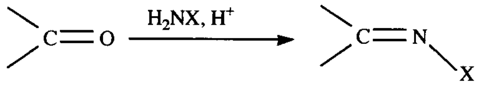
Aldehydes : R = H, alkyl or aryl; R' = H

Ketones : R, R' = alkyl or aryl

Fig. 2.29(b)

Condensation with derivatives of ammonia

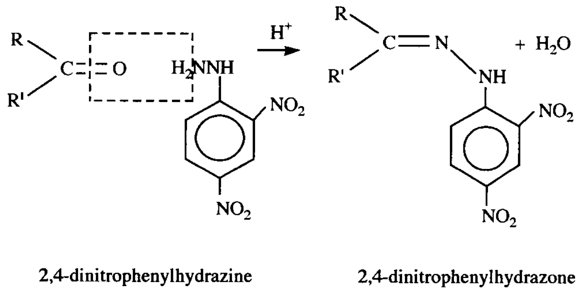
Under acidic conditions aldehydes and ketones undergo condensation reactions with a variety of ammonia derivatives, Fig. 2.30.



H_2NX	Reagent	Product
X = OH	hydroxylamine	oxime
= NH_2	hydrazine	hydrazone
= NHAr	arylhydrazine	arylhydrazone
= $NHCONH_2$	semicarbazide	semicarbazone

Fig. 2.30

Of these, hydrazone formation, and in particular formation of hydrazones using 2,4-dinitrophenylhydrazine, is probably the most familiar reaction. Historically, aldehydes and ketones were difficult to purify and identify. Many were oils and as such were more difficult to purify and identify than solids. They were routinely converted to the corresponding 2,4-dinitrophenylhydrazone which had two positive effects. One was the fact that the hydrazone was a solid and could therefore be purified by recrystallisation. It could then be identified using the technique of melting points and mixed melting points. The second was the fact that in forming the hydrazone the weight of the sample was increased, resulting in easier handling and characterisation, Fig. 2.31.



Aldehydes : R = H, alkyl or aryl; R' = H

Ketones : R, R' = alkyl or aryl

Fig. 2.31

Hydrazones are often orange-yellow solids and the reaction of a compound with 2,4-dinitrophenylhydrazine to give an orange-yellow precipitate is normally taken as indicative of the presence of a carbonyl functional group.

One of the advantages of incorporating nitro groups into the hydrazone molecule is the fact that compounds containing nitro groups tend to form crystals more easily and therefore lend themselves to purification by recrystallisation. They are also good for producing single crystals for crystallographic analysis.

Mechanism of reaction of aldehydes and ketones with hydrazine related compounds

In each case the reaction proceeds by nucleophilic attack of the ammonia derivative on the carbonyl carbon of the protonated carbonyl group, Fig. 2.32.

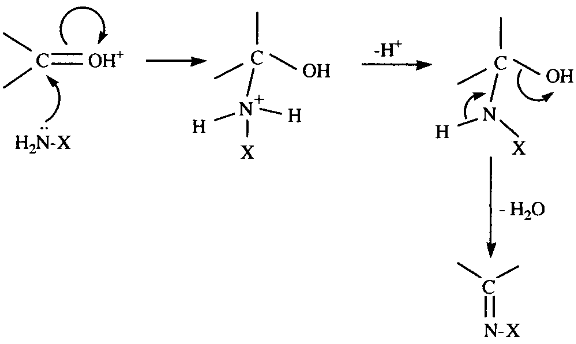


Fig. 2.32

Some other reactions which have mechanistic similarities to these and are of synthetic significance include:

1. the addition of ammonia, which can be followed by reduction using hydrogen over a catalyst such as nickel to produce primary amines;

2. the addition of hydrogen cyanide in cyanohydrin formation - cyanohydrins are a precursor of α-hydroxycarboxylic acids;

3. the addition of Grignard reagents, which is a method of producing secondary alcohols from aldehydes and tertiary alcohols from ketones;

4. the addition of alcohols in hemi-acetal, acetal, hemi-ketal and ketal formation - acetals and ketals are often used to protect the aldehyde and ketone functional groups during complex synthetic procedures.

These reactions are not discussed further here.

Oxidation of Aldehydes and Ketones

This is an area where the difference between aldehydes and ketones is most evident. Aldehydes are readily oxidised to carboxylic acids while ketones are not. The reason for this stems directly from the structural difference between aldehydes and ketones. Aldehydes have a hydrogen on the carbonyl carbon, ketones do not. In the oxidation reaction this hydrogen is lost and replaced by a hydroxyl group, Fig. 2.33. The analogous reaction for a ketone would involve removal of an alkyl or aryl group and this does not occur.

Oxidation of aldehydes

Aldehydes are easily oxidised to carboxylic acids. In fact they will quickly show signs of air oxidation if left in contact with air.

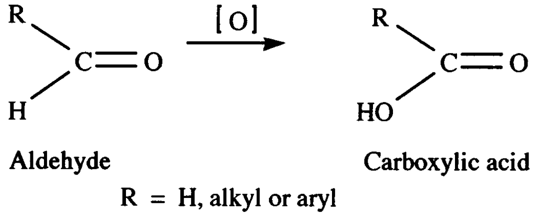


Fig. 2.33

In the laboratory the oxidation of aldehydes can be achieved using chromium(VI) salts or potassium manganate(VII) (potassium permanganate) under acidic conditions, Fig. 2.34.

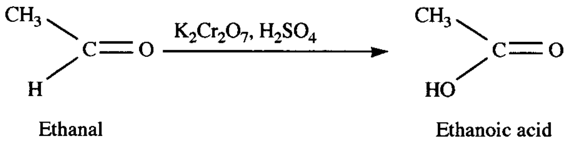


Fig. 2.34

Mechanistically, the reaction is thought to proceed by nucleophilic attack of chromate or dichromate ion on the carbonyl carbon. The stoichiometry and experimental details of this reaction are treated in the practical notes.

Aldehydes can be oxidised under very mild conditions using ammoniacal silver ions. The silver is reduced to silver metal and the aldehyde oxidised to the carboxylate ion. This reaction is regularly used to distinguish between aldehydes and ketones as ketones do not act as weak reducing agents. The ammoniacal silver nitrate reagent is known as Tollens' reagent and a positive result leaves a silver mirror on the inside of the reaction vessel (e.g. test-tube). The reaction equation can be balanced using oxidation numbers since the carbonyl carbon of the aldehyde undergoes an increase in oxidation number of 2 and the silver ions undergo a reduction in oxidation number of 1. Thus, two silver ions react with one aldehyde molecule. An example is given in Fig. 2.35.

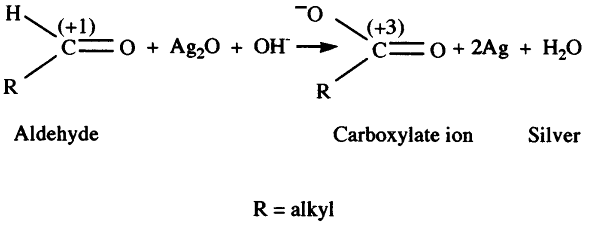


Fig. 2.35

In a similar reaction copper(II) ions can be reduced under alkaline conditions to produce red copper(I) oxide, Fig. 2.36. Again this reaction has some application in distinguishing aldehydes and ketones. The copper(II) ions are held in solution in Fehling's solution complexed to tartrate ions and in Benedict's solution using citrate ions.

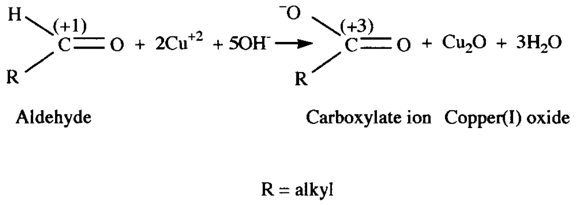


Fig. 2.36

While these tests are useful for simple compounds they are far from absolute in their results. For example, α-hydroxy ketones give a positive test with Tollens' and Fehling's reagents.

Oxidation of methyl ketones

While ketones are not as readily oxidised as aldehydes it is not true to say that they cannot be oxidised at all. Severe or specific conditions, however, are required. Methyl ketones undergo a very specific oxidation process when reacted with halate(I) (hypohalite ion) under alkaline conditions, Fig. 2.37. The reaction is known as the haloform reaction, since the methyl group of the ketone is converted to trihalomethane (i.e. haloform). The other product is a carboxylic acid. It should be noted here that the carbon skeleton has been shortened by one carbon in the process.

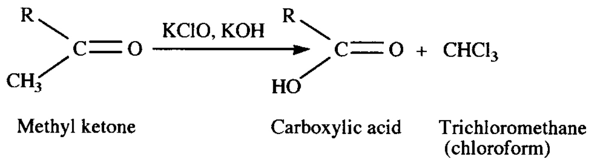


Fig. 2.37

Reduction of aldehydes and ketones

Both aldehydes and ketones can be reduced. Under differing conditions they may be reduced to alcohols or directly to the hydrocarbon.

Reduction to alcohols

Reducing agents such as lithium aluminium hydride can be used. In the case of aldehydes a primary alcohol results and in the case of ketones a secondary alcohol is produced, Fig. 2.38.

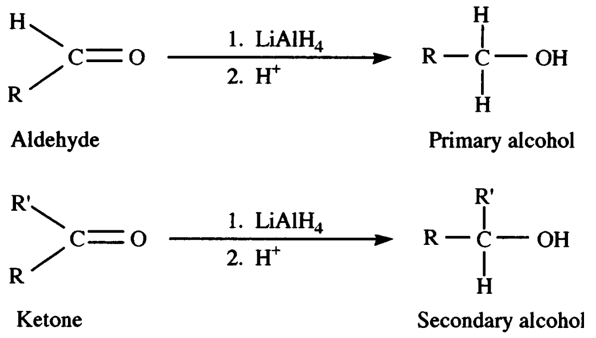


Fig. 2.38

This reduction can also be achieved by hydrogenation using hydrogen gas over a nickel, platinum or palladium catalyst. It is this catalytic route which is preferred industrially in the reduction of aldehydes and ketones, Fig. 2.39.

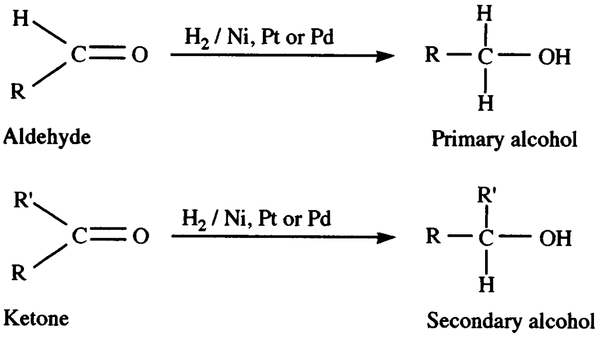


Fig. 2.39

Reduction to hydrocarbons

Aldehydes and ketones can be reduced to hydrocarbons using the Clemmensen reduction and the Wolff-Kischner reduction. The details of these reactions are not discussed here. It is interesting to note that the Clemmensen reduction and the Wolff-Kirshner reduction are complementary as the Clemmensen reduction is suitable for base-sensitive compounds while the Wolff-Kirshner reduction is suitable for acid-sensitive compounds.

Reactions of carbanions

Hydrogens α to a carbonyl group in aldehydes and ketones (and esters) are very slightly acidic. In fact tautomerism occurs, with proton switching as described in Fig. 2.28(a) and Fig. 2.28(b), p. 38.

Many reactions proceed via the enol form even though the equilibrium normally favours the carbonyl form by several orders of magnitude.

Where strong bases are used the enolate ion can be generated quantitatively. The enolate ion is stabilised by resonance where the charge is shared between the α-carbon and the oxygen. This possibility of placing the charge on a hetero-atom such as oxygen is good in terms of stabilisation, Fig. 2.40. Small quantities of weak base increase the equilibrium concentration of enol and enolate ion, thus enhancing reaction rates for reactions which go through the enol form.

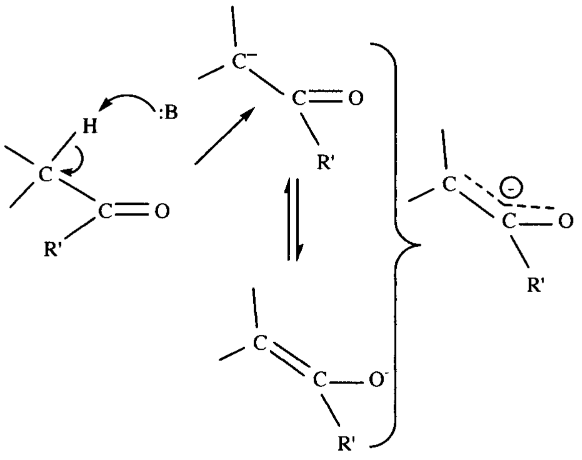


Fig. 2.40

Acids also increase the rate of enolisation and hence the rate of reactions which go through the enol form. The acid is a true catalyst in these reactions as it is not consumed in the process. This contrasts with bases where they are not true catalysts as they accept a proton and usually remain protonated at the end of the process.

Reactions which proceed via the enol form include the following.

Halogenation α to a carbonyl

Successive hydrogens on a carbon α to a carbonyl group in an aldehyde or ketone can be substituted by a halogen by direct reaction with the halogen in the presence of base or trace catalytic quantities of acid, Fig. 2.41.

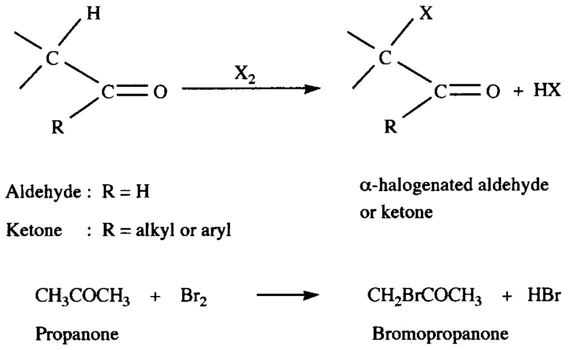


Fig. 2.41

Aldol condensation

The aldol condensation reaction is a reaction of synthetic importance which occurs between two molecules of an aldehyde or ketone in the presence of dilute acid or base. The reaction yields a β-hydroxyaldehyde or β-hydroxyketone. Essentially, the reaction is the reaction of one molecule of aldehyde or ketone with the enol of that aldehyde or ketone. It is not discussed further here.

The Wittig reaction

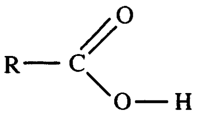
The Wittig reaction is named after the German chemist Georg Wittig who first reported it in 1954 while working at the University of Tübingen in Germany. The reaction can be used to make asymmetric alkenes using aldehydes and ketones. The conversion occurs under mild conditions and is specific in the placement of the alkene function.

Again, this reaction is of synthetic significance though details of the reaction are not discussed here.

CHAPTER 3 CARBOXYLIC ACIDS

3.1 Introduction

Carboxylic acids are characterised by the presence of the carboxyl group (-COOH). Saturated aliphatic monocarboxylic acids are compounds of the general formula RCOOH, where R is a hydrogen, alkyl or substituted alkyl group, Fig. 3.1. Aromatic carboxylic acids have R equal to an aryl group, Fig. 3.1.

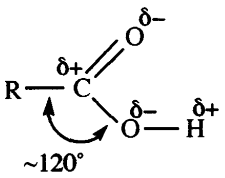


R = H, alkyl or aryl

Carboxylic acids

Fig. 3.1

The carboxyl group has a trigonal planar arrangement of atoms about the carboxyl carbon. The bond angles are about 120°. The high difference in electronegativity between carbon and oxygen and between hydrogen and oxygen results in significant polarity within the molecule, Fig. 3.2.



R = H, alkyl or aryl

Fig. 3.2

The presence of the carboxyl group dictates the main chemical and physical characteristics of the compounds. Like aldehydes and ketones the uncrowded nature of the carboxyl carbon and polarity of the carbonyl group have a major influence on the chemistry of carboxylic acids. In addition, the hydrogen of the carboxyl group is acidic and is readily lost as H^+. Thus, carboxylic acids have a number of reactions typical of acids. The R group attached to the carboxylic carbon may be an alkyl group which is open-chain or branched in nature. It may contain multiple bonds, a halogen or indeed an aromatic group, Fig. 3.3.

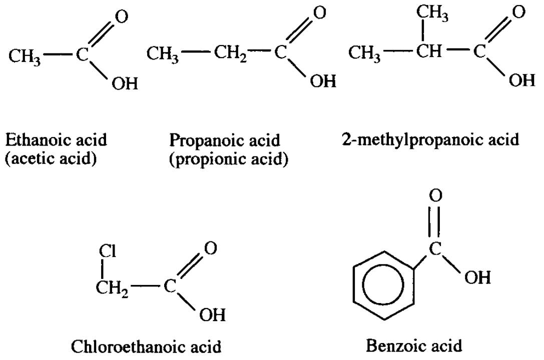


Fig. 3.3 *Some examples of carboxylic acids*

The chemistry of carboxylic acids is similar for most of the carboxylic acids but there are differences in chemical behaviour associated with some members. These differences are consistent with, and can be explained by, consideration of their structural differences. The chemistry of carboxylic acids will be treated in a general way and any notable differences or exceptions in behaviour will be referred to and explained as they arise in the following material.

3.2 Naming of the Carboxylic Acids

Nomenclature of the Aliphatic Carboxylic Acids

Saturated aliphatic monocarboxylic acids form a homologous series of the general formula $C_nH_{2n+1}COOH$ ($n \geq 0$). They can be viewed essentially as alkanes where three of the hydrogen atoms of a terminal carbon have been replaced by a doubly-bonded oxygen forming a carbonyl group, C=O, and a hydroxyl group, -OH, to form the carboxyl functional group, -COOH. Their names are derived from that of the 'parent' alkane with an 'oic acid' replacing the final 'e' to signify the presence of the carboxyl functional group. Thus, the name of the carboxylic acid derived from methane is methanoic acid, the acid derived from ethane is ethanoic acid, etc. Since the carboxyl group has to occur on a terminal carbon of the carbon chain or side chain (the -COOH group has a valency of 1, hence it cannot occur internally in a chain) there is no need to include a number as part of the name. However, numbers will occur in the name to indicate the location of other groups attached to the basic skeleton of the molecule. The names of the first ten members of the aliphatic carboxylic acids are given in Table 3.1. Isomerism in acids up to C_4 is considered below.

IUPAC Name	Common Name	Formula
Methanoic acid	Formic acid	HCOOH
Ethanoic acid	Acetic acid	CH_3COOH
Propanoic acid	Propionic acid	C_2H_5COOH
Butanoic acid	Butyric acid	C_3H_7COOH*
Pentanoic acid		C_4H_9COOH*
Hexanoic acid		$C_5H_{11}COOH$*
Heptanoic acid		$C_6H_{13}COOH$*
Octanoic acid		$C_7H_{15}COOH$*
Nonanoic acid		$C_8H_{17}COOH$*
Decanoic acid		$C_9H_{19}COOH$*

Table 3.1 *Names of aliphatic carboxylic acids (*More than one structurally isomeric carboxylic acid exists for this formula.)*

Structure of the Carboxylic Acids - Building Up the Aliphatic Carboxylic Acids (C_1 - C_4)

When considering isomerism in carboxylic acids it is convenient to view carboxylic acids essentially as alkanes where three of the hydrogen atoms of a terminal carbon have been replaced by a doubly-bonded oxygen forming a carbonyl group, C=O, and a hydroxyl group, -OH, to form the carboxyl functional group, -COOH. Thus, methanoic acid has only one possible isomeric structure as all of the hydrogens in methane are identical. Similarly, ethanoic acid has only one isomer as all six of the hydrogens in ethane occupy identical environments, Fig. 3.4.

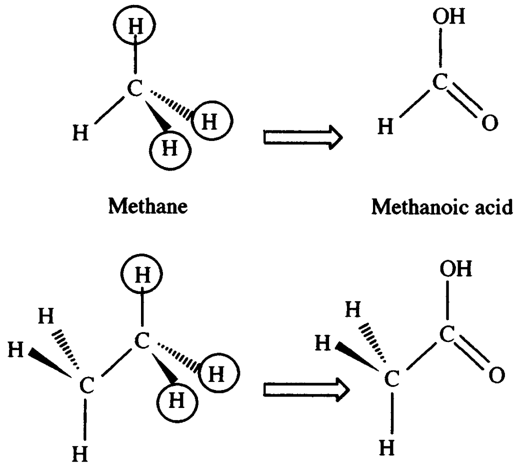


Fig. 3.4

Propane has only one isomer and has hydrogens in two distinct environments. One of these environments has hydrogens on a carbon which is 'internal' (i.e. it is bonded to two other carbon atoms and so has only two hydrogens on it). The second has hydrogens on terminal carbons in identical environments and so only one isomer of propanoic acid exists, Fig. 3.5.

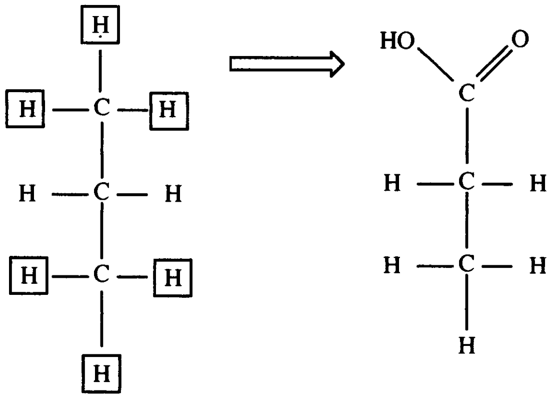


Fig. 3.5

Butane has two isomers: butane (*n*-butane) and 2-methylpropane (isobutane). Each has one unique environment, with hydrogens on a terminal carbon atom of the skeleton of the molecule. This gives rise to two isomers of the formula C_3H_7COOH. Their names are butanoic acid and 2-methylpropanoic acid (isobutanoic acid), Fig. 3.6.

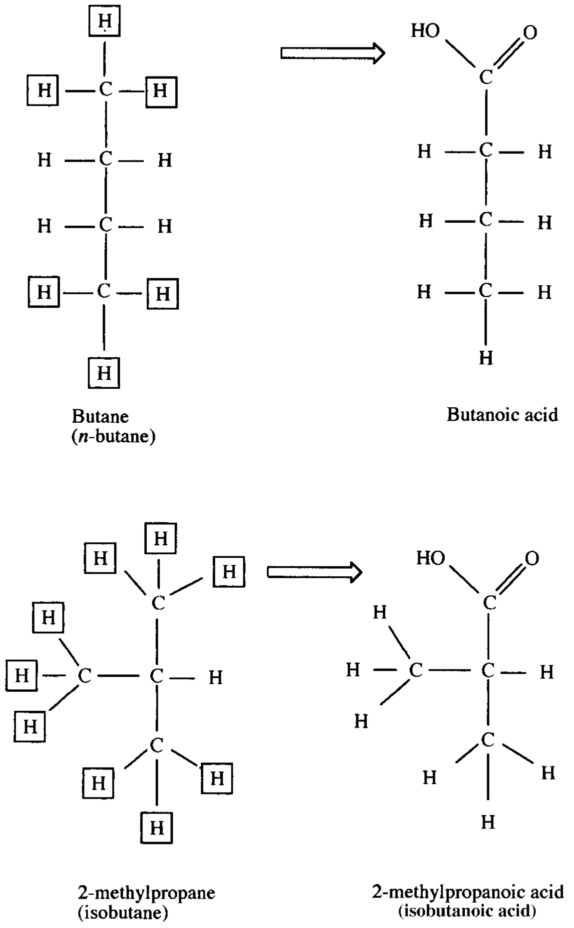


Fig. 3.6

3.3 Physical Properties of Aliphatic Carboxylic Acids

Though the hydrocarbon fragment of the molecule is essentially non-polar, the very high polarity of the carboxyl group makes carboxylic acids polar compounds. They are more polar than aldehydes and ketones and indeed alcohols. Consequently, they have elevated melting and boiling points when compared with alkanes of similar molecular mass. The high polarity of the hydroxyl group combined with the polarity of the carbonyl group provides the ability to form strong hydrogen bonds where the molecules effectively exist as dimers, Fig. 3.7.

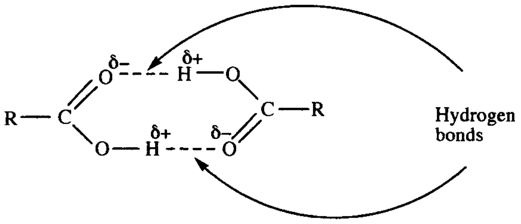


Fig. 3.7 *Hydrogen-bonded dimer*

The melting and boiling points of the lower carboxylic acids are summarised in Table 3.2 and some comparative data for compounds of similar molecular mass are summarised in Table 3.3.

Name	**Formula**	**m.p./°C**	**b.p./°C**	**Sol. in H_2O/(g/100 g)**
Methanoic acid	HCOOH	8.0	100	∞
Ethanoic acid	CH_3COOH	16.6	118	∞
Propanoic acid	C_2H_5COOH	-22.0	141	∞
Butanoic acid	C_3H_7COOH	- 6.0	164	∞
Pentanoic acid	C_4H_9COOH	-34.0	187	3.7

Table 3.2 *Some physical data for straight-chain carboxylic acids*

The polarity of carboxylic acids is high and sufficient to make the first members of the series essentially infinitely soluble in water. However, this solubility falls dramatically at carbon number five and only slight solubility is observed when one advances to higher carbon numbers. After that the hydrocarbon end of the molecule is large enough to render them insoluble in water. They are however soluble in less polar organic solvents such as alcohols and ethers.

Name (M_r)	**Formula**	**m.p./°C**	**b.p./°C**	**Sol. in H_2O/ (g/100 g)**
Ethanoic acid(60)	CH_3COOH	16.6	118	∞
Propan-1-ol (60)	C_3H_7OH	-126.0	97	∞
Propanal(58)	C_2H_5CHO	- 81.0	47	16
Propanone(58)	CH_3COCH_3	- 94.0	56	∞
Butane(58)	C_4H_{10}	-138.0	0	insol.
Octane(114)	C_8H_{18}	- 57.0	126	insol.

Table 3.3 *Some physical data for organic compounds of similar molecular mass*

Table 3.3, which shows some comparative data, gives evidence for the high polarity and strong hydrogen bonding in carboxylic acids. The comparison of boiling points with that of octane (*n*-octane) shows evidence for the boiling points of acids being similar to those of the corresponding hydrocarbon of double the molecular mass of the acid.

The lower carboxylic acids have particularly strong, irritating and unpleasant odours. However, beyond C_5 the volatility of the compounds decreases sufficiently to make then less offensive.

3.4 Acidity of Carboxylic Acids

The hydrogen of a carboxylic acid can be readily removed as an H^+. In dilute solution the lower acids dissociate slightly, Fig. 3.8.

$$\text{R-COOH} \rightleftharpoons \text{R-COO}^- + H^+$$

Fig. 3.8

This contrasts with the low acidity of the hydroxyl hydrogen of alcohols where no similar dissociation is observed. While the polarity of the O-H bond is certainly a factor in the liberation of the H^+ ions in carboxylic acids, the very low acidity of alcohols shows this polarity is not sufficient to render carboxylic acids proton donors. The reason for this acidity rests in the stability of the conjugate base of the carboxylic acid. The negative charge is distributed over the two oxygen atoms by resonance, forming two identical ions. This gives the $RCOO^-$ ion good stability, Fig. 3.9. This type of stabilisation is not possible in an alkoxide ion where the charge is localised on one oxygen. Consequently, alcohols are not acidic.

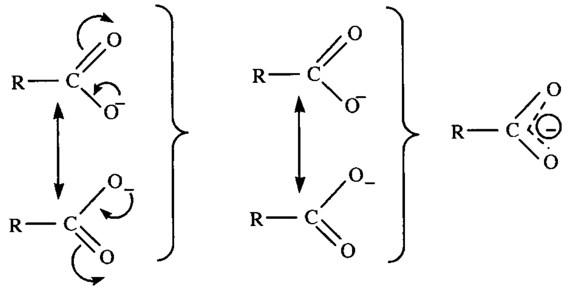


Fig. 3.9 Resonance stabilisation of the carboxylate ion

Relative Acidity of Carboxylic Acids

To compare the acidities of a selection of simple carboxylic acids the pK_a values of a number of acids are given in Table 3.4. For a carboxylic acid RCOOH which dissociates according to the equation

$$\text{RCOOH} \rightleftharpoons \text{RCOO}^- + H^+$$

K_a and pK_a are defined as

$$K_a = \frac{[\text{RCOO}^-][H^+]}{[\text{RCOOH}]}$$

and

$$pK_a = -\log_{10} K_a$$

To help with the ensuing discussion the acids are placed in order of increasing acid strength.

Acid	**Formula**	K_a	pK_a	**Conjugate base**
Ethanoic	C_3HCOOH	1.75×10^{-5}	4.76	CH_3COO^-
Methanoic	HCOOH	17.7×10^{-5}	3.75	$HCOO^-$
Chloroethanoic	$CH_2ClCOOH$	136×10^{-5}	2.87	CH_2ClCOO^-
Dichloroethanoic	$CHCl_2COOH$	5530×10^{-5}	1.26	$CHCl_2COO^-$
Trichloroethanoic	CCl_3COOH	23200×10^{-5}	0.63	CCl_3COO^-

Table 3.4 *Relative acidities of carboxylic acids*

The key to understanding the relative acidities of these acids lies in understanding the stabilities of their conjugate bases. We know that strong acids have weak conjugate bases. We can therefore conclude that the relative strengths of the conjugate bases has CH_3COO^- being the strongest base and CCl_3COO^- the weakest. The full list is given in Fig. 3.10.

$$CH_3COO^- > HCOO^- > CH_2ClCOO^- > CHCl_2COO^- > CCl_3COO^-$$

Fig. 3.10

The reason for this pattern can be easily explained when the nature of the 'R' group of the carboxylic acid is considered. The methyl group, $-CH_3$, in the ethanoate ion is net electron releasing along the σ-bond to the carboxylate carbon when compared with hydrogen in the case of the methanoate ion. Thus, in the ethanoate ion the methyl group pushes electron density towards the negative carboxylate ion and so lowers its stability. This makes the ethanoate ion less stable than the methanoate ion. Thus, the ethanoate ion is the stronger conjugate base, Fig. 3.11. Consequently, ethanoic acid is the weaker acid of the two.

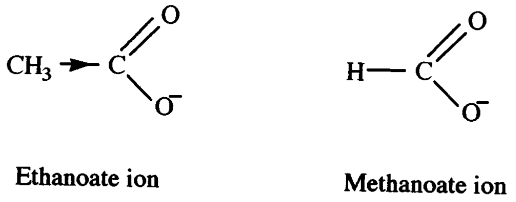


Fig. 3.11

Again by comparison with the hydrogen on the methanoate ion the chloromethyl group in the chloroethanoate ion is net electron withdrawing along the σ-bond to the carboxylate carbon (owing to the highly electronegative chlorine on the methyl group). Now the chloromethyl group is pulling electron density away from the carboxylate ion and so making it more favourable for it to hold the negative charge, Fig. 3.12.

Fig. 3.12

This makes the chloroethanoate ion a weaker conjugate base than methanoate and so chloroethanoic acid is a stronger acid than methanoic acid.

The dichloromethyl group is more electron withdrawing than the chloromethyl group and the trichloromethyl group is more electron withdrawing still. Thus, the relative stabilities of the conjugate bases are explained on the basis of the ability of the 'R' group to remove electron density from the vicinity of the negative charge of the carboxylate ion. Hence, the relative acidity of the acids listed in Table 3.4 is explained.

3.5 Preparation of Carboxylic Acids

As outlined in Chapter 1 carboxylic acids are produced when primary alcohols are oxidised. It is not surprising that this process provides a major route to carboxylic acids. Grignard reagents react with carbon dioxide to produce the magnesium salt of the carboxylic acid and the free acid can be generated using mineral acid. Hydrolysis of nitriles is a third important method of preparing carboxylic acids. There are a number of specific methods used for the large-scale production of ethanoic acid and these are dealt with separately.

Oxidation of Primary Alcohols

The oxidation of primary alcohols gives the corresponding carboxylic acid, Fig. 3.13.

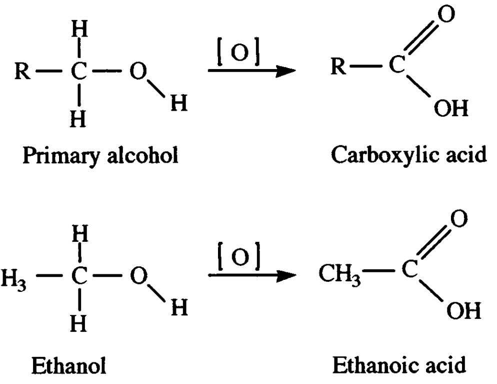


Fig. 3.13

The oxidation of primary alcohols to give the corresponding carboxylic acids is not constrained by the same difficulty of 'over oxidation' which troubles the production of aldehydes as they are not that easily oxidised further, Fig. 3.14.

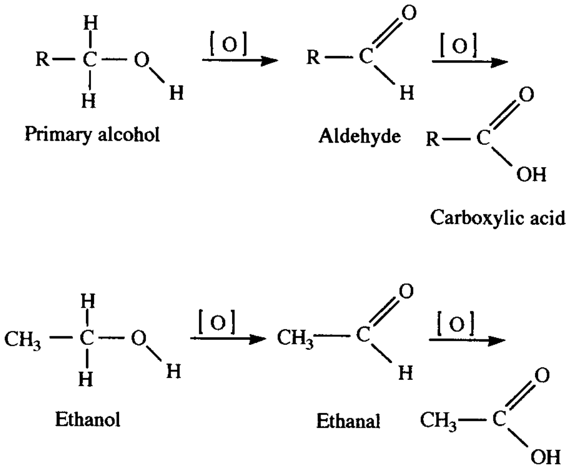


Fig. 3.14

The oxidation described in Fig. 3.14 can be achieved using acidified solutions of chromate or dichromate ions (see practical notes below). The yields are usually considerably better than in the preparation of aldehydes as the acids are far less volatile and there is less likelihood of over oxidation.

These reaction pathways are often employed in the laboratory. However, they are expensive methods and have the added problem of using heavy metal reagents and so large-scale waste treatment and disposal problems arise if they are used in bulk manufacture (see industrial preparations below).

Carboxylic Acids from Grignard Reagents

The reaction of Grignard reagents with carbon dioxide produces a magnesium compound of the carboxylic acid from which the free acid can be generated using mineral acid, Fig. 3.15.

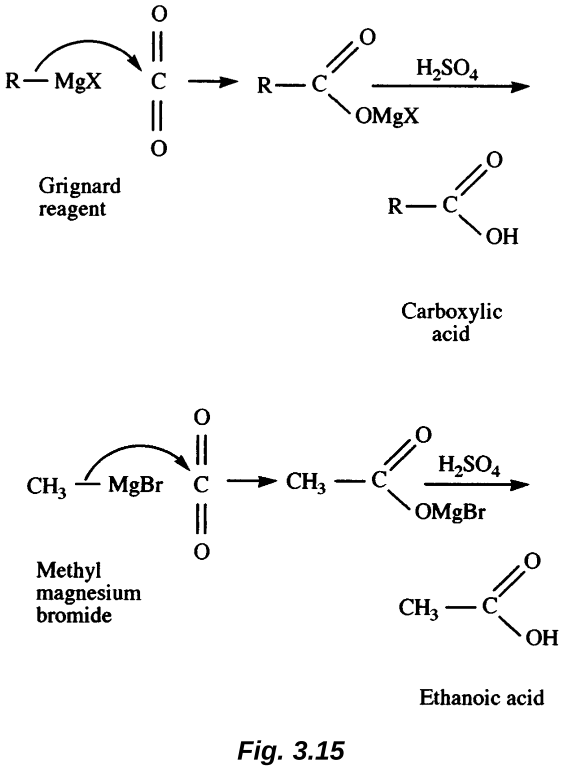


Fig. 3.15

Carboxylic Acids from the Hydrolysis of Nitriles

Nitriles (or cyanides) are important synthetic precursors to carboxylic acids, Fig. 3.16. Carboxylic acids one carbon longer than the alkyl halide are produced.

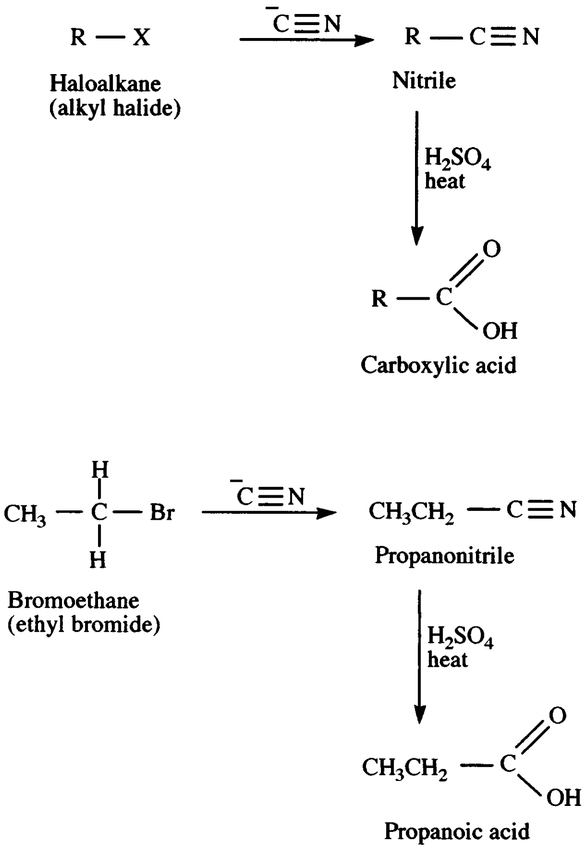


Fig. 3.16

Industrial Preparations of Ethanoic Acid

1. Air oxidation of ethanol

Common in the industrial preparation of ethanoic acid in vinegar is air oxidation of the ethanol in poor quality wines, cider or alcohol produced by the fermentation of cereal. This oxidation is achieved in the presence of *Bacterium aceti* at about 37 °C and can take weeks, Fig. 3.17. Vinegar is a 3 - 7% (w/v) solution of ethanoic acid. These weakly acidic solutions are produced by the bacterial route.

The dilution of concentrated industrial ethanoic acid to produce vinegar for consumption is illegal.

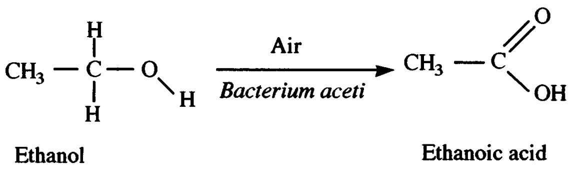


Fig. 3.17 Air oxidation

2. **Catalytic dehydrogenation followed by air oxidation**

   This involves the catalytic dehydrogenation of a primary alcohol to give the aldehyde as described earlier in Chapter 2, followed by the air oxidation of the aldehyde to the carboxylic acid.

3. **Air oxidation of small alkanes**

   Alkanes between C_4 and C_7 can be air oxidised at temperatures of about 200 °C in the presence of manganese(II) ethanoate or cobalt(II) ethanoate, Fig. 3.18. The reaction cleaving butane to give ethanoic acid produces methanoic acid and propanoic acid as side products.

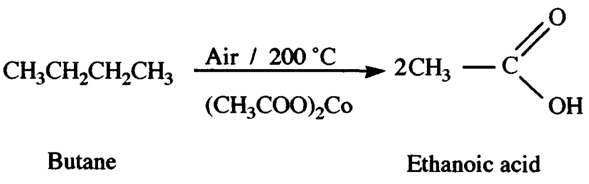


Fig. 3.18

The simple laboratory preparation of ethanoic acid is given at the end of section 3.7 where the reactions of ethanoic acid are also investigated.

3.6 Social and Applied Information on Carboxylic Acids

Methanoic Acid (Formic Acid), HCOOH

This is the first member of the aliphatic monocarboxylic acids. It was first isolated in 1749 by Margraf by distillation of red ants. Indeed the name formic acid comes from the Latin word for ant which is *formica*. The acid has a pungent, irritating odour and will cause blisters on contact with the skin. This blistering is very evident after nettle stings, since stinging nettles contain formic acid in their leaves. Unlike other carboxylic acids, formic (methanoic) acid contains the arrangement of atoms of the aldehyde functional group also, and consequently has the ability to give a positive test with Tollens' reagent (see p. 54).

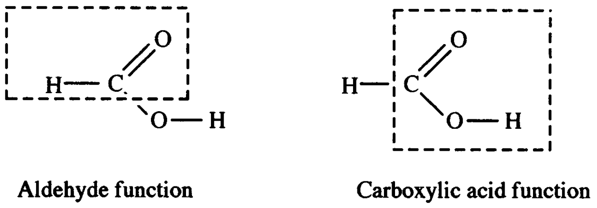


Fig. 3.19 Methanoic acid (formic acid)

Ethanoic Acid (Acetic Acid), CH_3COOH

This acid has been known from ancient times, but it was first prepared in 1723 by the German chemist, **Georg Ernst Stahl** (1660-1734). Ordinary vinegar contains between 3 and 7% w/w ethanoic acid.

The flavour of vinegar is due to other substances. Commonly available in shops is malt vinegar which is produced by bacterial oxidation of alcoholic liquids prepared from malt. There are also cider vinegars and wine vinegars. These products are found to contain sugars, phosphoric acid, alcohol and glycerol and may also have flavours added from herbs, e.g. tarragon and dill. Pure ethanoic acid (glacial acetic acid) is a colourless crystalline solid which melts at 17 °C. Thus, we find ethanoic acid frozen in bottles in winter. It boils at 118 °C. One important use of ethanoic acid is in the manufacture of cellulose acetate, which can be used for overhead transparency film. In thin films it is called cellophane and recent developments have resulted in the manufacture of a thread-like material which can be woven. This is sold under the trade names of 'Tricel' or 'Dicel'.

Propanoic Acid (Propionic Acid), C_2H_5COOH

Propanoic acid is the third member of the aliphatic acids. Its chief use is in the preparation of calcium propanoate, $(C_2H_5COO)_2Ca$, which is a preservative.

Butanoic Acid (Butyric Acid), C_3H_7COOH

This acid is produced when butter has 'gone off'. It has a rancid smell. It is also present in human sweat. Its smell can be detected by humans in concentrations as low as 10^{-11} mol l^{-1} and by dogs at 10^{-17} mol l^{-1}. The ability of dogs to track a person stems from their ability to detect carboxylic acids in the sweat and body odours. Each person produces their own characteristic combination of carboxylic acids. Goats are believed to produce the greatest concentration of carboxylic acids in their body odour.

Ethanedioic Acid (Oxalic Acid), $(COOH)_2$

This is a diprotic acid. It is found in rhubarb leaves. This acid and its salts are poisonous. It is also present in spinach. The high toxicity of rhubarb leaves is, however, probably linked to some other compound which is present. In fact, it is the acid anion of ethanedioic acid which is toxic. Normally, when treating people who have swallowed an acid, a base such as sodium hydrogencarbonate is administered to neutralise the acid. However, in the case of oxalic acid poisoning such treatment will increase the anion production and make the poisoning worse. A base which forms an insoluble salt must be added, e.g. calcium carbonate or magnesium hydroxide (milk of magnesia), to neutralise the acid. Historically, it was an important poison as it was difficult to detect.

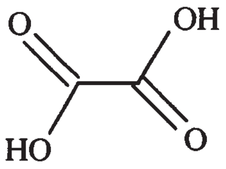


Fig. 3.20

Benzoic Acid, C_6H_5COOH

This is a white solid which forms needle-like crystals when crystallised from hot water. It has a sharp melting point of 121 °C and can be used in the calibration of thermometers in a melting point apparatus. Benzoic acid and its sodium salt are used as food preservatives.

Citric Acid, $C_6H_8O_7$

Citric acid is present in citrus fruits. It is present in almost all soft drinks. Coca-Cola is an exception. Phosphoric acid is used in it, though citric acid is used in Diet Coke. Citric acid is manufactured in Ringaskiddy, Co. Cork, by ADM by a fermentation process.

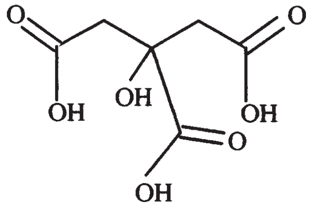


Fig. 3.21 *Citric acid*

(See also the appendix for information on fats, fatty acids and soaps.)

3.7 Reactions of Aliphatic Carboxylic Acids

The chemistry of carboxylic acids, RCOOH, is mainly dictated by the carboxyl (-COOH) functional group. Three features of the functional group contribute to the understanding and predicting of the chemical behaviour of this series of compounds. Firstly, acidity of the hydrogen on the carboxyl group makes possible a series of reactions commonly associated with other acids, Fig. 3.22.

$$\text{R-COOH} \rightleftharpoons \text{R-COO}^- + H^+$$

Fig. 3.22

The second relates to polarity of the carbonyl group and the possibility of nucleophilic attack at the carbonyl carbon, Fig. 3.23.

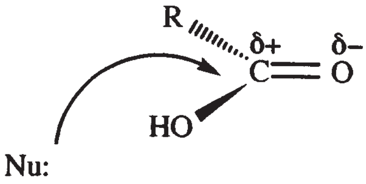


Fig. 3.23

The third relates to the ability of acids to form an enol and the slight acidity of the hydrogens on a carbon α– to a carbonyl group. This allows halogenation of carboxylic acids similar to that observed in aldehydes and ketones. It also allows a variety of useful alkylation and condensation reactions in acid derivatives such as esters. Reactions of this type are not discussed further here.

Reactions Involving Acidity of the Carboxyl Hydrogen

Reactions of carboxylic acids involving the release of an H^+ ion parallel much of the chemistry of mineral acids. The acidity of carboxylic acids is, however, much lower and the reactions, when they occur, are generally much less vigorous.

Effect on Litmus Indicator

Like mineral acids, water-soluble carboxylic acids will change the colour of blue litmus to red. It is worth noting that the acidity depends on the presence of water. Glacial ethanoic acid does not cause a change in the colour of dry blue litmus paper.

Reaction with Sodium Hydrogencarbonate

The reaction of carboxylic acids with sodium hydrogencarbonate liberates carbon dioxide gas and produces the salt of the acid, Fig. 3.24. It should be noted that pure glacial ethanoic acid will not liberate carbon dioxide from carbonates or hydrogencarbonates. The presence of water is necessary to release the H^+ ions from the acid.

$$RCOOH + NaHCO_3 \longrightarrow RCOONa + H_2O + CO_2$$

$$\underset{\text{Methanoic acid}}{HCOOH} + NaHCO_3 \longrightarrow \underset{\text{Sodium methanoate}}{HCOONa} + H_2O + CO_2$$

$$\underset{\text{Ethanoic acid}}{CH_3COOH} + NaHCO_3 \longrightarrow \underset{\text{Sodium ethanoate}}{CH_3COONa} + H_2O + CO_2$$

Fig. 3.24

Reaction with Sodium Carbonate

The reaction of carboxylic acids with sodium carbonate again liberates carbon dioxide gas and produces the salt of the acid, Fig. 3.25.

$$2RCOOH + Na_2CO_3 \longrightarrow 2RCOONa + H_2O + CO_2$$

$$\underset{\text{Methanoic acid}}{2HCOOH} + Na_2CO_3 \longrightarrow \underset{\text{Sodium methanoate}}{2HCOONa} + H_2O + CO_2$$

$$\underset{\text{Ethanoic acid}}{2CH_3COOH} + Na_2CO_3 \longrightarrow \underset{\text{Sodium ethanoate}}{2CH_3COONa} + H_2O + CO_2$$

Fig. 3.25

Reaction with Magnesium

The reaction of carboxylic acids with magnesium is also similar to the reaction of magnesium with dilute mineral acids. Hydrogen gas is evolved, though the reaction is less vigorous, Fig. 3.26. Water is necessary as discussed above.

$$2RCOOH + Mg \longrightarrow (RCOO)_2Mg + H_2$$

$$\underset{\text{Methanoic acid}}{2HCOOH} + Mg \longrightarrow \underset{\text{Magnesium methanoate}}{(HCOO)_2Mg} + H_2$$

$$\underset{\text{Ethanoic acid}}{2CH_3COOH} + Mg \longrightarrow \underset{\text{Magnesium ethanoate}}{(CH_3COO)_2Mg} + H_2$$

Fig. 3.26

Reaction with Zinc

The reaction of aqueous carboxylic acids with zinc is also similar to the reaction of zinc with dilute mineral acids. Hydrogen gas is evolved, though the reaction is less vigorous, Fig. 3.27.

$$2RCOOH + Zn \rightarrow (RCOO)_2Zn + H_2$$

$$2HCOOH + Zn \rightarrow (HCOO)_2Zn + H_2$$

Methanoic acid — Zinc methanoate

$$2CH_3COOH + Zn \rightarrow (CH_3COO)_2Zn + H_2$$

Ethanoic acid — Zinc ethanoate

Fig. 3.27

Reactions Involving Nucleophilic Attack on the Carbonyl Group

Reactions of carboxylic acids involving attack of a nucleophile on the carbonyl carbon are very important and form the basis of much of the chemistry of carboxylic acids. The conversion of carboxylic acids to esters, acid chlorides and amides all mechanistically involve attack on the carbonyl group leading to replacement of the hydroxyl group, -OH, of the acid.

Esterification

A carboxylic acid and an alcohol undergo a condensation reaction to produce an ester. Esters are sweet fruity-smelling compounds and the reaction of an acid and an alcohol in the presence of a small amount of sulphuric acid to give an ester is a standard diagnostic test for the presence of acids and alcohols, Fig. 3.28 and Fig 3.29. The oxygen of the alcohol is always retained in the ester. The experimental verification of this was dealt with on p. 21.

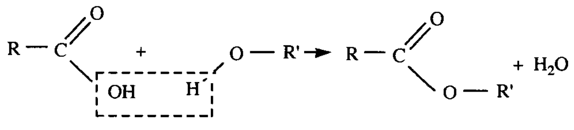


Fig. 3.28

$$HCOOH + C_2H_5OH \rightarrow HCOOC_2H_5 + H_2O$$

Methanoic acid — Ethanol — Ethyl methanoate

$$CH_3COOH + C_2H_5OH \rightarrow CH_3COOC_2H_5 + H_2O$$

Ethanoic acid — Ethanol — Ethyl ethanoate

$$CH_3COOH + CH_3OH \rightarrow CH_3COOCH_3 + H_2O$$

Ethanoic acid — Methanol — Methyl ethanoate

Fig. 3.29

The reaction is in fact an acid-catalysed equilibrium process and is more correctly represented in Fig. 3.30.

$$CH_3COOH + C_2H_5OH \xrightleftharpoons{H^+} CH_3COOC_2H_5 + H_2O$$

Ethanoic acid — Ethanol — Ethyl ethanoate

Fig. 3.30

The sulphuric acid is primarily present as a catalyst as it protonates the carboxylic acid (see mechanism below). The strong dehydrating properties of concentrated sulphuric acid may also suggest that it assists pushing the reaction to the right (application of Le Chatelier's principle). However, given the fact that only very small amounts of sulphuric acid are added this is unlikely to be a very significant function of the acid. At room temperature, or slightly above it, most combinations of carboxylic acids of low molecular mass and alcohols have an equilibrium constant, K_c, whose value is of the order of 4. This means that equimolar quantities of acid and alcohol will, at equilibrium, only give about 66% conversion to the ester. For this reason the synthesis of esters in a laboratory situation is normally carried out via the acid chloride route (discussed below) where very high yields are attainable.

The mechanism of the reaction involves protonation of the carboxylic acid by the stronger sulphuric acid. The carbonyl group is then attacked by an alcohol molecule acting as a nucleophile and a water molecule is expelled. The protonated ester then loses a proton and so the ester is formed and the proton regenerated, Fig. 3.31.

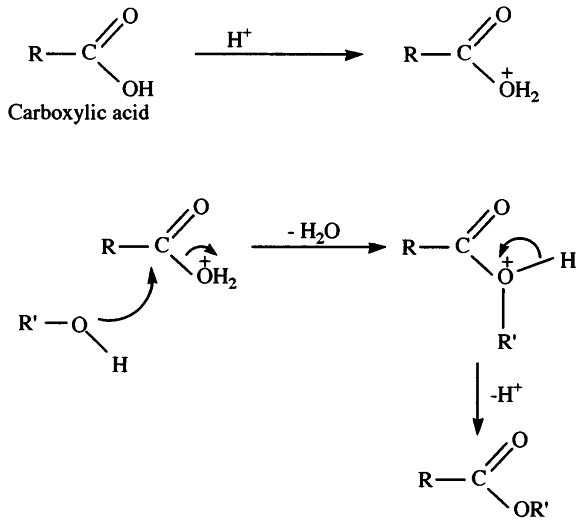


Fig. 3.31

Formation of Acid Chlorides

Acid chlorides are formed when the hydroxyl group of a carboxylic acid is replaced by chlorine. This is achieved using any one of a number of reagents. Thionyl chloride, $SOCl_2$, phosphorus(III) chloride, PCl_3, or phosphorus(V) chloride, PCl_5, are all suitable, Fig. 3.32.

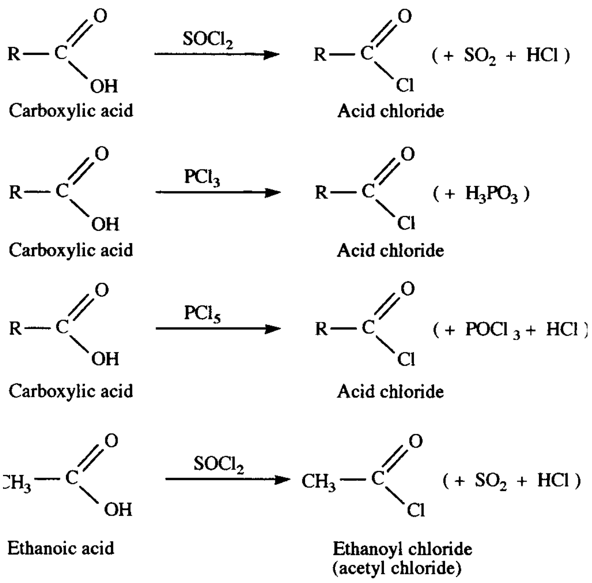


Fig. 3.32

The conversion of a carboxylic acid to an acid chloride can be quantitative and the reaction of an acid chloride with a dry (water free) alcohol can also be quantitative. Thus, by converting a carboxylic acid to the acid chloride and then to the ester a very high yield is possible. Fig 3.33.

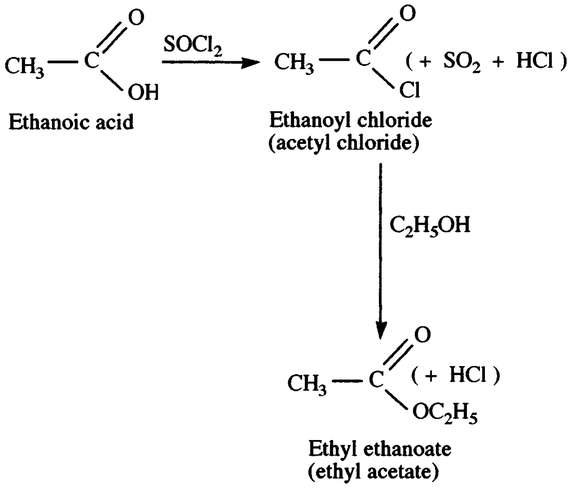


Fig. 3.33

Reduction of Carboxylic Acids

Carboxylic acids (and esters) are reduced by lithium aluminium hydride, $LiAlH_4$, to the parent primary alcohol, Fig. 3.34.

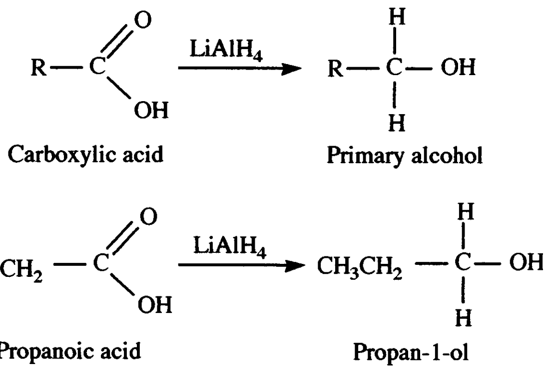


Fig. 3.34

Substitution of Hydrogens on the Carbon α to the Carboxylic Acid Group

In a similar fashion to the α-halogenation of aldehydes and ketones, the reaction of carboxylic acids with chlorine takes place in the presence of trace quantities of phosphorus and can continue to replace, successively, all the hydrogens on a carbon α to a carboxyl group, Fig. 3.35.

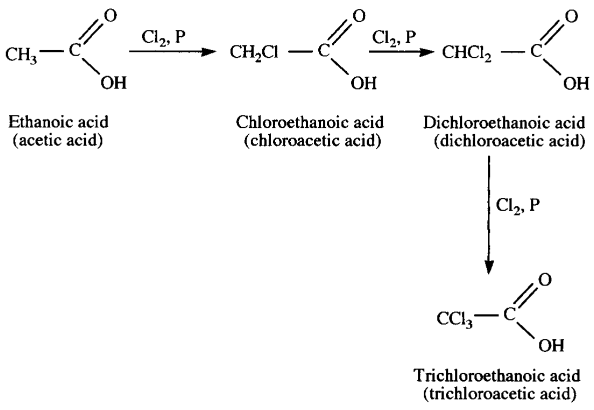


Fig. 3.35

Anomalous Behaviour of Methanoic Acid

Methanoic acid, HCOOH, exhibits almost all of the reactions described above for carboxylic acids except those involving reactions at the carbon α to the carboxylic acid group because there is no α carbon.

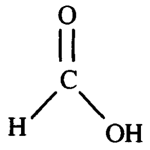
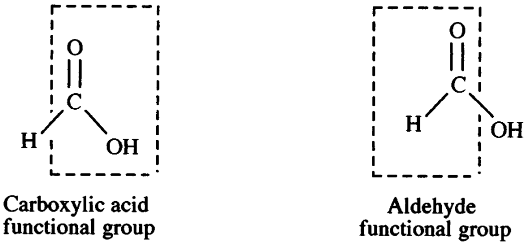


Fig 3.36 *Methanoic acid - no carbon α- to the carboxylic acid group*

In addition, methanoic acid can masquerade as an aldehyde as it also has a -CHO group, Fig. 3.37.



Carboxylic acid functional group

Aldehyde functional group

Fig. 3.37

This allows methanoic acid to give a positive silver mirror test with Tollens' reagent. The methanoic acid is converted to carbon dioxide or carbonate ion in the reaction, Fig. 3.38.

$$HCOOH + Ag_2O \longrightarrow 2Ag + CO_2 + H_2O$$

Fig. 3.38

Methanoic acid is decomposed by heat at a temperature of 160 °C, yielding carbon dioxide and hydrogen, Fig. 3.39.

$$HCOOH \xrightarrow{160\ ^\circ C} CO_2 + H_2$$

Fig. 3.39

Methanoic acid is dehydrated by warm concentrated sulphuric acid, yielding carbon monoxide, Fig. 3.40.

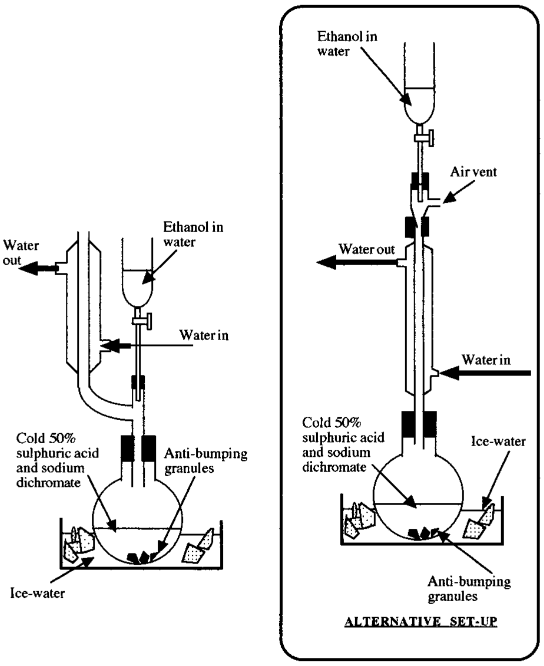
$$HCOOH \xrightarrow[-H_2O]{\text{Warm conc. } H_2SO_4} CO$$

Fig. 3.40

Experiment 3.1

Preparation and Properties of Ethanoic Acid

Ethanoic acid can be prepared in the laboratory by the oxidation of ethanol using sodium dichromate in sulphuric acid. The amount of oxidising agent is normally kept in excess in this reaction as the product does not readily undergo further oxidation. Once the oxidation reaction is driven to completion (by refluxing the reaction mixture after the initial vigorous reaction has subsided) the product is isolated by distillation.



$$3C_2H_5OH + 2Na_2Cr_2O_7 + 8H_2SO_4 \longrightarrow 3CH_3COOH + 2Cr_2(SO_4)_3 + 2Na_2SO_4 + 11H_2O$$

$$3C_2H_5OH + 2Cr_2O_7^{2-} + 16H^+ \longrightarrow 3CH_3COOH + 4Cr^{3+} + 11H_2O$$

Fig. 3.41 *Step 1 - oxidation of ethanol*

Notes on Step 1

1. The oxidising agent is in excess and placed in the 50% sulphuric acid. This is possible since the product is not readily oxidised.

2. The alcohol is added as a water solution to dilute the alcohol and to make the reaction less vigorous. The reaction flask must be shaken (if no other method of stirring or mixing is employed) after each small addition of alcohol/water mixture. This ensures complete mixing of the contents and avoids a build-up of unreacted alcohol in the reaction vessel. When the addition is complete the flask should be shaken again for two minutes before the mixture is refluxed.

3. Even with the alcohol diluted it is advisable to cool the reaction vessel during the dropwise addition of the alcohol as the reaction is very exothermic. Should the reaction become too vigorous (a) stop the addition and (b) make the cooling more efficient by adding more ice and salt to the cooling bath.

4. The mixture in the reaction vessel before the addition is an orange colour ($Cr_2O_7^{2-}$ is formed in the acidic solution regardless of whether one starts with a chromate or dichromate salt). On adding the alcohol the reaction mixture changes colour to green as Cr^{3+} is produced.

5. The purpose of the reflux for 30 minutes is to drive the reaction to completion.

6. The function of the boiling-chips is to prevent the reaction mixture from bumping.

7. The alternative set-up can be used where a two-necked flask is not available. The air vent is necessary to allow for expansion of the gases inside the reaction vessel as the system heats up and also the displacement of air as the addition is made.

8. The conversion of an alcohol to a carboxylic acid constitutes a four-electron loss in redox terms. Since each Cr(VI) present undergoes a formal gain of three electrons the ratio of alcohol to Cr(VI) reacting is 3:4.

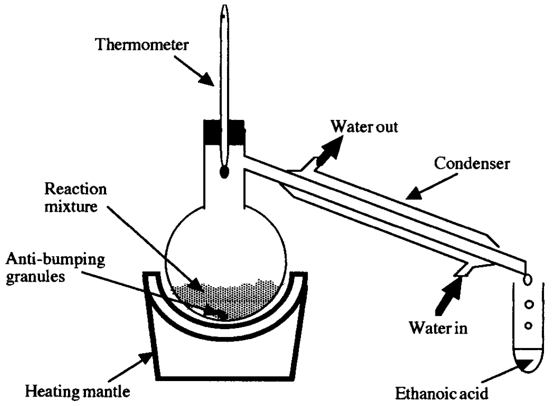


Fig. 3.42 *Step 2 - isolation of ethanoic acid by distillation*

Notes on Step 2

1. After allowing the reaction vessel to cool the assembly is rearranged to that of distillation. A fraction boiling at 110 °C - 120 °C corresponds to crude ethanoic acid. It can be further purified by redistillation.

2. Note direction of water flow through the condenser in all these experiments (in at the bottom, out at the top).

3. The thermometer bulb should be slightly below the side arm. In order to register the boiling point temperature the bulb should have some liquid as well as vapour in contact with it. In the position shown the bulb is in contact with vapour rising from below and condensed vapour dropping from above.

4. Again, boiling chips are needed.

Tests on the Collected Ethanoic Acid

1. **Physical properties**
   Ethanoic acid is a colourless liquid with a pungent odour.

2. **Combustion**
   Ethanoic acid burns with a clean flame (it has to be heated before ignition as not enough vapour is present over the cold liquid to generate an air mixture that will sustain a fire).

   $$CH_3COOH + 2O_2 \rightarrow 2CO_2 + 2H_2O$$

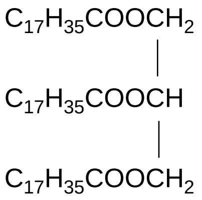
3. **Esterification**
   Reaction with alcohol under acidic conditions to form an ester: a few cm^3 of ethanoic acid and a few cm^3 of ethanol are treated with a few drops of concentrated sulphuric acid and the mixture heated gently for 1-2 minutes (a hot water bath is suitable for this purpose). The fruity odour of the ester is detected.

$$CH_3COOH + C_2H_5OH \overset{H_2SO_4}{\rightleftharpoons} \underset{\text{ethyl ethanoate}}{CH_3COOC_2H_5} + H_2O$$

Stearic Acid, $C_{17}H_{35}COOH$

Stearic acid is a common animal fatty acid. It has a saturated straight hydrocarbon chain attached to the carboxylic acid group.

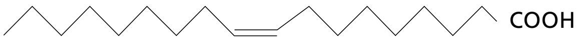
Tristearin,



$$\begin{array}{r} C_{17}H_{35}COOCH_2 \\ | \\ C_{17}H_{35}COOCH \\ | \\ C_{17}H_{35}COOCH_2 \end{array}$$

Tristearin is the ester formed between the triol glycerol and three stearic acid molecules. It is a principal component of beef fat and cocoa butter.

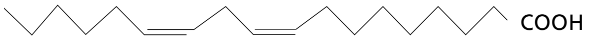
Oleic Acid, $C_{17}H_{33}COOH$



Oleic acid is an unsaturated fatty acid. It has a double bond between carbon number 9 and carbon number 10.

Unsaturated fatty acids tend to be oils rather than solids. Pork, lamb and poultry tend to have a higher proportion of unsaturated fats than beef fat. Vegetable oils tend to be unsaturated. Seeds have a higher concentration of oils than the stems of plants. The oils serve as a more concentrated food or energy source than carbohydrate. Hence, vegetable oils are often extracted from seeds. Oleic acid is the principal component of olive oil.

Linoleic Acid, $C_{17}H_{31}COOH$



Linoleic acid is an unsaturated fatty acid. It has two double bonds in the carbon chain. It is the main component of corn oil, soya bean oil and many other vegetable oils.

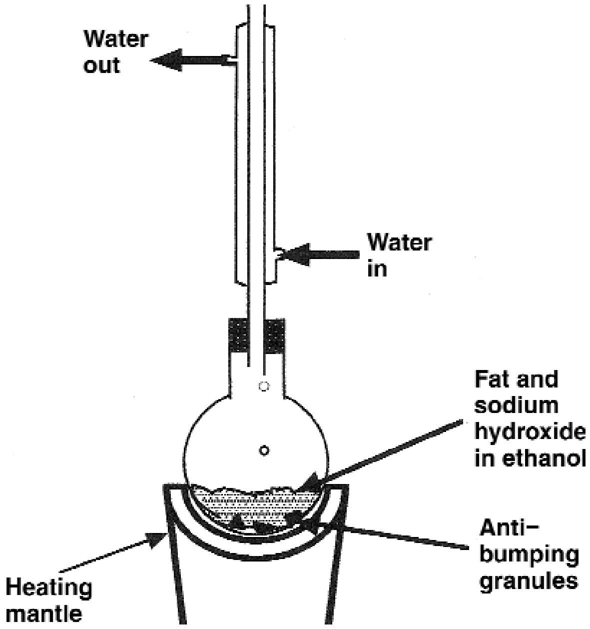
Soaps

Soaps are formed by the hydrolysis of fatty acid esters to produce salts of the fatty acids. The hydrocarbon end of the molecule is hydrophobic (water repelling) and the carboxylate end is hydrophilic (water attracting). The hydrophobic end dissolves in grease and the hydrophilic end dissolves in the water.

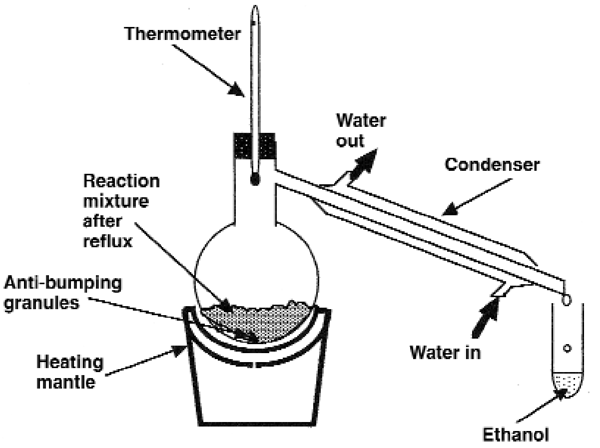
Experiment A.1

Soap Formation (Saponification)

Soaps are salts of fatty acids (long chain carboxylic acids). Fats are esters formed by the condensation of fatty acids and glycerol (propane-1,2,3-triol). Soaps are manufactured by the base hydrolysis of these fats (esters). In this experiment the fat is hydrolysed using sodium hydroxide in ethanol solution. The ethanol is then removed by distillation. The residue (a mixture of the excess sodium hydroxide, glycerol and the soap) is dissolved in the minimum of hot water and poured onto brine (saturated salt solution). The soap is isolated from the brine by filtration (the sodium hydroxide and the glycerol dissolve in the brine but the soap does not).

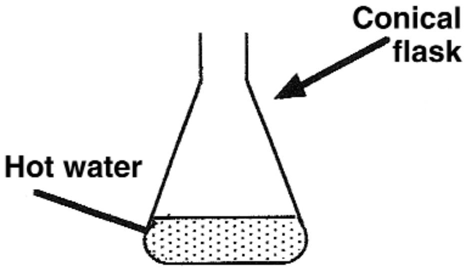


Step 1 Reflux
(Base hydrolysis of esters)

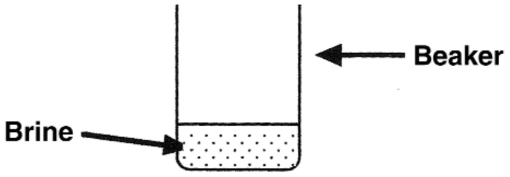


Step 2 Distillation

(Removal of ethanol)

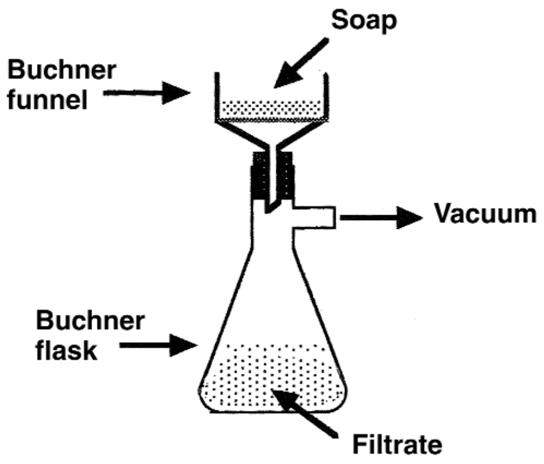


Step 3 Dissolving Residue in Hot Water



Step 4 Pouring Onto Brine

(Salting out the soap)



Step 5 Filtration

(Isolation of the soap)

Notes on the procedure

1. Fats are esters of fatty acids and glycerol. Animal fats tend to be formed from saturated fatty acids (e.g. stearic acid, $C_{17}H_{35}COOH$, and palmitic acid, $C_{15}H_{31}COOH$) while vegetable fats tend to be formed from unsaturated fatty acids (e.g. linoleic acid, $C_{17}H_{31}COOH$ and linolenic acid, $C_{17}H_{29}COOH$). Hydrolysis using sodium hydroxide leads to the sodium salt of the fatty acids whereas hydrolysis using potassium hydroxide leads to the potassium salt of the fatty acids. Hard washing soaps (e.g. blocks of ‘Sunlight’) are generally sodium salts of the saturated fatty acids. Softer soaps (i.e. toilet soaps) are generally potassium salts of a blend of fatty acids which are largely unsaturated. These soaps are often blended with essential oils and perfumes.

2. The purpose of the reflux is to speed up the hydrolysis reaction and to drive it to completion.

3. The ethanol is present as a solvent since NaOH is not soluble in fat.

4. If the mixture following the reflux were poured onto the brine without the ethanol first being distilled off soap would still be isolated. However, the yield would not be as high since the ethanol would help retain some of the soap in the brine/ethanol mixture. It is normal for the filtered soap to be washed with a very small

amount of ice-water to remove any traces of NaOH which may remain. A small quantity of cold water is used since a larger quantity of water or warm water would dissolve the soap and so decrease the yield greatly.

5. Anti-bumping granules are added to the flask at the start to prevent bumping of the reaction mixture.

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MODULE 7

Stoichiometry II

CONTENTS

Chapter 1 **Thermochemistry**

Chapter 2 **Chemical Kinetics**

Chapter 3 **Chemical Equilibrium**

Chapter 4 Calculations

Appendix

CHAPTER 1

THERMODYNAMICS

1.1 Thermodynamics

Thermodynamics and Thermochemistry

Thermodynamics is the general study of the conversion of energy from one form into another. However, we are concerned here only with that section of thermodynamics which deals with the energy changes which take place during a physical or a chemical change. Because chemists are concerned with physical changes such as changes of state or phase or crystalline state, as well as with chemical changes, a study of the energy changes which take place during such reactions, whether physical or chemical, is called thermochemistry.

The Law of Conservation of Energy

It is helpful for this discussion to call the substances involved in the physical or chemical change 'the system' and everything else not directly involved in the physical or chemical change 'the surroundings'. A boundary (container) separates the system from the surroundings and allows energy but no materials to be exchanged between the two, see Figure 1.1. Together the system and the surroundings compose 'the universe'. The law of conservation of energy states that energy may convert from one form into another but cannot be created or destroyed. Therefore, during the physical or chemical change, energy may be gained by the system from the surroundings or lost by the system to the surroundings but the total amount of energy in the universe is conserved.

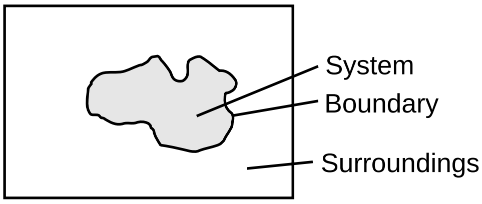


Fig. 1.1 *The universe*

Internal Energy, Heat and Work and the First Law of Thermodynamics

The system has a certain amount of internal energy, U, at any instant. This internal energy is the sum of all the kinetic energies, potential energies, vibrational energies, rotational and electronic energies of all the individual substances present, in addition to the energies which these substances possess at 0 K. The internal energy of a system cannot be determined directly but changes in internal energy during a physical or chemical process, ΔU, can be defined as

$$\Delta U = U_{\text{products}} - U_{\text{reactants}}$$

and can be calculated by measuring the amounts of energy added to or lost from the system during the reaction. Note that ΔU is positive when the products have more energy than the reactants, i.e. if the products gained energy from the surroundings during the physical or chemical change.

Energy is usually transferred to and from the system in two ways: heat energy, Q, may be added to or lost from the system, and mechanical work, W, may be done on or by the system. Heat energy, by convention, is taken as positive if it is absorbed by the system. Heat may be transferred to the system by conduction, convection or radiation from a heat source in the surroundings. Typical laboratory heat sources are Bunsen burners and hot plates. Industrial heat sources are heat exchangers and furnaces. Heat is also transferred from the system to the surroundings by conduction, convection or radiation. In small-scale laboratory reactions the heat evolved in a reaction may be absorbed using a condenser or an ice bath or simply dissipated to the container and the air. In industrial processes, where significant quantities of heat are generated, heat exchangers are widely used to cool systems. The heat from a hot industrial system is used to generate steam or to preheat reactants for another part of the process. An isothermal reaction is one which occurs without an increase in temperature. This can be achieved if the rate of addition or removal of heat from the system is controlled so that the temperature does not fall or rise.

Doing work on the system means that the substances in the system are compressed and allowing the system to do work means the system expands. Work, by convention, has a positive sign if it is done on the system by the surroundings. Thus, during a physical or chemical change where the products have gained energy by comparison to the reactants, then either a certain quantity of heat energy was absorbed by the system or work was done on the system by the surroundings or a combination of the two processes occurred so that ΔU is positive according to the equation:

$$\Delta U = Q + W$$

This equation is the first law of thermodynamics.

Light energy and electrical energy are less common alternative energy inputs or outputs to thermal energy. (See section 1.3 below.)

In the laboratory most small-scale reactions are carried out at normal atmospheric pressure, e.g. in open beakers or other vessels. Occasionally in laboratories and often in industry, reactions are carried out at reduced pressure by partially evacuating the container or at increased pressure by compressing the reactant gases or by pumping air or an inert gas into the container. Therefore, work, W, in chemical or physical processes normally involves changes in the volume of the system at constant pressure. Either the substances of the system are compressed by the surroundings, gaining energy in the process (positive work) or they expand against the pressure of the surroundings, using energy to do so (negative work).

By definition, mechanical work is done when a constant force, F, moves a body a certain distance, d, in the direction of the force

$$W = F \text{ x } d$$

So the work done, on or by a body, during a reaction involving a change of volume but where pressure is fixed is

$$W = p \text{ x } A \text{ x } d$$

$$W = p\Delta V$$

Liquid and solid reactants and products are virtually incompressible and therefore they are not contributors to the mechanical work done in a physical change or in a chemical reaction.

In Fig. 1.2 a system exerts the same pressure on its surroundings as the surroundings exert on it and thus the system maintains a certain fixed volume. In Fig. 1.3 the system has undergone a physical or chemical change which produced a net decrease in the volume of the system, due to a reduction in the number of gaseous particles. As a result the system now exerts a smaller pressure on the surroundings than before. The surroundings have compressed the system reducing its volume and have added energy to the system.

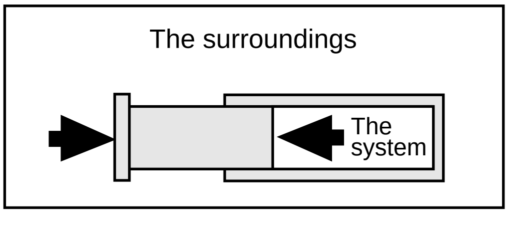


Fig. 1.2 *The universe, before a chemical reaction involving a reduction in volume at constant pressure, p*

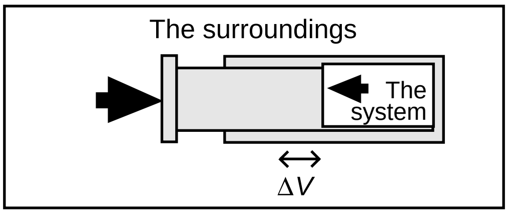


Fig. 1.3 *The universe, after a chemical reaction involving a reduction in volume at constant pressure, p*

Enthalpy

Keeping account of the change in internal energy in most physical and chemical processes therefore involves keeping account only of heat changes and volume changes. The heat change for a reaction which occurs at constant pressure is given a special name, the **enthalpy** change, ΔH, and relates thus to the other quantities mentioned.

$$\Delta U = Q + W$$
$$\Delta U = Q + p\Delta V$$
$$Q = \Delta U - p\Delta V = \Delta H$$

In Leaving Certificate Chemistry only the thermodynamics of chemical reactions which occur at constant pressure are considered, i.e. $\Delta H = Q$. If the reaction is carried out at constant pressure and constant volume, $\Delta H = \Delta U$.

Furthermore in Leaving Certificate Chemistry even where volume changes do occur, only thermal energy changes and not any energies associated with volume changes are considered, and in these cases $\Delta H \approx \Delta U$. This approximation is most valid when the reaction involves only liquids and solids because the change in volume during the reaction is small, but where gases are involved, the change in volume may be quite significant.

Note

Any property of a thermodynamic system which depends only upon the initial and final states and not the route taken between the states is referred to as a **state function**. For example, the potential energy of a rock on top of a mountain is the same whether it was carried up there today or moved there by geological action millions of years ago, provided the difference in initial and final heights in each case is the same. Thus potential energy is a state function. Internal energy is a state function as it depends only on the quantities of energy present initially and finally. Pressure, temperature and volume are also state functions. The amounts of work and thermal energy added to a system to bring about a particular change in the internal energy of the system may vary according to the relationship

$$\Delta U = Q + W$$

and depend on how the process is carried out. For example, if a certain quantity of air is pumped into a tyre to high pressure, mechanical work is done in compressing the air and its temperature increases, indicating an increase in internal energy. This is an example of an **adiabatic** process, i.e. one where no thermal energy enters or leaves the system. The same increase in internal energy of the air could have been brought about by adding heat energy to the air without changing its volume. In both cases the same initial and final internal energy conditions would have been observed but would have been achieved by different quantities of mechanical work and thermal energy, hence these properties are not state functions. However, the change in enthalpy, i.e. the heat change for a reaction which takes place at constant pressure, is a state function. Thus change in heat energy, Q, is a state function under these particular conditions since $Q = \Delta H$.

Endothermic and Exothermic Reactions

By convention, if ΔH is positive the reaction products have more energy than the reactants and the system gains energy from its surroundings as it proceeds, Fig. 1.4. The reaction is described as **endothermic** and, unless the reaction is conducted isothermally, is accompanied by a temperature fall, ΔT. After some time the surroundings supply the thermal energy to raise the temperature again, Fig. 1.5. Why should a reaction which *absorbs* energy be accompanied by a *fall* in temperature? The energy absorbed to convert reactants into products is obtained from the immediate surroundings, i.e. the solvent and the container lose energy and the temperature falls. (See section 1.6.)

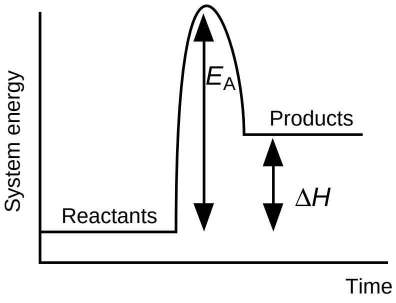


Fig. 1.4 *Endothermic process*

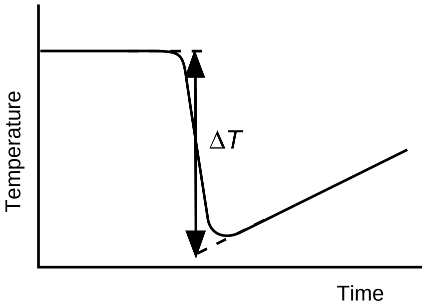


Fig. 1.5 *Endothermic process*

(See Experiments 1.1 and 1.2.)

Conversely, if ΔH is negative the reaction products have less thermal energy than the reactants and the system loses energy to its surroundings as it proceeds, Fig. 1.6. The reaction is described as **exothermic** and is accompanied by a temperature rise, ΔT, unless the experiment is conducted isothermally. After a time thermal energy is absorbed by the surroundings causing the temperature to fall again, Fig. 1.7.

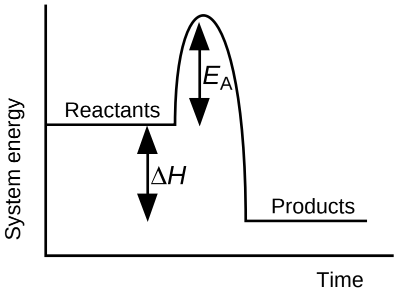


Fig. 1.6 *Exothermic process*

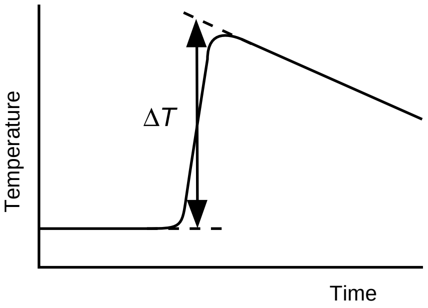


Fig. 1.7 *Exothermic process*

(See Experiments 1.3 and 1.4.)

Note that in both endothermic and exothermic reactions, the system absorbs a quantity of energy from the surroundings called activation energy, E_A, which is used to transform the reactants into a higher energy activated state before bond breaking to form products can occur. This energy is restored to the surroundings as the reaction proceeds. The rate of the reaction is dependent on the size of the activation energy. (See Chapter 2.)

Standard States

Standard enthalpies of reaction refer to the reactants and products of the chemical process in their standard states, i.e. in unit activity, in the normal state and most common allotropic form in which that substance is found at the pressure of 101 kN m^{-2} and temperature of 298.15 K. The activity of a solid, liquid or solvent is always taken as unity. The activity of a gas is unity if the gas has a partial pressure of normal atmospheric pressure. The activity of a solution is unity at a concentration of one mole per litre. Standard enthalpies of reaction are denoted by the symbol ΔH^{O}_{298}. If the temperature and activities of the process are not specified the symbol is just ΔH. Note that standard state conditions differ from standard temperature and pressure (s.t.p.) conditions. Thus, under standard state conditions, carbon is in the form of solid graphite, water is in the liquid state and oxygen is gaseous O_2 and not ozone. In addition, standard enthalpies are quoted with reference to one mole of a specified substance in the reaction, e.g. the standard enthalpy of combustion of hydrogen refers to the energy change involved when one mole of hydrogen gas combines with half a mole of oxygen gas in combustion to give one mole of water, with reactants and products in their standard states. The subscripts (s), (l), (g), and (aq) are sometimes used in equations to indicate solid, liquid, gaseous and infinitely dilute aqueous solutions. These state or phase symbols will only be used here where the state or phase is of particular significance.

Standard enthalpies of formation, combustion, solution, etc.

Some enthalpies have specific names. Standard enthalpies of formation, ΔH^{θ}_{f}, refer to the formation of a mole of a substance from its elements in their standard states.

$$\Delta H^{O}_{f} = H^{O}_{\text{substance}} - H^{O}_{\text{elements}}$$

By convention, all elements in their standard states have standard enthalpies of formation of zero. Hence *relative* standard enthalpies of formation of compounds are available.

Standard enthalpies of combustion refer to the combustion of a mole of a substance in excess oxygen to produce the normal oxide, unless otherwise specified; thus carbon dioxide rather than carbon monoxide, etc.

Standard enthalpies of solution refer to dissolving one mole of a substance in excess water to form an infinitely dilute solution, the dissolving occurring at standard conditions.

Standard enthalpy of neutralisation refers to an acid reacting with a base to form *one mole of water*, under standard conditions.

Sometimes reactions cannot go to completion under standard conditions. For example water does not form a vapour at the pressure of of 101 kN m^{-2} and the temperature of 298.15 K. So the standard enthalpy of vaporisation of water refers to the amount of energy required to change one mole of liquid water, initially at standard conditions, to water vapour at constant pressure. Similarly the standard enthalpy of atomisation of carbon is the amount of energy required to change one mole of solid graphite, initially at standard conditions, to separate gaseous carbon atoms at constant pressure. The unit for each of these standard enthalpies is the kilojoule per mole.

An enthalpy of reaction refers to a specific chemical reaction as written. The unit is then just kilojoule.

1.2 Burning and Exploding!

Fuels

A fuel is a substance which when oxidised releases energy. Most fuels in common use are elemental carbon or organic compounds. The oxidising agent is normally oxygen in the air. When carbon is burned in excess air the combustion product is carbon dioxide. An organic fuel will burn to form the combustion products carbon dioxide and water and possibly oxides of nitrogen and sulphur, etc., if these other elements are present in the fuel. There are a number of inorganic fuels also, e.g. hydrogen and sulphur and there are alternative oxidising agents, e.g. chlorine gas.

Nuclear fuels release energy associated with changes which occur in the nucleus. Such reactions are not chemical reactions and therefore are not discussed here. Alternative forms of acquiring energy, including harnessing the wind and sea are mechanical processes and are not discussed here. However, the use of solar energy to bring about endothermic chemical reactions in nature, e.g. photosynthesis, or to bring about simple reactions in the laboratory, e.g. the reaction between chlorine gas and methane, or simple physical changes, such as heating water in solar panels, are of course part of the discussion.

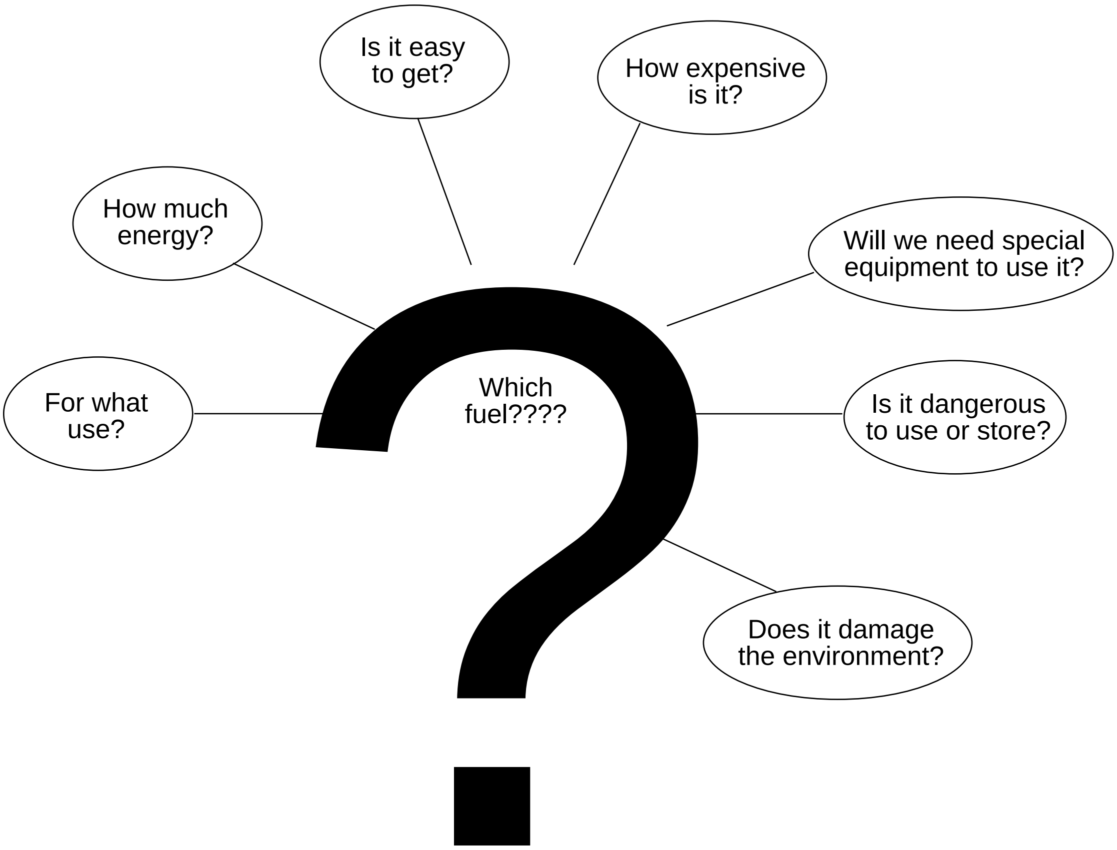


Fig. 1.8 *Which fuel?*

Types of fuel

There is a wide selection of materials which may be classified as fuels. Included are the fossil fuels, oil, gas, turf (peat), lignite, coal, anthracite. Included also are renewable fuels: timber, alcohol, oils from plants, hydrocarbons from biological sources and hydrogen from electrolysis. Fuels can also be classified according to their state: solid fuels, liquid fuels, gaseous fuels.

How does one select from this variety of fuels the most suitable one? Fuels must be considered for a particular purpose under the following headings:

Kilogram calorific content

Fuels can be directly compared in terms of their energy efficiency by comparing the energies released upon burning the same mass of each fuel, namely a kilogram. The energy released by one kilogram is termed the kilogram calorific value of the fuel and since a kilogram of any fuel, when burned, releases a considerable quantity of energy, the unit is megajoule per kilogram, MJ kg^{-1}. (See also ‘Counting Calories’, section 1.4.) Kilogram calorific data are obtained by burning a small sample of each fuel in a bomb calorimeter and scaling up the energy released in the experiment to give the energy which would be released upon burning a kilogram of that fuel. In this way, turf is found to be rather inefficient and peat briquettes, produced when water is compressed out of the turf, a little more efficient but still less efficient than coal, which in turn is less efficient than anthracite. Table 1.1 shows the kilogram calorific values of common fuels. Petrol is found to provide slightly more energy per kilogram than diesel oil but the most efficient fuel in terms of energy provided per kilogram is hydrogen, with methane in second place.

If a set of liquid fuels is to be compared, the results may be quoted in terms of energy released per litre of fuel.

Fuel	Kilogram calorific value/MJ kg^{-1}
Wood (dried beech, chestnut, pine)	17-19
Turf	15.9
Peat briquettes	19.31
Lignite	21.6
Coal	33.5
Anthracite	34.6
Coke	30.7
Methanol	22.3
Ethanol	29.8
Petrol (C_8H_{18})	48.35
Kerosene (aviation)	46.5
Diesel (marine)	44.3
Methane	55.7
Propane/Butane	49.4
Hydrogen	142.9
Some of these fuels do not have fixed composition so data for their kilogram calorific values is variable[1,2,3,4].	

Table 1.1 *Kilogram calorific values of fuels*

Availability

The most efficient fuel in terms of energy release is not always readily available. Traditionally, communities have used the most readily available fuel for cooking, heating, lighting, etc. Thus, turf was used in homes in Ireland for cooking and heating, and fish oils or beeswax were used for lighting. Traditional industries, e.g. tanning, brewing, textile making, etc., also used the locally available fuel. Coal deposits do exist in Ireland but mining coal in Ireland presents some formidable economic and technological challenges and all of our coal for domestic use and electricity generation is imported[5]. Until recently our natural gas deposits have been inaccessible. Hydrogen gas, despite its great efficiency, is not a readily available fuel. When considering the availability of a fuel, a city dweller, a rural household, a travelling family, a mountaineering expedition and a space shuttle mission have different priorities. A further consideration in choosing a fuel to run machines in a factory, a hospital heating system, or the central heating at home is whether the fuel will continue to be available in the future.

Equipment

Anthracite has a greater calorific value than coal but can only be burned in closed stoves where the temperature is high enough to overcome the high activation energy associated with burning this fuel. Gas cookers, domestic gas fire jets and Bunsen burners are all designed to burn a single gaseous fuel. Adjustments must be made to equipment for different flame characteristics if the gas supply is changed. Car and other vehicle engines are designed to use a specific fuel. One cannot change from petrol to diesel to gas without making rather drastic adjustments to the ignition and timing systems. This is because all fuels have different ways of igniting, different rates of combustion, different exhaust products. The cost, size and maintenance of combustion apparatus and fuel storage apparatus must be also considered when selecting a fuel.

Cost

Cost is related to availability, transport, demand in the world market, global politics, etc. Rather complex interplays between social and economic issues arise here. For example, whatever objections one might have to the nuclear fuel industry, the fact that nuclear fuel is accepted in other countries, helps keep the costs of oil, coal, gas, etc., low, by reducing the demand for them. Thus Ireland benefits indirectly from other countries' decisions to use nuclear power. Another example to illustrate the complexity of the background to the cost of fuels is the link between world politics and the dependence of our lifestyles on transport. We rely to a great extent on transport to enjoy a high-convenience, hectic lifestyle which includes increasingly global travel for business or holidays, exports of fresh Irish dairy produce and fresh fish and shellfish to restaurants in Europe, entertainment by visiting opera tenors, ballet companies, soccer teams, etc., pizza deliveries, Interflora, enjoyment of exotic fruits all year round, etc. We are therefore very dependent on a low-cost supply of fuels from the oil industry to operate the ships, planes, trains, buses, trucks, cars, motorcycles, which sustain this frantic movement of goods and people. The reliability of this transport system at a reasonable cost depends upon maintenance of good political relations between oil-rich nations and oil-poor nations.

Hazards

One of the reasons that hydrogen gas is not used to a greater extent as a fuel is the nature of the hazards associated with handling it. It not only has a very high energy content but is very reactive and very easily ignited. The Hindenburg airship disaster of 1937 illustrates the flammability of bulk hydrogen. The Hindenburg was a rigid German airship which began the first aerial transatlantic commercial service in 1936. The 200 000 m^3 of hydrogen gas in this case was not used to power the airship but to give it lift. The airship was driven by four diesel engines at a top speed of 132 km hr^{-1}. It could accommodate 70 passengers who travelled in great luxury. In 1937, while manoeuvring to land at New Jersey, 35 passengers, crew and ground staff were killed when the hydrogen ignited. This ended travel using hydrogen airships although helium airships are now used in a limited way. Because helium is twice as dense as hydrogen it cannot achieve the same lift.

All fuels, being flammable, have associated risks. Gaseous fuels have the ability to form explosive mixtures when mixed with air in certain flammable proportions. Liquid fuels can have low flash points, fire points and spontaneous ignition temperatures. Flash point is the minimum temperature at which the vapours above a fuel will ignite when a flame is applied momentarily.

Fire point is the minimum temperature at which there is sufficient vaporisation of the fuel so that a fire will continue when a flame is applied.

Spontaneous ignition temperature is the minimum temperature at which a fuel will ignite without the application of a flame.

Solid fuels are generally more difficult to ignite but have been known to ignite spontaneously under certain circumstances.

Storage

Hydrogen again poses difficulties. Its molecules are so small they tend to diffuse between the molecules of which the container is made. Heavy metal cylinders are used to store hydrogen and other gaseous fuels, often at high pressure to reduce bulk. This adds to transport costs, handling difficulties, etc. Heaps of coal have been known to undergo spontaneous combustion during storage in ships' holds, on quay sides, etc. Gas pipelines seek to avoid multiple storage points, one for each customer, by delivering the fuel upon demand. However, damage to pipelines, leakage, cost of installation and maintenance then must be considered. Timber, turf and coal are bulky fuels and must be kept dry to ensure easy ignition.

Pollution

The term 'smokeless' fuel is a little confusing. A smokeless fuel does produce gaseous combustion products but these products are transparent (sooty particles are not produced), odourless and not noxious. Methane is a perfect example of a smokeless fuel - it burns to produce carbon dioxide and water vapour. The gas jet of a cooker, Bunsen burner, or other gas-fired appliance is designed to entrain the correct volume of air to ensure complete combustion. Thus no sooty particles, which indicate incomplete combustion, are observed. The two gaseous products cause minimal damage to the environment. The water vapour re-enters the water cycle of condensation, return to the seas, re-evaporation, rainfall, photosynthesis, etc. The carbon dioxide returns to the carbon cycle which keeps atmospheric carbon dioxide concentrations at a constant value of 0.03% by absorption of the gas in photosynthesis or absorption of the gas in the waters of the seas, lakes, rivers, etc. However, there is an imbalance in the carbon cycle resulting from the reduction of the photosynthetic capability of the earth due to deforestation, and also from an increase in the global consumption of fossil fuel reserves. Thus atmospheric carbon dioxide levels are increasing and one concern of environmentalists is the influence of this increasing carbon dioxide concentration on the greenhouse effect and global warming. There is great debate about the extent of global warming and the extent to which carbon dioxide is a contributor.

Turf and peat briquettes are considered to be smokeless fuels and may be burned in the so-called 'smokeless zones' of Cork and Dublin. They produce small quantities of soot and relatively large quantities of ash. Ash is non-volatile inorganic material and remains in the grate. It does not enter the atmosphere but must be disposed of in landfill sites.

Coal is a very smoky fuel by virtue of its tendency to undergo inefficient, incomplete combustion, particularly in the open domestic fire. The chimney gases contain large quantities of carbon particles, a product of incomplete combustion, carbon monoxide, again a product of incomplete combustion, and carbon dioxide and water vapour. Low temperature combustion of coal gives rise to phenols and other aromatics. In addition, since coal contains a small but non-negligible percentage of sulphur compounds, the combustion products contain sulphur dioxide gas, a serious atmospheric pollutant which causes respiratory difficulties and contributes to the formation of acid rain.

Anthracite, because it is burned in closed hot stoves, undergoes complete smokeless combustion. It does contribute to a small extent to the sulphur dioxide problem.

Petrol burns inefficiently in a car engine, producing carbon particles, carbon monoxide, carbon dioxide, water vapour and sulphur dioxide gas. In addition there are unburned hydrocarbon fuel molecules and various oxides of nitrogen present. The latter can be represented by the general formula, NO_x, and are formed when the high energy spark from the spark plug in the combustion chamber breaks the triple bond in the nitrogen gas in the air. The nitrogen atoms then react with oxygen in the air to form the oxides of nitrogen in different proportions. The purpose of a catalytic converter fitted to the exhaust system of a petrol-driven car is to reduce the damage to the environment of these combustion gases. The catalytic converter converts carbon monoxide to carbon dioxide, unburned fuel to carbon dioxide and water vapour and NO_x to nitrogen. Unleaded fuel must be used since lead is a powerful catalytic poison of rhodium, platinum and palladium, the metals used as catalysts in the converter[6].

Diesel oil burns incompletely and its major mode of pollution is by adding soot and carbon monoxide to the atmosphere. Hydrogen is the perfect fuel in terms of pollution, producing only water vapour.

Explosives[7]

An explosive is a material which undergoes a rapid exothermic chemical reaction in which the explosive solid or liquid is converted to large quantities of gases and the speed of the reaction is faster than the speed of sound through the material. The more rapid the reaction and the greater the number of moles of gaseous products, the greater the power of the explosion. The word explosive conjures up images of warfare and terrorism but controlled explosions have several very important peaceful applications, including mining for coal and metals underground, making shafts and tunnels and blasting the rock containing the coal or ore. Civil engineering relies on blasting pathways for railways, roads, canals and tunnels and for demolition work. The aerospace industry uses explosives in ejector seats and in propulsion of rockets into space. Antenna dishes, turbine blades, etc., can be shaped by explosions. Fires in oil wells can sometimes be blasted out by explosions; this works on the same principle as blowing out a candle, i.e. removing the flame from the fuel.

Low explosives

In a low explosive, a chemical reaction, initiated by applying a flame, takes place between an oxygen-rich compound and a fuel, i.e. two separate substances are involved. Blackpowder, first discovered about 1250, but not used for blasting until the 17th century, is an example of a low explosive. It is a mixture of carbon, sulphur and potassium nitrate. Carbon and sulphur act as the fuels and the potassium nitrate supplies the oxygen. For blasting, it was packed into a hole drilled in a rock, the hole was plugged with clay and a fuse made of twine was lit. The effectiveness of the explosion was determined by how finely ground the materials were, how well they were mixed and how tightly they were packed together. Blackpowder generates a lot of smoke when exploded, but despite this and the fact that its effectiveness was quite unpredictable, it remained the only important explosive until about 1850.

Another example of a low explosive is an ammonium nitrate and carbon mixture. The explosive reaction is

$$2NH_4NO_{3(s)} + C_{(s)} \rightarrow 2N_{2(g)} + CO_{2(g)} + 4H_2O_{(g)}$$

Here three moles of solid material are converted to seven moles of gaseous products.

Fireworks are low explosives containing blackpowder and colouring agents which are metal salts. The heat generated in the explosion, initiated by lighting a fuse, excites the electrons in the metal atoms and the characteristic flame colour of the metal is observed in the fragments from the disintegrating firework, white from magnesium salts, red from strontium salts, etc. Arrangements of pastes, syrups and packaging determine the shape of the display when lit.

Dust explosions occur when a combustible material, very finely divided into powder form and mixed with air in the form of a dust cloud, is ignited by a flame or spark. The combustible substance could be coal dust, flour, custard powder, etc. Many serious explosions have taken place in food factories in this way. In factories where flammable dust can accumulate all equipment must be earthed to avoid the build-up of static electricity which can generate sparks.

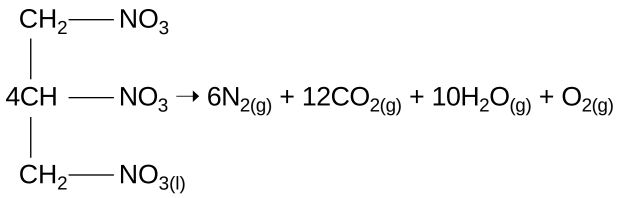
High explosives

High explosives involve a chemical reaction which takes place within the molecules of a single substance, the molecules of which are oxygen rich and can also act as a fuel. Since only one substance is involved, and therefore no grinding or mixing is necessary, the behaviour of high explosives is more predictable than that of low explosives. High explosives are not set off by applying a flame but by detonation. Detonation means starting an explosive reaction using a shock wave.

Alfred Bernhard Nobel (1833-1896), the Swedish industrial chemist, was the first to realise that nitroglycerine must be detonated and was responsible for two important developments in explosives. Firstly, he absorbed the very unsafe nitroglycerine liquid onto clay. These sticks of clay, containing the nitroglycerine, became known as dynamite and were much safer to handle than nitroglycerine on its own. Gelignite is another ‘safe’ high explosive, where nitroglycerine is absorbed into a jelly-like material. Secondly, Nobel worked on making safe detonators to set off the explosion in a controlled fashion. A detonator contains a chemical which reacts very quickly to form a gas. Shock waves formed as the gas is generated detonate the dynamite. The chemical reaction in the detonator can be started by lighting a fuse made of twine, a trail of blackpowder or a shock from the firing pin in a gun.

Nobel left the fortune accumulated by his inventions in trust to award the ‘Nobel Prizes’. These prizes are currently awarded annually for the promotion of Peace, Literature, Physics, Chemistry, Physiology and Medicine. The prizes were first awarded in 1901 and are administered by the Nobel Foundation in Stockholm.

In the intermolecular explosion of nitroglycerine the following reaction takes place.



$$4\begin{array}{l} CH_2-NO_3 \\ | \\ CH-NO_3 \\ | \\ CH_2-NO_{3(l)} \end{array} \rightarrow 6N_{2(g)} + 12CO_{2(g)} + 10H_2O_{(g)} + O_{2(g)}$$

In this reaction there are 29 gaseous product moles for every 4 moles of reactant. The volume occupied by the products is much larger than that occupied by the liquid explosive. However, the reaction is so rapid that large quantities of gases are generated in a small space at high pressure and high temperature (exothermic reaction). The gases are not confined, or are confined only by a thin container, and they expand against the atmosphere or container, exhibiting great destructive power as the energy is dissipated into the container, walls, structures, etc.

Celluloid, the first synthetic plastic, contains enough oxygen to behave like a high explosive when given a shock. Celluloid was used to make early movie film but had to be replaced by a less hazardous material, cellulose acetate, as the former burns vigorously. Table tennis balls are made of celluloid.

Modern high explosives are often plastic-type materials whose shapes can be moulded to improve the accuracy of the required blast. Precisely directed shock waves can achieve the desired effect with the minimum use of explosive and minimal damage to the surroundings. Safer detonating devices, some of which are electrically operated or remote controlled (e.g. by radio waves), have also been developed.

Another modern explosive development is the car safety ‘air bag’. Most new cars have at least one air bag fitted to minimise the shock of collision in an accident. The air bag is actually inflated by nitrogen gas and not air and this gas is generated by a mini explosion. A microprocessor fitted to the vehicle continually records speed and acceleration. If this information matches any crash pattern for speed and acceleration stored in the microprocessor, then an electrical signal deploys the air bag by initiating an explosion. The gas generator contains a mixture of sodium azide, potassium nitrate and silicon dioxide. The reactions which occur are:

$$2NaN_{3(s)} \rightarrow 2Na_{(s)} + 3N_{2(g)}$$

$$10Na_{(s)} + 2KNO_{3(s)} \rightarrow K_2O_{(s)} + 5Na_2O_{(s)} + N_{2(g)}$$

$$K_2O_{(s)} + 5Na_2O_{(s)} + 6SiO_{2(s)} \rightarrow K_2SiO_{3(s)} + 5Na_2SiO_{3(s)}$$

Sodium azide, NaN_3, is a high explosive detonated by the electrical signal from the microprocessor. The first two reactions generate inert nitrogen gas to inflate the plastic ‘air’ bag which cushions the driver or passenger when the sudden acceleration in a crash causes the head and neck to jerk forward violently. The third reaction produces a safe, stable, non-flammable compound from the oxides of potassium and sodium. The oxides themselves are corrosive. The air bag inflates in milliseconds. Note that sodium azide is extremely toxic and since most air bags, fortunately, are not used during the lifetime of a car, it is desirable that unused air bags are removed from scrap vehicles and if possible recycled[8].

(See Experiment 1.5, p. 26.)

1.3 Is Heat the Only Form of Energy Allowed?

Chemiluminescence and Bioluminescence

When there is a decrease in energy as a reaction proceeds from reactants to products, this energy is not always released in the form of thermal energy. Sometimes light is emitted as a reaction occurs. A glow of light energy often accompanies exothermic combustion reactions, e.g. burning coal or a candle. However, in these cases the energy released is predominantly thermal with only a small proportion of light energy. If a reaction proceeds exothermically, but with light energy being the predominant form of energy released, the phenomenon is called **chemiluminescence** or cold light. Unfortunately there is no reaction, emitting cold light, simple enough chemically to be discussed in a Leaving Certificate class. However, a chemiluminescence reaction can be demonstrated without writing a formula or naming the reactants and products. Chemiluminescence reactions such as that suggested in Experiment 1.6 are used by the emergency services, in 'survival' situations, e.g. they have been used in climbing expeditions to Everest. They also work underwater[9]. (See Experiment 1.6, page 27.)

If a biological process releases light energy the phenomenon is called **bioluminescence** and is exhibited by glow worms, fireflies and many marine creatures. In Thomas Hardy's book 'The Return of the Native' two rivals play dice by the light of thirteen glow worms. The female firefly uses her glowing abdomen to attract a mate. Sometimes the bioluminescence is used instead to attract prey. A glow in a ship's wake at night is caused by bioluminescent microorganisms.

The reverse effect is also well known, i.e there are examples of endothermic reactions absorbing light energy rather than heat energy. One very important example is of course photosynthesis. The fading of watercolours demonstrates this effect also. Blue shades are the most fugitive, i.e. fade fastest, and therefore the tonal balance as well as the overall brightness of watercolour paintings change over time. Paint catalogues classify colours according to their permanence in light. Another example of a photochemical reaction from the Leaving Certificate syllabus is the homolytic fission of chlorine which takes place during the free radical substitution reaction of methane with chlorine and absorbs uv from sunlight.

$$Cl_{2(g)} \rightarrow 2Cl^{\bullet}_{(g)} \quad \Delta H = 242 \text{ kJ mol}^{-1}$$

Dentists use a small uv source to activate the catalyst to initiate certain addition polymerisation reactions to make certain dental materials in the mouth. (Some modern catalysts may be activated with blue light.) This involves breaking the bond in an unstable organic peroxide molecule to form free radicals. The reaction is endothermic and fuelled by light.

Electricity

Instead of heat or light, chemical reactions can emit energy in the form of electricity. One example is the so-called 'galvanic' pain experienced when a piece of metal makes contact with a metal filling in a tooth and the saliva in the mouth. The electrical current generated stimulates nerve endings in the tooth, causing the painful sensation and may lead to corrosion of cavity fillings. This reaction is 'exothermic'. All electrical cells and batteries produce electrical energy as the result of chemical reactions.

Electricity can also be used to fuel a chemical reaction. The electrolysis of water in the Hofmann voltameter is just one example of an endothermic reaction which takes place as the result of absorbing electrical energy.

$$H_2O_{(l)} \rightarrow H_{2(g)} + {}^{1}/_{2}O_{2(g)} \ \Delta H = 285.8 \text{ kJ mol}^{-1}$$

Recharging a battery is an example of using electrical energy to bring about a chemical reaction.

Electricity is used also to extract metals from their ores. (See Experiment 1.7, p. 27.)

1.4 Zeroth Law of Thermodynamics

It is worth mentioning the zeroth law of thermodynamics. This law gets its name from the fact that it was discovered after the other laws of thermodynamics but is so fundamental to the understanding of thermodynamics. We have been assuming it intuitively already. It states that if two bodies are in thermal equilibrium with a third body, e.g. a thermometer, then the first two bodies are in thermal equilibrium with one another. This means that there will be a net heat flow from a hot body to a cold one but if two bodies are at the same temperature neither experiences a net loss or gain of heat energy relative to the other.

1.5 Calorimetry

The process of experimentally measuring the amount of heat energy involved in a physical or chemical change is called **calorimetry**. A calorimeter is the container in which the physical or chemical change takes place and there are three types to consider, namely sealed and open metal calorimeters and open calorimeters made of a material which is an insulator.

For the most accurate work either a sealed or an open metal calorimeter is used. The metal calorimeter may be well insulated or it may be immersed in water. In the latter case the heat absorbed by the water must be calculated.

For work not requiring the same degree of accuracy, the calorimeter may itself be constructed of an insulating material, e.g. expanded polystyrene. In calculations, the heat absorbed or released by the calorimeter is considered negligible and is ignored.

The quantity of heat lost or gained by a substance is easily calculated since all materials have associated with them the physical property of specific heat capacity. The specific heat capacity, c, of a substance is the quantity of energy required to change the temperature of 1 kg of that substance by 1 K. Specific heat capacities are defined at constant volume, c_v, and at constant pressure, c_p. Specific heat capacities of gases at constant pressure are somewhat bigger than specific heat capacities at constant volume, because at constant pressure the substance is allowed expand against the surroundings as it is heated and this requires additional energy. For liquids and solids c_p and c_v values are very similar since the degree of expansion upon heating is small. Since our work is nearly always carried out at atmospheric (constant) pressure we use c_p values. The units for both are J kg^{-1} K^{-1}. Thus the quantity of energy required to raise the temperature of mass m of the substance, and thus increase its temperature by $\Delta\theta$, is simply $mc\Delta\theta$. The same quantity of energy is lost when mass m of the substance cools by $\Delta\theta$. Tables of specific heat capacity data are readily available[3,10]. Subscripts can be used to denote different substances in calculations, e.g. c_w is the specific heat capacity of water and c_c is the specific heat capacity of copper. Heat capacity, C, is the energy required to change the temperature of a body by 1 K. If the body is made of the same material throughout $C = mc$.

Measuring Enthalpies of Combustion

Bomb calorimetry

A closed metal calorimeter, called a bomb calorimeter, is used to measure heats of combustion, to compare efficiencies of fuels and to measure the energy content of foodstuffs, Fig. 1.9. The bomb is a thick-walled steel vessel into which oxygen at high pressure can be pumped. This ensures that the substance burns in an excess of oxygen and the normal oxide is formed. The sample is held in a platinum crucible and ignited electrically. The platinum will not burn and will not react with the sample even under the conditions of high temperature and pressure which exist inside the bomb during reaction. The bomb is immersed in a vessel of water in a container designed to eliminate energy transfer to or from the surroundings. The bomb and surrounding water may then be considered to be the universe, the combustion reaction taking place in the bomb is the system and the water and insulated container with lid act as the surroundings.

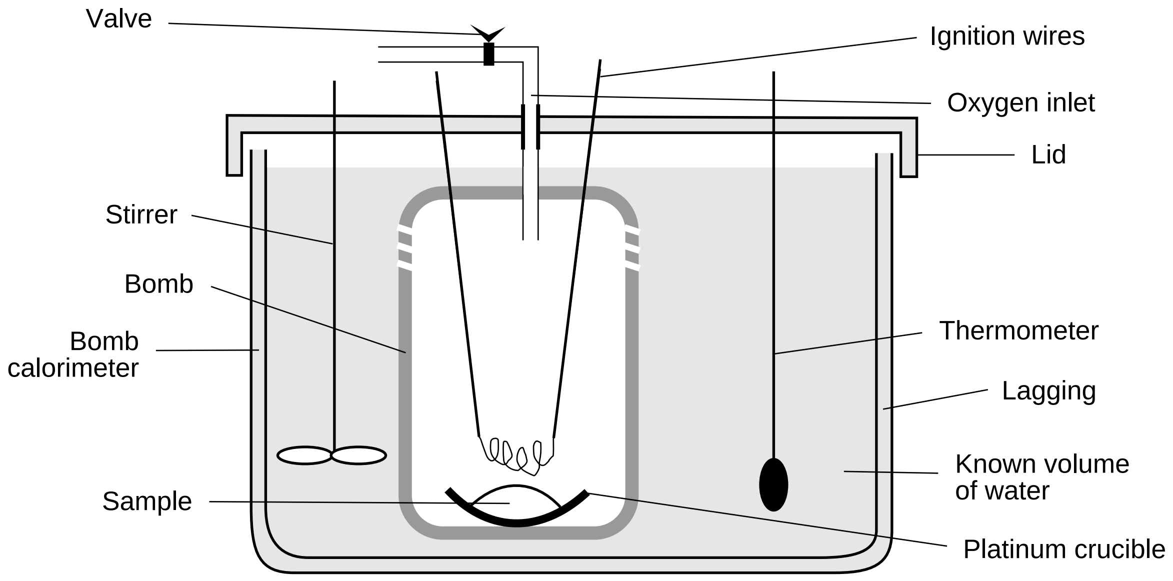


Fig. 1.9 *Bomb calorimeter*

A bomb calorimeter is a specialised piece of equipment and, because of the high temperature and pressure at which the combustion occurs, requires a skilled operator and is not normally found in a school laboratory.

The energy, ΔE, released in a combustion reaction is transferred to the steel container and to the water.

$$\Delta E = C_{bc}\Delta\theta_w$$

where C_{bc} is the heat capacity of the bomb and $\Delta\theta_w$ is the increase in temperature of the water. The heat capacity of the bomb calorimeter, C_{bc}, may be determined by measuring the electrical energy required to bring about a certain rise in temperature. Alternatively, the heat capacity of a bomb calorimeter may be determined by burning a known mass of a substance of known heat of combustion, e.g. benzoic acid, and measuring the resultant temperature increase.

Consider carrying out the combustion of 2 g of sucrose ($C_{12}H_{22}O_{11}$) in excess oxygen in a steel bomb calorimeter immersed in water in an insulated container. The energy released in the combustion is calculated from the formula above and the energy released upon burning a mole of sucrose (342 g) is proportionately larger than that released when 2 g is burned. Corrections can be made for the energy involved in igniting the sucrose and for the fact that this reaction is not carried out at constant pressure.

Estimating heats of combustion using an open metal calorimeter

A crude estimate for the heat of combustion of an easily ignited sample can be found in an open system in a school laboratory. A known mass of an easily ignited sample is placed in a metal crucible under a beaker containing a known volume of water at a known temperature, Fig. 1.10. The sample is ignited with a lighting taper and the flame and product gases transfer energy to the beaker of water. There are considerable heat losses to the surroundings, e.g. the energy absorbed by the metal crucible, the beaker and its stand are not included in the calculation and not all of the energy from the product gases is transferred to the water - as the combustion gases rise from the lighting sample the air in contact with these gases will absorb heat from them. To reduce heat transfer from the hot gases to the air in the room, cardboard shields are placed around the apparatus.

Consider the combustion of 2 g of a combustible substance by this method. The energy, ΔE, released in the combustion reaction is assumed to be transferred completely to the water,

$$E = m_w c_w \Delta\theta_w.$$

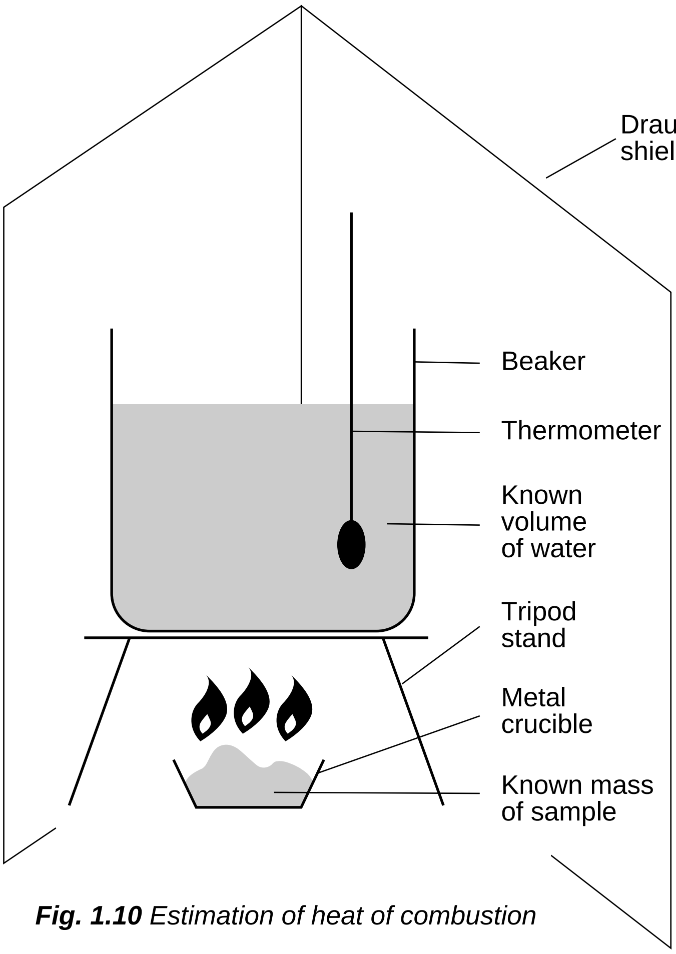


Fig. 1.10 *Estimation of heat of combustion*

The increase in temperature of the water, $\Delta\theta_w$, can be measured with a thermometer. Note that m_w must be in kilograms. The energy released upon burning a mole of the flammable substance is proportionately larger than that released when 2 g are burned.

Measuring Enthalpies of Solution

Using a metal calorimeter

Heats of solution or heats of neutralisation or various other heats of reaction (provided no gaseous reactants or products are involved) are easily measured using a simple open metal calorimeter, lagged with insulating material to reduce heat loss to the surroundings, Fig. 1.11.

For example, to measure the heat of solution of sodium hydroxide, 2 g of sodium hydroxide are dissolved in 200 cm^3 of water in a metal calorimeter of known mass. The energy, ΔE, transferred to the solution is given by

$$\Delta E = m_w c_w \Delta\theta_w + m_c c_c \Delta\theta_c$$

where m_w and m_c are the masses of the water and the calorimeter, respectively, and c_w and c_c are the specific heat capacities of water and the metal from which the calorimeter is made, respectively. The rises in temperature of the water and the calorimeter, $\Delta\theta_w$ and $\Delta\theta_c$, respectively, are assumed equal to one another because of the good thermal conductivity of the metal. The energy released upon dissolving a mole of sodium hydroxide (40 g) is proportionately larger than E. If the temperature rises during the experiment the reaction is exothermic and the calculated heat of solution is given a minus sign.

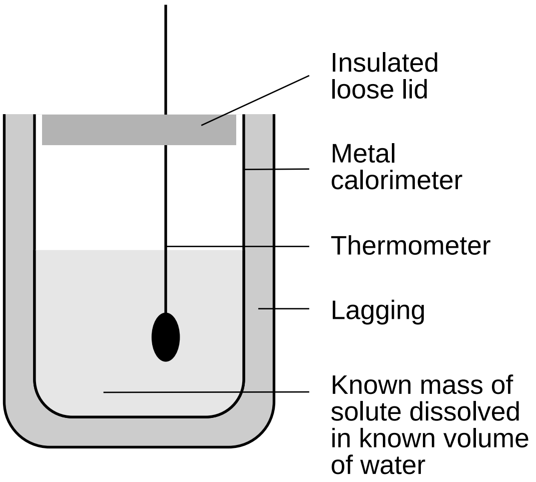


Fig. 1.11 *Measuring heat of solution*

For precise work, it should be borne in mind that the energy released or absorbed when the solute dissolves is transmitted to or absorbed from the solution, not just to or from the water. Therefore, the specific heat capacity of the solution at the actual concentration used in the experiment should be used in the calculation and not the specific heat capacity of water. The mass of the solution should be used in calculations instead of the mass of the solvent where accuracy is important.

Using an insulated calorimeter

Now consider carrying out the same experiment to measure the heat of solution of sodium hydroxide by dissolving 2 g of sodium hydroxide in 200 cm^3 of water in a styrofoam cup, Fig. 1.12. Negligible heat is transferred to the surroundings and the calculation is

$$\Delta E = m_w c_w \Delta\theta_w$$

The energy released upon dissolving a mole of sodium hydroxide (40 g) is proportionately larger. (See Experiments 1.4 and 1.8, pp. 26 and 28.)

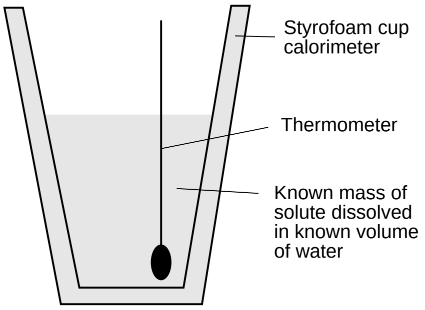


Fig. 1.12 *Measuring heat of solution*

1.6 Hess's Law

It is a necessary consequence of the first law of thermodynamics that if a series of chemical and/or physical changes takes place, the algebraic sum of the enthalpies of each of the individual changes is equal to the enthalpy for the process occurring in a single step. The Swiss-Russian chemist **Germain Henri Hess** (1802-1850) first stated in the 1840s that only the initial and final states of the reactants and products, and not the route taken, accounted for the energy change in a process. This law is often referred to as Hess's law of heat summation and is very useful in calculating, from known enthalpy changes, the enthalpy changes for processes which cannot be measured experimentally. For example, the enthalpy of formation of ethane is not measurable experimentally because carbon and hydrogen form a mixture of hydrocarbons when they react directly. We require, therefore, the standard enthalpy for the following reaction from calculation.

$$2C_{(s)} + 3H_{2(g)} \rightarrow C_2H_{6(g)}$$

The heats of combustion of carbon, hydrogen and ethane have been determined experimentally.

$$H_{2(g)} + {}^1/_2O_{2(g)} \rightarrow H_2O_{(l)},\ \ \Delta H = -285.8 \text{ kJ mol}^{-1}$$

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)},\ \Delta H = -393.5 \text{ kJ mol}^{-1}$$

$$C_2H_{6(g)} + 3{}^1/_2O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)},\ \ \Delta H = -1560 \text{ kJ mol}^{-1}$$

Consider, then, that the formation of one mole of ethane directly from its elements (Route A in italics in Fig. 1.13) has the same initial and final states as burning two moles of carbon and three moles of hydrogen to form two moles of carbon dioxide and three moles of water and then (somehow) converting the two moles of carbon dioxide and three moles of water to one mole of ethane and three and a half moles of oxygen (Route B). The practical difficulties actually involved in reversing the combustion of ethane can be conveniently ignored and from the first law of thermodynamics we can say that the same quantity of energy released in combustion is gained if the reaction is reversed, the ΔH value being simply inverted (additively). Since the quantity of oxygen consumed in the combustion steps is equal to that produced in the final step there is no overall loss or gain of oxygen. The carbon dioxide and water produced in the combustion of carbon and hydrogen are intermediates and are used up in the final step of Route B to produce ethane. According to Hess the enthalpy of reaction by Route A is equal to the algebraic sum of the enthalpies of each of the reactions of Route B.

$$\Delta H = -787 - 857.4 + 1560 = -84.4 \text{ kJ}$$

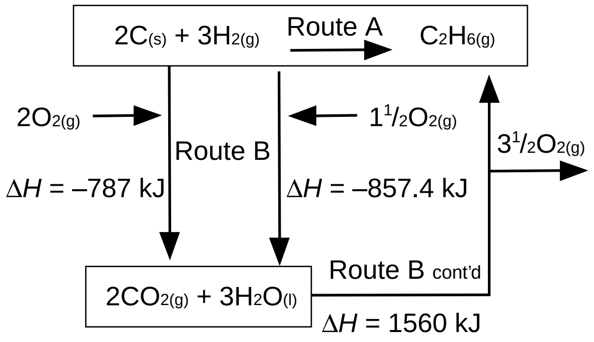


Fig. 1.13 *Equivalent routes in terms of energy*

Algebraically, the three reactions of Route B are equivalent to the single reaction of Route A. Intermediates and any substances used but reformed in the processes 'cancel'.

$$2C_{(s)} + \cancel{2O_{2(g)}} \rightarrow \cancel{2CO_{2(g)}}, \ \Delta H = -787.0 \text{ kJ mol}^{-1}$$

$$3H_{2(g)} + \cancel{1\tfrac{1}{2}O_{2(g)}} \rightarrow \cancel{3H_2O_{(l)}}, \ \Delta H = -857.4 \text{ kJ mol}^{-1}$$

$$\cancel{2CO_{2(g)}} + \cancel{3H_2O_{(l)}} \rightarrow C_2H_{6(g)} + \cancel{3\tfrac{1}{2}O_{2(g)}}, \ \Delta H = +1560 \text{ kJ mol}^{-1}$$

$$2C_{(s)} + 3H_{2(g)} \rightarrow C_2H_{6(g)}, \ \Delta H = -84.4 \text{ kJ mol}^{-1}$$

Fig. 1.14 is another way of illustrating Hess's law. The diagram represents an exothermic reaction which can proceed by several pathways. The enthalpy change for the reaction, i.e. the thermal energy released, is simply the difference between the energies of the reactants and products. Whether the reaction route has no intermediates, one intermediate or several does not alter this figure. A similar illustration may be made for an endothermic reaction.

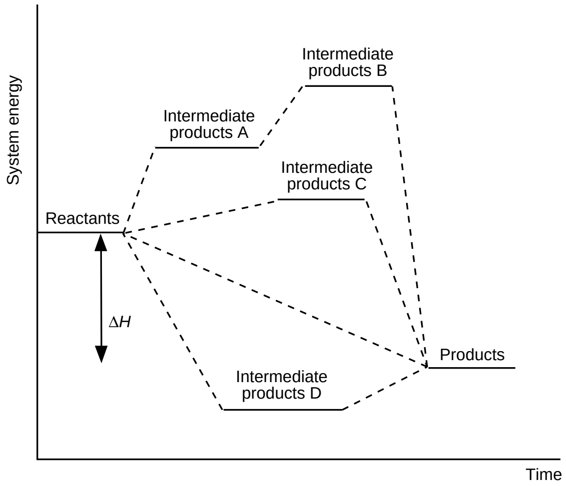


Fig. 1.14 *The enthalpy change is independent of the reaction pathway*

Enthalpies of Reaction from Enthalpies of Formation

Consider also the following statement.

Heat of reaction = Σ(Enthalpies of formation of products) – Σ(Enthalpies of formation of reactants)

Heat of reaction = $\Sigma\, \Delta H_f$ (products) – $\Sigma\, \Delta H_f$ (reactants)

This statement can be easily justified from Hess's law, diagramatically. Remember that enthalpies of formation are relative values, all elements in their standard states having being assigned an enthalpy of formation of zero. This allows very rapid calculations of enthalpies of reaction to be carried out, given a table of enthalpies of formation. Fig. 1.15 depicts an endothermic reaction. A similar illustration may be made for an exothermic process.

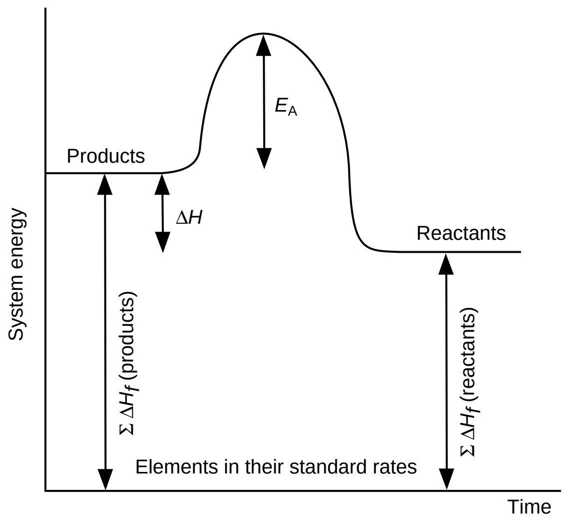


Fig. 1.15 *Heat of reaction =* $\Sigma\ \Delta H_f$ *(products) –* $\Sigma\ \Delta H_f$ *(reactants)*

Dieting

According to a Gallup opinion poll in 1992, at least 20% of the British population at any one time is trying to lose weight[11]. Of course, not all diets are intended to cause weight loss, sometimes a person might be medically advised to gain weight. Counting calories is an established practice in attempts to control weight. Every time we count calories we're making use of Hess's law and calorimetry. The body releases the same quantity of energy from a certain mass of a foodstuff in the slow multi-step metabolic processes of digestion and aerobic cellular respiration as is released in the rapid combustion of the same mass of the same foodstuff. The reactants are the same, namely the foodstuff and oxygen, and so are the products, namely carbon dioxide and water vapour. According to Hess the route of reaction is unimportant and so the energy content of a food for the purposes of sustaining body functions and tissue can be experimentally determined by simply burning it in a bomb calorimeter.

Counting calories

Traditionally the energy content of food and other fuels has been measured in 'Calories'. The 'Calories' referred to in this way are actually kilocalories (kcal). The calorie itself, which is defined as the quantity of energy required to change the temperature of 1 g of water by 1 K, is simply too small to be useful for food energy content. Neither the Calorie (kcal) nor the calorie, however, is an SI unit and nutritional information supplied on food packaging in the EU provides the energy content information in the approved SI energy unit, the joule, J, usually with kilocalorie information also. A joule is defined in terms of mechanical work: one joule is the work done (energy used) when a force of one newton moves a body a distance of 1m in the direction of the force. In fact, since joules are also very small the information is usually quoted in kilojoules, kJ.

Food labelling

Most food packaging has a panel which gives nutritional information about the contents. These panels comply with the 1990 EU Directive on Nutrition Labelling for Foodstuffs which requires that the information on it refers to 100 grams or 100 millilitres of the foodstuff as sold, and gives the energy value in kJ and kcal and the amounts of protein, carbohydrate, sugars, fat, saturates, fibre and sodium in grams and the amount of any other nutrient for which a claim is made[12]. Despite the fact that packaging prioritises the SI unit, most dieters persist with 'counting the Calories' rather than the kilojoules.

Enthalpies of Neutralisation

Hess was also the first person to observe that the heat of neutralisation of a strong acid and strong base is almost a constant. The explanation for this fact is that all strong acids and bases are fully dissociated in solution. When the acid and base are mixed, a salt is formed but its ions remain dissociated and water is also formed. Essentially, the only reaction involving the breaking or formation of bonds is the making of water and therefore the only thermal energy change expected is that associated with the production of water from its ions, which of course is a constant. The neutralisations of strong acids and bases written ionically illustrate these points.

For example, the equation for the reaction between nitric acid and sodium hydroxide is usually written as

$$HNO_{3(aq)} + NaOH_{(aq)} \rightarrow NaNO_{3(aq)} + H_2O_{(l)}$$

Rewriting this equation to show the dissociated ions gives

$$H^+_{(aq)} + NO_3^-{}_{(aq)} + Na^+_{(aq)} + OH^-_{(aq)} \rightarrow Na^+_{(aq)} + NO_3^-{}_{(aq)} + H_2O_{(l)}$$

Rewriting this equation again, omitting the ions which do not undergo any chemical change gives the reaction

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$$

The formation of water from its ions has the enthalpy value –57.2 kJ mol^{-1}.

Repeating the procedure for another strong acid and base gives the same result. The usual equation for the reaction between hydrochloric acid and potassium hydroxide is

$$HCl_{(aq)} + KOH_{(aq)} \rightarrow KCl_{(aq)} + H_2O_{(l)}$$

Ionically

$$H^+_{(aq)} + Cl^-_{(aq)} + K^+_{(aq)} + OH^-_{(aq)} \rightarrow K^+_{(aq)} + Cl^-_{(aq)} + H_2O_{(l)}$$

Omitting the ions which do not change chemically

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$$

The formation of water from its ions has the enthalpy value –57.2 kJ mol^{-1}.

The reaction between sulphuric acid and sodium hydroxide produces sodium sulphate and water:

$$H_2SO_{4(aq)} + 2NaOH_{(aq)} \rightarrow Na_2SO_{4(aq)} + 2H_2O_{(l)}$$

Written ionically

$$2H^+_{(aq)} + SO_4^{2-}{}_{(aq)} + 2Na^+_{(aq)} + 2OH^-_{(aq)} \rightarrow 2Na^+_{(aq)} + SO_4^{2-}{}_{(aq)} + 2H_2O_{(l)}$$

Omitting the ions not involved in any chemical change

$$2H^+_{(aq)} + 2OH^-_{(aq)} \rightarrow 2H_2O_{(l)}$$

The formation of water from its ions has the enthalpy value –57.2 kJ mol^{-1}, that is, –114.4 kJ per two moles of water. However, the definition of enthalpy of neutralisation refers to the formation of one mole of water, so the enthalpy of neutralisation of sulphuric acid by sodium hydroxide to form one mole of water may be represented by the equation

$$^1/_2H_2SO_{4(aq)} + NaOH_{(aq)} \rightarrow {}^1/_2Na_2SO_{4(aq)} + H_2O_{(l)},\ \Delta H = -57.2\ \text{kJ mol}^{-1}$$

The enthalpies of neutralisation of acids and bases when one or both reacting species are weak are not constant. Most of these enthalpies are less than –57.2 kJ mol^{-1}, but sometimes the value is greater. Some examples include:

$$HCl_{(aq)} + NH_4OH_{(aq)} \rightarrow NH_4Cl_{(aq)} + H_2O_{(l)},\ \Delta H = -52.2\ \text{kJ mol}^{-1}$$

$$HCN_{(aq)} + KOH_{(aq)} \rightarrow KCN_{(aq)} + H_2O_{(l)},\ \Delta H = -11.7\ \text{kJ mol}^{-1}$$

$$HCN_{(aq)} + NH_4OH_{(aq)} \rightarrow NH_4CN_{(aq)} + H_2O_{(l)},\ \Delta H = -5.4\ \text{kJ mol}^{-1}$$

$$HF_{(aq)} + NaOH_{(aq)} \rightarrow NaF_{(aq)} + H_2O_{(l)},\ \Delta H = -68.6\ \text{kJ mol}^{-1}$$

The reason these four enthalpies of neutralisation are reduced below or increased above the –57.2 kJ mol^{-1} value which we now expect for a reaction involving the formation of water from its ions, is that there are now additional processes occurring. Any weak acid or weak base is not fully dissociated in aqueous solution. When the acid and base solutions are mixed, they can only fully neutralise one another if the weak acid and/or base completely ionises. These reactions are endothermic. The acid anion or the base cation produced upon ionising the weak acid or base are then hydrated by water ions. This stabilises the ions and therefore releases energy. So the net energy released in such neutralisations is the energy released upon formation of water from its ions, less the energy required to fully dissociate the weak acid and/or base involved, plus the energy associated with hydrating the acid anion and/or base cation. In most cases the latter energy is insignificant and the result is dictated by the first two processes. In the case of neutralising hydrogen fluoride, however, the latter process is very significant.

1.7 Bond Energy

Definition

For a diatomic substance, A-B, in the gaseous state, **bond energy** is defined as the energy required to break the bonds in one mole of the substance and to separate the neutral atoms formed completely from one another at standard pressure and at a specified temperature, usually 298 K. The same amount of energy is released if the neutral atoms are brought together to form the same bond. The bond energy of the A-B bond, therefore, is the energy required for the following endothermic process:

$$AB_{(g)} \rightarrow A_{(g)} + B_{(g)}$$

The bond energy of one of the bonds in a polyatomic substance of formula AB_X is the energy required to break one mole of those bonds and separate the neutral fragments completely, again at standard pressure and at a specified temperature, usually 298 K. The bond energy of the A-B bond is the energy required for the following endothermic process

$$AB_{X(g)} \rightarrow AB_{(X\text{-}1)(g)} + B_{(g)}$$

or the energy released if this process is reversed.

For example, the bond energy of breaking one C-H bond in a mole of methane molecules is

$$CH_{4(g)} \rightarrow CH_{3(g)} + H_{(g)},\ \Delta H = 435 \text{ kJ mol}^{-1}$$

Each of these two definitions for bond energy refers to the breaking of a specific bond in a *specific* compound. The average bond energy (or average bond dissociation energy or average bond enthalpy), however, is the average energy required to break a specific bond in *a wide selection of compounds containing that bond*. All of these processes are carried out at constant standard pressure and at a specified temperature, usually 298 K. The average bond energy of the C-H bond can be calculated by breaking all the bonds in methane and dividing by four.

$$CH_{4(g)} \rightarrow C_{(g)} + 4H_{(g)},\ \Delta H = 1660 \text{ kJ mol}^{-1}$$

$$E_{av}(\text{C-H}) = 1660 \div 4 = 415 \text{ kJ mol}^{-1}$$

A better value for the C-H average bond energy can be calculated by averaging the C-H bond energy data of a large number of organic compounds, the average energy of the C-H bond is then 412 kJ mol^{-1}.

Uses of Bond Energy Data

Average bond energy data can be used to calculate the enthalpy change for a reaction. The principle is quite simple. The energy required to break all the reactant molecules into neutral gaseous atoms at infinite separation is the sum of the average bond energies of all the bonds in the reactants, ΔH_1. Similarly, the energy released when these neutral gaseous atoms at infinite separation are assembled to form the products is the sum of the average bond energies of all the bonds in the products, ΔH_2. According to Hess's law, the algebraic sum of the energies for these two stages is equal to the enthalpy change for the reaction taking place in a single step, $\Delta H = \Delta H_1 + \Delta H_2$, see Fig. 1.16. The result obtained for the enthalpy of reaction by this method is less accurate than that obtained from summation of enthalpies for a series of reactions. This is because *average* bond energy data were used rather than heat of combustion data or other *specific* data for the specific reactants and products of the reaction.

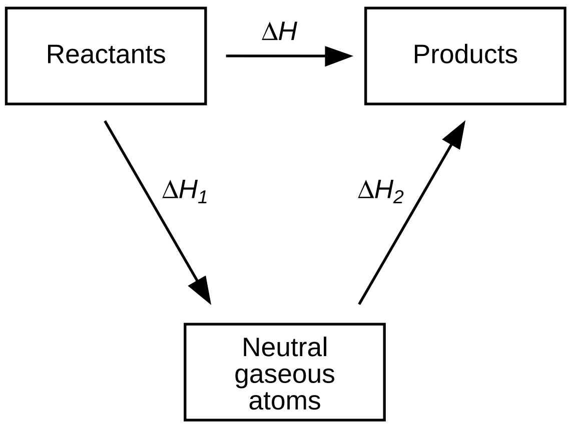


Fig. 1.16 *Bond energy calculations*

Bond energy values provide data to compare bond strengths, see Table 1.2.

Bond	Bond energy/ kJ mol^{-1}
Cl-Cl	242
Br-Br	193
I-I	151
F-F	158
H-H	436
O=O	496
N≡N	944
C-C	348
C$\overset{\cdots}{-}$C	518
C=C	612
C≡C	837

Table 1.2

For example the bond energies of the Cl-Cl, Br-Br and I-I bonds are 242, 193 and 151 kJ mol^{-1}, respectively. The decrease can be explained in terms of atomic size: the electrons of the covalent bond are farther from the iodine nuclei and more effectively shielded from the iodine nuclei by electrons in inner shells than is the case in bromine or chlorine. This is despite the larger positive nuclear charges of the iodine atoms. The F-F bond, however has a value of 158 kJ mol^{-1}, which breaks the trend of halogen-halogen bonds strengthening progressively down the group. The reason for the weak F-F bond is the anomalously low electron affinity of fluorine and the large repulsions between the non-bonding electrons of the fluorine atoms of the bond. The small n = 2 energy level accounts for the low electron affinity of fluorine and the strong repulsions between the non-bonding electrons of molecular fluorine.

Another interesting set of bonds to compare is that comprised of H-H, O=O and N≡N which have the following bond energies: 436, 496 and 944 kJ mol^{-1}. (Strictly speaking, the oxygen molecule does not have a double bond; it is a diradical.) These figures indicate that the triple bond of nitrogen is stronger than the double bond of oxygen which in turn is stronger than the single bond of hydrogen, but there is not a linear progression. The figures indicate that the triple bond in nitrogen has an extremely high bond energy and hence is difficult to break, accounting for the inertness of nitrogen gas. The oxygen double bond on the other hand is broken by not much more energy than that required to break a single H-H bond and this accounts for the reactivity of oxygen gas. Several factors must be considered to account for the differences in these bond strengths. Small atomic size of the atoms involved generally contributes to bond strength and this is one of the reasons why the single bond of hydrogen is almost comparable in strength to the oxygen double bond. The underlying reason for the large discrepancy in bond energy values in the cases of N_2 and O_2 lies in the difference in the arrangement of electrons in the molecular orbitals formed in the two molecules.

In a polar covalent bond, there is another contributing factor influencing bond energies, namely, the greater the electronegativity difference between the atoms of the polar covalent bond the greater the bond strength. The electronegativity difference indicates polarity and hence an electrostatic attraction between the atoms in addition to the covalent bonding between them.

A third set of average bond energy values worth comparing is the series consisting of the carbon-carbon single bond, C–C, the aromatic carbon-carbon bond, C$\overset{\cdots}{-}$C, the carbon-carbon double bond, C=C and the carbon-carbon triple bond, C≡C, which have values of 348, 518, 612 and 837 kJ mol^{-1}, respectively. There is a progressively stronger bond formed when more than one pair of electrons is shared between the two carbon atoms but again it is not a linear progression. To understand the difference in carbon-carbon bond strengths, the carbon-carbon bonds in ethane, ethene, ethyne and benzene are examined. In ethane, there is a single sigma bond between the two carbon atoms. In benzene there is a sigma bond and a delocalised aromatic bond between the two carbon atoms. In ethene there is a sigma bond and one pi bond between the carbon atoms, in ethyne there is one sigma bond and two pi bonds at right angles to one another.

A **sigma** molecular orbital (or bond) is formed along the axis joining two atoms and is cylindrically symmetrical about this axis. Such bonds are formed by the end-on overlap of two orbitals which are in phase, see Fig. 1.17.

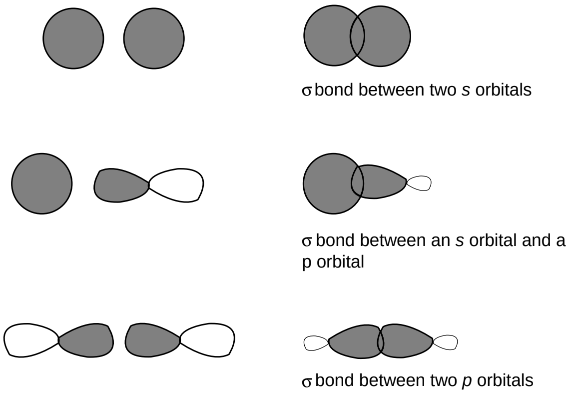


Fig.1.17 *Sigma (σ) bonds*

A **pi** molecular orbital (or π bond) is formed in a plane at right angles to the axis joining two atoms. It is formed by sideways overlap of two orbitals parallel to one another and in phase. There is a change in the sign of the wave function when such a molecular orbital is rotated through 180˚ around the bond axis. Sideways overlap is less efficient than end-on overlap and therefore pi bonds are generally weaker than sigma bonds formed between the same atoms.

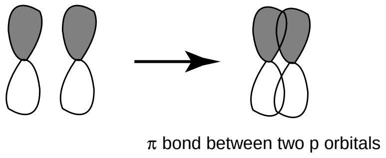


Fig. 1.18 *Pi (π) bonds*

1.8 Second and Third Laws of Thermodynamics

The Second Law of Thermodynamics

Next we must consider briefly the second law of thermodynamics which can be stated in various ways. From a chemical point of view, it can be expressed thus: a physical or chemical change can only be spontaneous if it tends towards minimum energy and maximum disorder. A spontaneous reaction is one which will occur, given enough time.

A Leaving Certificate student might wonder why endothermic reactions take place spontaneously. Such reactions are observed to happen and are not always particularly slow, e.g. ammonium chloride dissolves readily in water with a considerable temperature drop, liquids evaporate, e.g. enormous volumes of seawater evaporate daily despite the large specific latent heat of vaporisation of water, etc. That energy is absorbed from the surroundings to enable the reaction to occur is obvious but the student might be interested to learn that all spontaneous endothermic reactions are accompanied by an increase in molecular disorder which in turn is associated with a release of energy. In any spontaneous endothermic chemical or physical process, the energy released by the increase in molecular disorder in the system must be greater than the enthalpy change for the reaction.

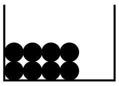
The explosion of N_2O_5 to form nitrogen(IV) oxide and oxygen is endothermic. It is accompanied by a large increase in disorder and therefore would be predicted to be spontaneous. The overall energy of the system tends to decrease, obeying the second law.

$$N_2O_{5(s)} \rightarrow 2NO_{2(g)} + {}^1/_2O_{2(g)}$$

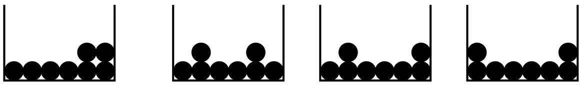
Conversely, a physical or chemical change can only bring about a more orderly set of products if the reaction is exothermic.

The Third Law of Thermodynamics and Entropy

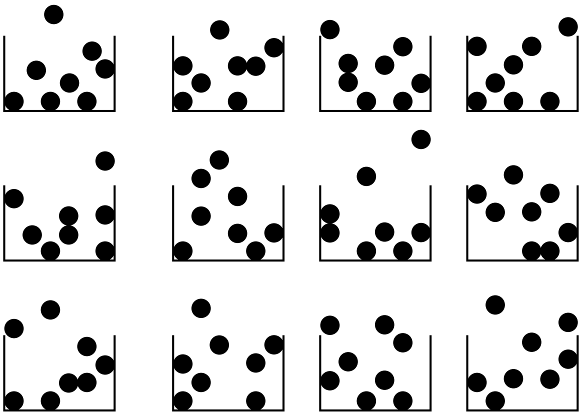
Disorder, or entropy, *S*, is defined as relating to the number of different microscopic ways of making a certain macroscopic situation. The third law of thermodynamics states that the entropy of a pure crystalline substance at absolute zero is zero since there is only one way of arranging its molecules with no disorder, i.e. there is zero disorder. As the substance is heated to room temperature the molecules begin to vibrate about their fixed positions and the disorder increases as the vibrations increase. Entropy is obviously related to temperature. A flawless crystal has only one perfectly ordered state at 0 K. As temperature increases the sample melts and in the liquid at a given temperature there are several different equivalent ways of arranging the molecules in contact with one another. Further heating supplies more energy to the molecules and, in the gas state at a given temperature, there is a great degree of freedom of movement of the molecules. Consequently there are several more ways of bringing about the same macroscopic observation so the entropy has increased significantly once more. For example, in an imaginary sample consisting of eight molecules only one way of arranging a flawless lattice exists, there are several ways of arranging the molecules in a liquid sample, some of which are shown, and several more ways of arranging the molecules in the gaseous state, again some of which are shown, see Fig. 1.19.



Pure crystal at 0 K, zero disorder, zero entropy



Liquid showing four states of equal disorder to macroscopic observer, increased entropy



Gas showing twelve states of equal disorder to macroscopic observer, entropy further increased

Fig. 1.19 *Entropy increases with temperature*

Entropy is therefore related to probability. Mathematically, entropy, *S*, is defined as

$$S = k \ln \Omega$$

where k is a constant and Ω represents the thermodynamic probability, i.e. the number of different ways of bringing about the same macroscopic observation by distribution of the molecules in various positions and energy states. The energy associated with an entropy change is $T\Delta S$, where T is temperature in kelvin, and ΔS is the entropy change associated with the physical or chemical change. By convention, $T\Delta S$ is negative upon release of energy or increased disorder.

There is a high probability of a disordered arrangement of molecules occurring since there are so many disorderly ways of arranging a sample of molecules. There is only one way of arranging a set of molecules in perfect order. This situation has an effectively zero probability of occurrence, given the usual very large number of molecules in a sample.

Number of ways of achieving perfect order in a sample =1
Number of molecules in sample = N
Probability of perfect order = $1/N \rightarrow 0$ since N is very large.

Spontaneity[13]

A chemical reaction is spontaneous only if there is a decrease in energy associated with its occurrence. This energy is called the free energy for the reaction and is designated ΔG. By our usual convention ΔG must be negative if energy is released.

$$\Delta G = \Delta H - T\Delta S$$

If an exothermic reaction is to be always spontaneous then it must be accompanied by an increase in disorder or if the reaction tends towards greater order, the $T\Delta S$ term must not exceed the ΔH term as temperature rises. If an endothermic reaction is to be ever spontaneous then it must be accompanied by a large increase in disorder so that the $T\Delta S$ term exceeds the ΔH term.

1.9 Experiments

Experiment 1.1

To Demonstrate an Exothermic Reaction

Teacher demonstration/student experiment

Materials

Commercial 'hand warmer' for combating cold weather conditions (fuel sticks type)

Safety

Wear safety spectacles.

Procedure

1. Allow the students to handle and examine the contents of the 'hand warmer'.
2. Light the fuel stick as instructed on the pack and place as instructed in the insulated case.
3. Allow the students to note the change in temperature by handling the pack.

Conclusion

There is a rise in temperature associated with the reaction which occurs when the fuel sticks smoulder. This is an exothermic reaction.

Discussion

The 'hand warmer' contains a fuel which burns exothermically.

Experiment 1.2

To Measure the Temperature Rise Associated with an Exothermic Reaction

Student Experiment

Materials

Expanded foam polystyrene cup
Fitted lid with hole
Thermometer, graduated to 0.2 ˚C if available
Elastic bands
Stop clock or clock/watch with seconds-hand
Graph paper
Balance
Spatula
Clock glass
Volumetric flask, 100 cm^3
Graduated cylinder, 50 cm^3 or 100 cm^3
Zinc powder
Copper sulphate solution, approximately
1 M $CuSO_4$

Safety

Wear safety spectacles. Copper sulphate is toxic if swallowed or inhaled. Avoid breathing the dust. Zinc dust is flammable. Do not use water in the case of a fire.

Procedure

1. Prepare the copper sulphate solution from copper sulphate. Use 25 g $CuSO_4\bullet 5H_2O$ in deionised water to make 100 cm^3 of approximately 1 M solution.
2. Weigh out, using the balance, 6 g of powdered zinc on the clock glass.
3. Place 30 cm^3 of copper sulphate solution,

measured with a graduated cylinder, in the polystyrene cup. Arrange the thermometer in the hole of the lid using elastic bands to keep it at a suitable height.

4. Take the initial temperature readings of the copper sulphate solution at 30 second intervals for three minutes with the thermometer and lid in place.

5. After a further 30 seconds add the zinc to the copper sulphate solution and keep recording the temperature at 30 second intervals for a further 5 minutes.

$$Zn_{(s)} + CuSO_{4(aq)} \rightarrow ZnSO_{4(aq)} + Cu_{(s)}$$

6. Draw a graph of temperature versus time on graph paper.

Conclusion

There is a rise in temperature associated with this reaction.

Discussion

Avoid using granulated zinc as the rate of reaction is too slow to produce a measurable increase in temperature in a suitably short period of time.

The correct temperature rise is read from a line drawn vertically at a time corresponding to the mean temperature. This is the line drawn vertically at the midpoint of the sharp temperature rise shown in the sketch, Fig. 1.20. The extrapolation of the temperature (after addition) versus time curve back to the time of addition makes an allowance for the heat loss to the surroundings.

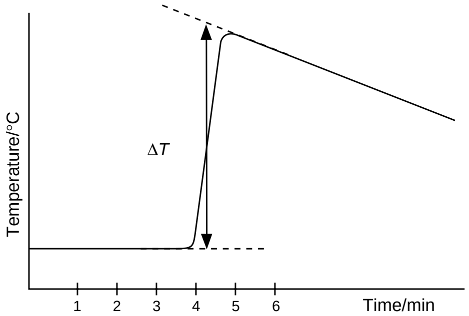


***Fig. 1.20** Temperature change during an exothermic reaction*

There is no calculation of heat loss suggested here. The students need only concern themselves with the temperature rise and the accurate graphing of the results. Comment on the use of the Celsius scale rather than the Kelvin scale.

Experiment 1.3

To Demonstrate an Endothermic Reaction

Teacher demonstration/student experiment

Materials

Commercial ‘instant ice pack’, e.g. Coldypack from Smith & Nephew for bruising and inflammation.

Safety

Wear safety spectacles. Ammonium nitrate is oxidising and, when dry, explosive when heated, particularly if impure.

Procedure

1. Allow the students to handle gently and examine the contents of the 'ice pack’.

2. Break the inner bag in the ‘ice-pack’ as instructed in the directions for use.

3. Allow the students to observe the change in the appearance of the pack and note the change in temperature by handling the pack.

Conclusion

There is a fall in temperature associated with the reaction which occurs when the chemicals in the bag are mixed. This is an endothermic reaction.

Discussion

The ‘ice-pack’ contains ammonium nitrate crystals which dissolve endothermically in water. There are other reusable packs available which contain a gel which is pre-cooled in a refrigerator before use as an ice-pack or warmed in a microwave oven for use as a hot pack. The obvious advantage is that this pack may be reused several times. The disadvantages are that the initial cost is high and the pack is not ready for instant use and so is unsuitable for use in a first aid kit.

Project

Design a chemical system, using chemistry from the syllabus, which could be used to make a hand-warmer which, like the ice-compress of this experiment, operates by dissolving one substance in another or otherwise. Bear hazards in mind.

Experiment 1.4

To Measure the Temperature Fall Associated with an Endothermic Reaction

Student Experiment

Materials

Expanded foam polystyrene cup
Fitted lid with hole
Thermometer, graduated to 0.2 ˚C
Elastic bands
Stop clock or clock/watch with seconds-hand
Graph paper
Balance
Spatula
Clock glass
Graduated cylinder, 50 cm^3 or 100 cm^3
Ammonium chloride
Deionised water

Safety

Wear safety spectacles. Ammonium chloride is toxic if swallowed or inhaled. Avoid breathing the dust.

Procedure

1. Weigh out, using the balance, 5 g of ammonium chloride on the clock glass.

2. Place 30 cm^3 of deionised water in the polystyrene cup. Arrange the thermometer in the hole of the lid using elastic bands to keep it at a suitable height.

3. Take the initial temperature readings of the water at 30 second intervals for three minutes with the thermometer and lid in place.

4. After a further 30 seconds add the ammonium chloride to the water and keep recording the temperature at 30 second intervals for a further 5 minutes while using the thermometer as a stirrer and shaking to dissolve the ammonium chloride.

5. Draw a graph of temperature versus time on graph paper.

Conclusion

There is a fall in temperature associated with this reaction.

Discussion

The correct temperature fall is read from a line drawn vertically at a time corresponding to the mean temperature. This is the line drawn vertically at the midpoint of the sharp temperature fall shown in the sketch, Fig. 1.21. The extrapolation of the temperature (after addition) versus time curve back to the time of addition makes an allowance for the heat gain from the surroundings.

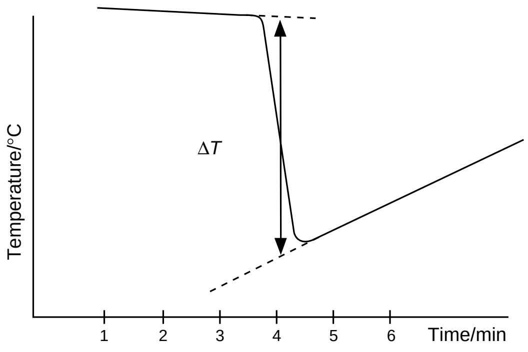


Fig.1.21 *Temperature change during an endothermic reaction*

There is no calculation of heat absorbed suggested here. The students need only concern themselves with the temperature fall and the accurate graphing of the results.

Experiment 1.5

To Demonstrate a Dust Explosion

Teacher demonstration

Materials

Container with **tightly fitting lid**, e.g. 2 litre plastic paint ‘can’ or cardboard catering ‘tin’ for coffee

Rubber tubing or polythene tubing, 1 m
Small funnel

Candle
Flammable powder, e.g. custard, lycopodium powder
Lighting taper
Matches

Safety

Do not set off bomb under light fittings. Fine dust in the air can cause breathing difficulties.

Procedure

1. Set up the apparatus as shown in the diagram, Fig. 1.22. The rubber tube is connected through a small hole made low down in the wall of the can. A small candle is placed at the bottom of the can. The candle is lit with the taper.

2. Place the lid firmly on the can.

3. Blow air into the can using the tube to disturb the powder and form a cloud of dust inside the can. Pinch the tubing immediately after blowing to avoid powder being blown back into the mouth.

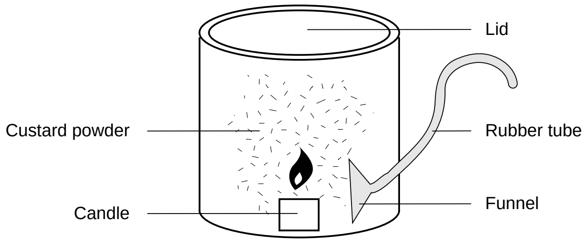


Fig. 1.22 *Controlled dust explosion*

Conclusion

The custard cloud was ignited by the candle flame, blowing the lid off the can with a loud bang.

Discussion

The lid is quite difficult to remove mechanically. Therefore the energy released in this explosion is quite significant.

Experiment 1.6

To Demonstrate Chemiluminescence

Teacher demonstration

Materials

Commercial light sticks for emergency lighting, e.g. LumicaLight
Thermometer
Elastic band

Safety

Wear safety spectacles. Do not cut or puncture tube. Check labelling for hazards.

Procedure

1. Examine the light stick. Note its initial appearance and temperature by attaching the thermometer to it using the elastic band. Remove the thermometer.

2. Darken the laboratory.

3. Bend the light stick as instructed in the directions for use.

4. Allow the students to note the energy emitted in the form of light and also to note, by reattaching the thermometer, that the temperature has not changed.

Conclusion

There is a release of energy associated with the reaction going on when the chemicals in the light stick are mixed. This is an ‘exothermic’ reaction although the temperature does not increase.

Discussion

What would happen if the light stick were heated/cooled before it was bent?

Experiment 1.7

To Demonstrate the Release of Electrical Energy by a Chemical Reaction

Teacher demonstration/student experiment

Materials

Magnesium ribbon
Copper plate
Sandpaper
Dilute sulphuric acid solution, approximately 2 M
Bulb, 2.2 V, 250 mA
Bulb holder

Two electrical leads with crocodile clips at one end and other ends connected to bulb holder

Safety

Wear safety spectacles. Sulphuric acid is corrosive. Hydrogen gas, which is highly flammable, is generated.

Procedure

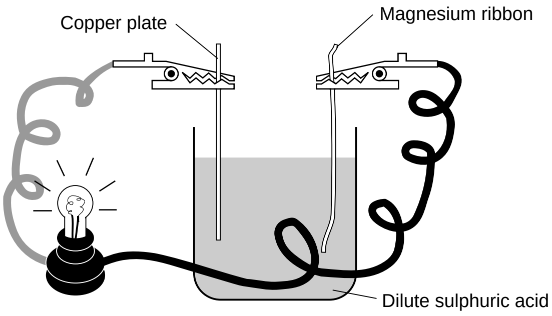


Fig. 1.23 *Chemical energy converted into light energy*

1. Set up the apparatus as shown in the diagram. Do not connect the two crocodile clips to the metal plates yet.

2. Complete the circuit.

3. Observe the bulb and any changes occurring in the electrolyte or at the electrodes.

Conclusion

There is a release of energy associated with the reactions going on at the electrodes. This is an ‘exothermic’ reaction because there is a release of electrical energy which is converted to light energy and thermal energy in the filament of the bulb. A variation of this experiment uses orange juice as the electrolyte and runs a clock.[14]

Discussion

The apparatus described here is a cell. The electrical energy produced by a cell can be used to bring about an endothermic reaction such as the electrolysis of water.

Experiment 1.8

To Determine the Enthalpy of Neutralisation of a Strong Acid and a Strong Base

Student Experiment

Materials

Expanded foam polystyrene cup
Fitted lid with hole
Glass beaker
Thermometer, graduated to 0.2 ˚C
Elastic bands
Pipette
Sodium hydroxide solution, 1.1 M
Hydrochloric acid solution, 1.0 M
Phenolphthalein indicator, two drops
Deionised water

Safety

Wear safety spectacles. Both sodium hydroxide solution and hydrochloric acid solution are corrosive and both of the solutions used are relatively concentrated. The polystyrene cup is not a very stable vessel, particularly with a thermometer in it - it could be stabilised by standing it in a beaker of suitable size and using a fitted lid with a hole for the thermometer. Phenolphthalein solution is highly flammable and toxic.

Procedure

1. Using a pipette measure out 50 cm^3 of the hydrochloric acid solution into the polystyrene cup. Add two drops of phenolphthalein indicator.

2. Take the initial temperature reading of the hydrochloric acid solution.

3. Measure 50 cm^3 of the sodium hydroxide solution into a beaker using a pipette.

4. Take the initial temperature reading of the sodium hydroxide solution.

5. Add the sodium hydroxide solution quickly to the hydrochloric acid solution. Check that the indicator changes colour and replace the lid.

$$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$$

6. Record the maximum temperature reading while using the thermometer as a stirrer, carefully, to ensure thorough mixing. Subtract the temperature readings to get the temperature rise for the reaction. Let $\Delta\theta_w$ be the temperature difference recorded during the reaction.

7. Calculate the total volume and mass of the solution. The total volume of solution = 50 cm^3 + 50 cm^3 = 100 cm^3 = 0.10 l. Then, on the assumption that all dilute aqueous solutions have approximately the same density as water, 1 kg l^{-1}, the mass is calculated from mass = density x volume = 1 x 0.10 = 0.10 kg. Let m_w be the mass of the mixture.

8. Calculate the heat rise in the mixture from

$$E_w = m_w c_w \Delta\theta_w$$

where c_w is the specific heat capacity of water. All dilute aqueous solutions may be assumed to have specific heat capacities approximately equal to that of water, taken to be 4180 J kg^{-1} K^{-1}.

9. Scale up this heat change for the formation of one mole of water. In this case 50 cm^3 of hydrochloric acid is completely neutralised. This corresponds to

$$\frac{50 \times 1.0}{1000} = 0.05 \text{ mol HCl}$$

and to the formation of 0.05 moles of water according to the balanced equation above. Therefore the formation of one mole of water would release

$$E_w \times \frac{1}{0.05}$$

Therefore

$$\Delta H = E_w \times \frac{1}{0.05} \text{ J mol}^{-1}$$

This is the enthalpy of neutralisation for this reaction and is nearly constant for all strong acids and bases. Note that the minus sign must be supplied to indicate an exothermic reaction.

Conclusion

The enthalpy of reaction can be determined by calorimetry. The reaction is exothermic.

Discussion

A more accurate temperature rise may be obtained by recording initial and final temperatures over a period of time and determining the temperature rise from a graph.

The acid and base solutions should be stored overnight in the same room, ideally the room where the experiment is to be carried out. This avoids having to take an average of two temperatures as the initial temperature and avoids the solutions tending to gain or lose heat to the surroundings before the solutions are mixed.

The purpose of the phenolphthalein is to indicate that the acid has been fully neutralised.

Using excess sodium hydroxide ensures complete neutralisation of the acid.

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CHAPTER 2 CHEMICAL KINETICS

2.1 Chemical Kinetics

Chemical kinetics is the study of the factors which control the rates at which chemical reactions take place. The rate of a chemical reaction is the rate of change in the concentration of one of the reactants or products. As is often the case with chemical properties, there is a wide variation in the rates of progress of chemical reactions. Some reactions take place so rapidly that they are described as 'instantaneous'. For very accurate work, 'instantaneous' reactions do actually have small but measurable times of reaction. One of the fastest known reaction types is the transfer of a proton in acid-base neutralisations[1,2]. Other reactions, under certain specific conditions, require minutes, hours or days to go to completion or reach equilibrium and others take years, or even millennia. In extreme cases, some energetically spontaneous chemical reactions take place so slowly that, in effect, the reactions must be said not to occur. It is convenient to compare reactions in terms of reaction half-life, i.e. the time it takes for the concentration of a specific reactant to be reduced to half its original value. Reactions with half-lives from zero to 1×10^{-11} seconds may be called *fast*.

Half-lives

Fast - Acid base neutralisations

Milliseconds - Explosion of a detonator

Seconds - Burning of a match head

Minutes - Removing unwanted hair with a depilatory cream

Hours - Paint 'drying'

Days - Iron rusting

Years - Tarnishing of oil paintings

Millennia - Formation of fossil fuels

Forever - Reaction between pure hydrogen and oxygen gases

(See Experiment 2.1, p. 45.)

How are Rates of Reaction Measured?

The rate, *r*, of a chemical reaction is defined as the change in the concentration of one of the reactants or products in unit time.

$$r \propto \frac{-\mathrm{d}[\mathrm{A}]}{\mathrm{d}t}$$

Sometimes, the rate of a chemical reaction is more loosely defined as the change in the mass, volume or concentration of one of the reactants or products in unit time. Thus, the rates of chemical reactions are expressed in various units, e.g. grams per second, moles per hour, millilitres per minute, etc. Mathematically, the rate of reaction is negative if one expresses it in terms of the decrease in the amount or concentration of one of the reactants with time and positive if it is expressed in terms of the increase in the amount or concentration of a product with time. The rate of a particular reaction varies with time, rates tending to slow down with time, principally because the concentrations of the reactants decrease with time. The numerical value of the rate of reaction also depends on temperature, initial concentration of reactants, presence of a catalyst, etc.

The terms instantaneous rate, average rate and initial rate need to be clarified. Fig. 2.1 shows the change in concentration of a product of a reaction with time. The **instantaneous rate** of reaction is the rate of change of concentration of the reactant or product at a particular time. The slope of the tangent to a graph of the change in concentration versus time at a particular time gives the instantaneous rate. The steeper the slope, the faster the rate. In Fig. 2.1, the instantaneous rate at t_1 is the slope of line a. The **average rate** of reaction is the total change in concentration of a product or a reactant over a given period of time divided by the time. In Figure 2.1 the average rate over time t_2 is represented by the slope of line b. The **initial rate** of reaction is the instantaneous rate at the moment the reaction begins. It is the slope of the tangent to the graph when time is zero, i.e. the slope of line c in Fig. 2.1. There is an important mathematical distinction between the instantaneous rate and the average rate, similar to the distinction between the terms actual speed and average speed for a moving object. Suppose a car accelerates towards a brick wall but brakes so that it comes to rest just before it strikes the wall. Its actual speed at any instant during the journey is the rate of change of its position at that instant - this is not constant as the car is accelerating at different rates throughout the journey. Its average speed is simply the total distance divided by the total time.

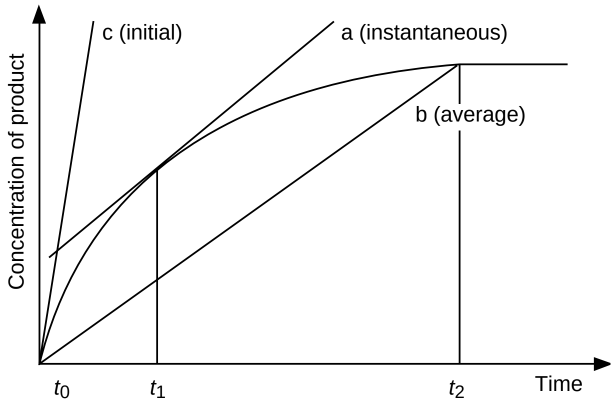


Fig. 2.1 *Instantaneous, average and initial rates of reaction*

Rates of reaction for fast reactions are obviously very difficult to determine experimentally because of the difficulties in monitoring the very rapid changes in concentration of a reactant or product. Special instrumental techniques have been developed to monitor very rapid changes in concentration.[3,4]

For slower reactions, rates are more readily determined, although it is easier to measure the concentration of one of the reactants or products as time goes by for some reactions than others. The procedure is relatively simple if the reaction produces one gaseous product from non-gaseous reactants, e.g. decomposition of hydrogen peroxide or reactions between an acid and a carbonate or hydrogencarbonate.

$$H_2O_{2(aq)} \longrightarrow H_2O_{(l)} + {}^1\!/{}_2O_{2(g)}$$

$$2HCl_{(aq)} + CaCO_{3(s)} \longrightarrow CaCl_{2(aq)} + CO_{2(g)} + H_2O_{(l)}$$

The gaseous product can then be collected in a graduated vessel over water, or in a gas syringe, and the increase in volume monitored with time. Alternatively, the reaction can be allowed to occur on a balance and the loss in mass of the reaction vessel and contents recorded with time. Other reactions which are relatively easily monitored are those where one of the reactants or products has a physical property which is related to its concentration. Physical properties which are useful in this way include optical activity (the ability of a substance to rotate the plane of polarisation of a beam of polarised light), colour, pH, electrical conductivity, etc. With modern instruments linked to microprocessors to detect and measure these properties, the data on changes in concentration can be collected as the reaction proceeds, graphed and interpreted, automatically.

A rather tedious method for measuring rates is the sampling technique. Here several identical reactions are set up under a certain set of conditions, and at regular time intervals the reaction in one sample is quenched (see Section 2.6), and a measurement is carried out at leisure to determine the concentration of one of the reactants or products at the time of sampling. Again, chemical analysis can be used to measure concentration, e.g. titration, or an instrumental analysis may be used to determine some physical property related to concentration. (See Experiment 2.2 p. 45.)

2.2 Reaction Mechanisms and Reaction Order

To study the kinetics of reactions, chemists divide reactions according to their order and examine reaction mechanisms.

A chemical equation is a summary of the overall starting materials and products of a chemical change which may proceed *via* a single step or a number of chemical steps involving several intermediates. A reaction mechanism is a complete description of all the intermediate species and their involvement in stepwise reactions which lead from the reactants to the final products summarised in a chemical equation. The actual steps or the mechanism of a reaction are notoriously difficult to establish as determining a mechanism involves the search for extremely short-lived and hence low-concentration intermediates which are, in addition, possibly unstable species. In such a multi-step process, some steps have faster rates than others and it is quite common for one step to be significantly slower than all the others. This step is called the **rate-determining step** and it determines the overall rate of the reaction.

Suppose a driver of a car has to travel through eight sets of traffic lights. Five sets of lights are green. The car is delayed at one set of lights for 30 seconds, at another for 15 seconds and at the third for 3 minutes. Which set of lights is most responsible for slowing down the rate of progress of the driver? Clearly the red light which causes a delay of three minutes is the rate-determining traffic light. The rate-determining step is the slowest step of all the chemical reactions which compose the reaction mechanism.

The **order** of a chemical reaction is the sum of the powers of the concentrations in the rate expression. The order of a chemical reaction may be zero, one, two, three or higher and not necessarily a whole number.

Zero order reactions, while uncommon, do exist. In these reactions the rate is determined by a factor other than the availability of a reacting species, e.g. the availabilty of catalyst surface area or free enzyme sites. The reaction cannot be speeded up by providing more reactant. Examples of zero order reactions are the gold-catalysed decomposition of hydrogen iodide and the enzyme-controlled decomposition of alcohol in the body.

The rate of decomposition of alcohol in the body is one of the chemical reactions whose kinetics sometimes interest people. This particular reaction has zero order. This means that the rate of decomposition of alcohol is <u>not</u> dependent on the concentration of alcohol in the body tissues. There is a limited number of enzymes in the liver capable of breaking down alcohol. The rate-determining factor is how quickly the enzymes' active sites become available to process the queue of alcohol molecules. This rate is a constant, given as approximately 5.3 g per hour for women and 7.3 g per hour for men. However, there can be a variation of ±50% in these figures for an individual. The alcohol consumed is distributed in the available body fluids. The body fluid distribution volumes for women and men are, respectively, 28 l and 40 l approximately; again there is individual variation. The current legal maximum permitted alcohol concentrations in blood and urine to be in charge of a motor vehicle in Ireland are 80 mg per 100 ml and 107 mg/100 ml, respectively. Samples of blood and urine taken from persons suspected of being 'over the limit' must be tested within ten days to avoid biochemical decomposition. The alcohol content of various drinks is often quoted in units - one unit is 8 g of ethanol and a glass of wine or measure of a spirit is the equivalent of one unit, a pint of lager is two units. The average man is brought to the limit by four units of alcohol and 2.8 units will bring an average woman to the limit for driving.

Most first order reactions are those where the decomposition of a single reactant is the rate-determining step. Examples include the decomposition of gaseous sulphuryl chloride (SO_2Cl_2) to produce sulphur dioxide and chlorine and of hydrogen peroxide to produce water and oxygen gas, and radioactive decay (although the latter is not a *chemical* reaction).

$$SO_2Cl_{2(g)} \longrightarrow SO_{2(g)} + Cl_{2(g)}$$

$$H_2O_{2(aq)} \longrightarrow H_2O_{(l)} + {}^1\!/_2O_{2(g)}$$

In these decompositions, the rate of reaction under a given set of conditions depends on the concentration of the decomposing substance, A.

The rate of decomposition, r, of A is proportional to the concentration of A. Note that the sum of the powers of the concentrations in the rate expression is one.

$$r \propto [A]$$

Mathematically the rate is expressed by

$$\frac{-d[A]}{dt} \propto [A]$$

and the tangent to the graph of concentration of A versus time at any point represents the rate of change of concentration at that instant.

Note that if

$$r \propto [A]$$

then

$$r = k[A]$$

where k is a constant under the conditions of the reaction and is called the rate constant for the reaction. The rate constant, k, for a reaction depends on temperature, the orientation of the colliding molecules, the frequency of collisions and the activation energy. (See section 2.3.)

Refer to Fig. 2.2 below to clarify a few points. It represents a simple non-reversible first order reaction of the type

$$A \longrightarrow C + D$$

The initial concentration of the reactant is x and is seen to decrease with time, while the concentration of one of the products is seen to increase with time to x. The second product behaves identically. When the reactant concentration falls to zero and the concentration of both products has risen to x, the reaction is complete. This occurs at the time marked t in the diagram. Note also the half-life of the reaction, $t_{1/2}$, when the concentration of the reactant is reduced to $x/2$.

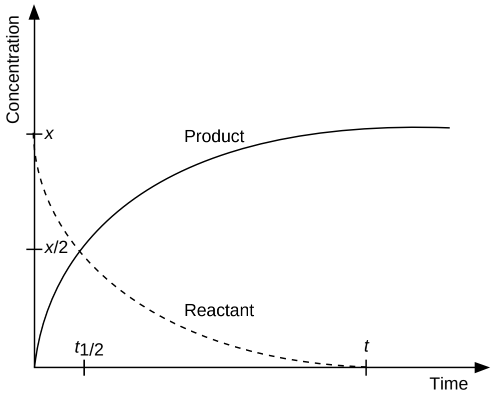


Fig. 2.2 *Change in reactant and product concentrations with time*

The decomposition of hydrogen peroxide to produce water and oxygen gas is an example of a first order reaction^1 which is suitable for laboratory demonstration.

In the bimolecular base-catalysed hydrolysis of ethyl ethanoate, the water may be kept in large excess compared to the ester and the change in the water's concentration with time is negligible, so the rate of reaction depends only on the concentration of the ester. This reaction, under these circumstances, is classified as a pseudo first order reaction. In general, pseudo order reactions are those where the observed order of reaction is less than the predicted order because of the experimental conditions, e.g. where one reactant is present in large excess with respect to the others.

Second Order Reactions

Many second order reactions involve bimolecular collisions in the rate-determining step. Examples include the alkaline hydrolysis of an ester, e.g.

$$CH_3COOC_2H_{5(l)} + NaOH_{(aq)} \longrightarrow CH_3COONa_{(aq)} + C_2H_5OH_{(aq)}$$

and other reactions of the type

$$A + B \longrightarrow C + D$$

The rate, *r*, of reaction of A is proportional to the products of the concentrations of both A and B.

$$r \propto [A][B]$$

$$\frac{-d[A]}{dt} \propto [A][B]$$

Note that if

$$r \propto [A][B]$$

then

$$r = k[A][B]$$

where *k* is the rate constant under the conditions of the reaction. Note that the sum of the powers of the concentrations in the rate expression is two.

Another example of a second order reaction is the decomposition of hydrogen iodide according to the equation

$$2HI_{(g)} \longrightarrow H_{2(g)} + I_{2(g)}$$

and other reactions represented by

$$2A \longrightarrow \text{products}$$

The rate, *r*, of reaction of A, is proportional to the product of the concentrations of A:

$$r \propto [A][A] = [A]^2$$

$$\frac{-d[A]}{dt} \propto [A][A] = [A]^2$$

Note that if

$$r \propto [A]^2$$

then

$$r = k[A]^2$$

where *k* is the rate constant under the conditions of the reaction. Note that the sum of the powers of the concentrations in the rate expression is also two.

The law of mass action is a principle introduced by the Norwegian chemists **Cato Guldberg** (1836-1902) and **Peter Waage** (1833 -1900) in 1863 and it has been used in writing the two rates of reaction expressions above. It states that the rate of a chemical reaction at a fixed temperature is proportional to the product of the active masses or activities of the reactants. The activity of a reactant, A, is usually its molar concentration, indicated by [A], but not invariably. For example, if one of the reactants is a solid in excess its activity is usually taken as 1. Thus, its concentration does not affect the rate mathematically. This is appropriate since the reaction rate is dependent on the other reactants encountering the reactant present in excess. The production of carbon dioxide gas in the reaction between dilute hydrochloric acid and excess calcium carbonate in the form of chips and the production of hydrogen gas in the reaction between dilute hydrochloric acid and excess zinc in the form of metal turnings are often used as laboratory demonstrations of rate laws. Since the two solids are in excess and have unit activities they have no mathematical effect on the rate. These reactions are both pseudo first order.

Reactions involving more than two molecules

The next simplest reaction mechanisms might be expected to be those involving trimolecular collisions and tetramolecular collisions, etc. However, trimolecular collisions in the gaseous state are approximately one thousand times less frequent than bimolecular collisions and tetramolecular collisions do not occur frequently enough to be even considered to account for any appreciable rate of reaction. Bear in mind also that not all collisions lead to reaction.

Consider traffic accidents - collisions between two cars are much more frequent than collisions between three vehicles and four-car collisions are less frequent again.

How then do reactions of the trimolecular type, e.g.

$$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$$

and the tetramolecular type, e.g.

$$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$$

occur? The answer is that reactions like these do not occur in a single step but in a series of simpler steps composed of bimolecular collisions and decompositions.

The order of a reaction is not predictable from its chemical equation and it is not necessarily an integer. The order is the sum of the powers of the concentrations in the rate expression. The acid-catalysed hydrolysis of cane sugar to form glucose and fructose is a first order reaction, actually pseudo first order, although there are two reactants.

$$C_{12}H_{22}O_{11(aq)} + H_2O_{(l)} \xrightarrow{H_3O^+} C_6H_{12}O_{6(aq)} + C_6H_{12}O_{6(aq)}$$

The following reaction might be expected to be second order, relying on bimolecular hydrogen and bromine collisions.

$$H_{2(g)} + Br_{2(g)} \longrightarrow 2HBr_{(g)}$$

In fact, this reaction is observed to have an order of 3/2. Studies have shown that the reaction between hydrogen and bromine is a chain reaction which occurs in the classic initiation, propagation and termination stages of chain reactions.

Initiation: $Br_2 \longrightarrow 2Br^\bullet$

Propagation: $Br^\bullet + H_2 \longrightarrow HBr + H^\bullet$

$H^\bullet + Br_2 \longrightarrow HBr + Br^\bullet$

Termination: $2Br^\bullet \longrightarrow Br_2$

The first propagation step is the slow rate-determining step and this step depends on the concentrations of hydrogen gas and bromine free radicals. The concentration of bromine free radicals from the initiation step is proportional to the square root of the concentration of bromine gas. Therefore the (simplified) rate of reaction expression becomes

$$r \propto [H_2][Br_2]^{1/2}$$

This is a good example to illustrate that the rate expression cannot be simply written down on the basis of the balanced equation.

The **molecularity** of a reaction is the number of species taking part in the rate-determining step. The molecularity of the reaction between bromine and hydrogen is two since there are two species, bromine free radicals and hydrogen molecules, taking part in the first propagation step or the slow rate-determining step.

2.3 Rate Determining Factors

As discussed above, the rate of a chemical reaction is determined by its reaction mechanism, and specifically by the rate at which the slowest step of the mechanism occurs, and is expressed mathematically by applying the law of mass action to the slow rate-determining step. The factors which restrict the speed of the rate-determining step in a reaction are in turn whether the molecules which participate in the rate-determining step collide (i) frequently, (ii) with the correct orientation for the formation of the required intermediate and (iii) effectively, i.e. with total kinetic energy equal to or greater than that required to lead to the higher energy intermediate state from which the products are formed.

The minimum amount of energy which colliding species must possess in order to react is called the activation energy, E_A. The activation energy is the energy required to form a high energy reaction intermediate from one or more reactant molecules. The intermediate has high energy because it is formed by weakening or completely breaking some of the bonds in the reactant molecules. Weakening or breaking bonds requires energy. The high energy intermediates are unstable and short lived, having lifetimes between 1×10^{-13} and 1×10^{-12} seconds[3].

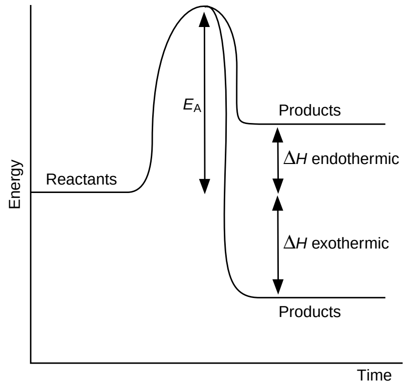


Fig. 2.3 *Reaction energy profile diagram*

The activation energy can be slightly greater, or much greater, than the sum of the average kinetic energies of the reacting molecules. In the former extreme, in many collisions the reacting molecules possess between them the activation energy. In the latter extreme, relatively few collisions between reacting species may be effective and this leads to a slow rate of reaction. Thus, activation energy accounts for the variation in rates of reaction from instantaneous to infinitely slow.

It is clear that the rate of a chemical reaction can be increased by several factors if these factors can

(i) increase the total number of collisions per unit time and thus increase the total number of effective collisions per unit time, or

(ii) increase the proportion of effective collisions without changing the number of collisions per unit time, or

(iii) provide an alternative reaction mechanism which involves intermediates with lower activation energies.

State of Reactants

Reactions between solids

In order to react, molecules must collide. Solid-solid reactions between powdered substances are possible but a reaction is dependent on intimate mixing and takes places between molecules on the surfaces of the solid particles. Some of these solid-solid reactions are actually quite rapid or even explosive, e.g. the MnO_2 catalysed decomposition reaction of potassium chlorate to potassium chloride and oxygen is quite rapid (minutes) upon heating the mixture and the reaction of the blackpowder mixture of carbon, sulphur and potassium nitrate is explosive. However, reaction does not take place between the citric acid and sodium hydrogencarbonate of an Alka Seltzer antacid tablet until it is put in water. Furthermore, the sodium hydrogencarbonate does not convert the acetylsalicylic acid (aspirin) in the Alka Seltzer into sodium acetylsalicylate until they are added to water. Sodium acetylsalicylate is more soluble than acetylsalicylic acid and more readily absorbed into the bloodstream to give rapid pain relief.

Heterogeneous reactions

Solid-liquid and solid-gas reactions are quite common and since there is a distinct boundary between the reacting species they are called heterogeneous reactions. In these reactions, the rate is increased by increasing the surface area of the solid or, if the liquid reactant is a solution, increasing the concentration of the solution or, if the second reactant is gaseous, the pressure of the gas. (See Experiment 2.3, p. 46.)

Reactions between gases or between liquids

Reactions involving fluids, i.e. liquids, solutions and gases, are very common. Because of the mobility of the molecules of fluids, collisions between reacting particles occur quite frequently. The collision frequency between reacting species in a gas is higher than in a solution where reacting molecules tend to undergo repeated vibrations (100 - 1000) in a cage of solvent molecules before undergoing a net displacement through the solution to eventually encounter one another.[3]

The Nature of the Bonding in Reacting Species

Ionic compounds, in general, react more quickly than covalent substances. Ionic compounds are normally solid and therefore tend to be dissolved in water for reaction. In aqueous solution, the ions of the ionic compound are fully dissociated, and although surrounded by a sphere of solvent molecules, have good mobility through the solution. In addition, collisions with ions of opposite charge are facilitated by the electrostatic attraction between them and thus reactions between oppositely charged ions in solution are rapid. Examples to illustrate rapid reactions between ionic compounds in solution are given in Experiment 2.4.

Covalent substances, in general, react more slowly than ionic compounds because bonds in the reactant molecules must be broken before reaction can proceed. Therefore, the colliding molecules must possess a certain minimum energy and not all collisions are effective collisions as mentioned above. A reaction which illustrates the relatively slow rate of reactions involving covalent molecules is described in Experiment 2.5. Covalent bond strengths show a wide variation according to whether the atoms joined by the bond are small or large and whether they are joined by single, double or triple bonds. (See Chapter 1, section 1.7, Bond Energy.)

Nitrogen gas, for example, consists of diatomic molecules containing triple bonds with a bond energy of 944 kJ mol^{-1}. This bond energy value accounts for the inertness of nitrogen gas. Nitrogen gas, extracted from air at relatively low cost, is used to provide an inert atmosphere in bags of potato crisps. The gas cushions the crisps and helps prevent them from being crushed before they reach the consumer but does not impair the flavour since its high-energy triple bond imparts very high activation energies to any reactions and makes them infinitely slow. If air is used for packaging, reactions between the oxygen in the air and the fat or oil molecules give a stale taste. This food packaging process is called gas flushing and is common for other foodstuffs also, e.g. biscuits, pizzas, etc.

Temperature

The temperature at which a reaction is carried out is the single most significant factor in controlling the rate of the reaction. According to the kinetic theory of gases, the average kinetic energy of the molecules of a gas is proportional to the absolute temperature. Liquid reactants or reactants in solution also possess greater kinetic energy at higher temperature. The greater the average kinetic energy of the molecules, the greater the average molecular speed and the greater the probability that in a collision reacting molecules will have enough energy to react, i.e. that the collision will be effective in leading to products.

The molecules of a gas at different temperatures have molecular speeds which approximately fit normal distribution curves. The statistical analysis of speed distribution of gaseous molecules at different temperatures was first carried out by the Scottish physicist **James Clerk Maxwell** (1831-1879) in 1860. He included correction factors which had been suggested by the Austrian physicist **Ludwig Edward Boltzmann** (1844-1906) and so the results are often described as the Maxwell-Boltzmann distribution. Fig. 2.4 shows the Maxwell-Boltzmann distribution of speeds for a gaseous sample at two different temperatures. Note that the curves are unsymmetrical because there is always a lower limit of zero to molecular speed, while there is no theoretical upper limit for molecular speed at any temperature. Thus the maxima for the curves correspond to the most probable speed at that temperature - the average speed is slightly to the right of the most probable speed on each curve - if the curves were symmetrical the most probable speed and the average speed would be equal. Heavy molecules have narrower, lower energy distributions than lighter ones at the same temperature, Fig. 2.5. At low temperature the standard deviation from the probable molecular speed is small whereas at higher temperature, and hence greater average kinetic energy, there is a greater range of possible molecular speed values for the molecules, a greater value for the standard deviation and a broader, flatter distribution curve.

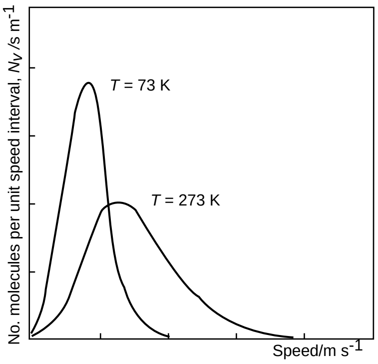


Fig. 2.4 *Speed disribution of molecules at different temperatures*

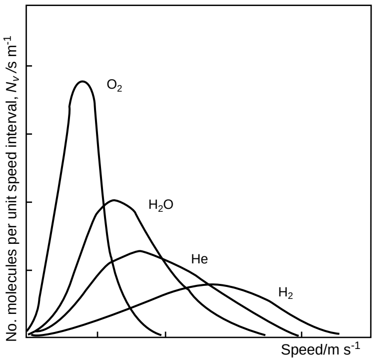


Fig. 2.5 *Speed distribution of molecules of different masses*

Since only the molecules with relatively high energy can become involved in successful collisions, and the activation energy is constant for a particular reaction, the higher temperature curve shows a greater number of molecules possessing the activation energy than the lower temperature curve. Increasing the temperature of a reaction mixture by 10 K increases the number of collisions by only about 2% but the number of effective collisions is increased by 200-300%. The reason there is a relatively small increase in the total number of collisions upon raising the temperature is that the molecules are very small in comparison to the intermolecular spaces. Collision rate, Z, can be shown to depend on the abundance of molecules in the sample, the masses of the colliding species, the diameters of the colliding species and the square root of absolute temperature[5]. Therefore, comparing the collision rates in a sample at two temperatures which differ by 10 K, is the same as comparing the square roots of their temperatures, if all other factors are unchanged.

$$\frac{Z_{283}}{Z_{273}} = \frac{\sqrt{283}}{\sqrt{273}} = 1.018$$

In this example there is only a 1.8% increase in the number of collisions per second upon raising the temperature 10 K.

To compare the fractions of molecules possessing a certain minimum energy, i.e. the activation energy, the areas of the molecular speed distribution curves for the two temperatures beyond the minimum specified molecular speed corresponding to the activation energy are compared. This is a much more significant ratio than that above. For a 10 K increase in temperature the two shaded areas in Fig. 2.6 are compared and the ratio of these areas is approximately 2:1. The rate of a reaction doubles upon increasing the reaction temperature 10 K. (See Experiment 2.6, p. 48.)

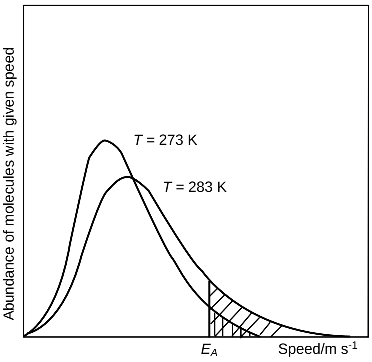


Fig. 2.6 *Speed disribution of molecules at different temperatures above a specified minimum corresponding to E_A*

There is one important set of exceptions to the general rule that the rate of reaction increases with increasing temperature and that is the case of biological systems. In most biochemical processes, the reactions are controlled by enzymes which are protein molecules, deactivated below a narrow optimum temperature range and denatured above that temperature range.

Concentration

For reactions which take place in solution, increasing the concentration of the reactants will bring about an increase in the rate of reaction. In concentrated mixtures, the distances and hence the times between collisions of reacting species, is reduced. If the number of collisions between reacting molecules per unit time is increased so will the number of effective collisions between the species. (See Experiment 2.7, p. 49.)

Pressure

In gaseous reactions, an increase of pressure on the reactants will reduce the volume of the mixture and bring about an increase in the rate of reaction. The increase in pressure has the same effect as an increase of concentration in a liquid reaction, i.e. it reduces the distances and hence the times between collisions of reacting species. If the number of collisions between reacting molecules per unit time is increased so will the number of effective collisions between the species.

Presence of a catalyst

A catalyst is a substance which influences the rate of a chemical reaction by participating in the reaction while not being consumed by it. Catalysis is discussed in the next section.

2.4 Catalysis

A catalyst is a substance which influences the rate of a chemical reaction by participating in the reaction while not being consumed by it. A catalyst participates in the reaction by providing an alternative reaction mechanism which is not available in the absence of the catalyst and which involves the catalyst in the rate-determining step. If the activation energy, E_{AC}, for the formation of the intermediate in the new rate-determining step is reduced compared to the activation energy, E_A, of the uncatalysed situation the reaction will proceed more quickly, (see Fig. 2.7). Conversely, if there is an increase in activation energy, the reaction rate is reduced and this situation is often referred to as negative catalysis, the word catalysis itself usually implying an increased rate. Catalysts have no effect on the enthalpy of reaction since they have no effect on the initial and final states of reaction, cf. Hess's law. In a reversible reaction, the catalyst lowers the activation energy for both reactions. This is of particular significance in equilibrium systems. The catalyst has no effect on equilibrium concentrations or equilibrium constants (see Chapter 3) since it favours neither forward nor reverse reaction but it does cause equilibrium to be established more quickly.

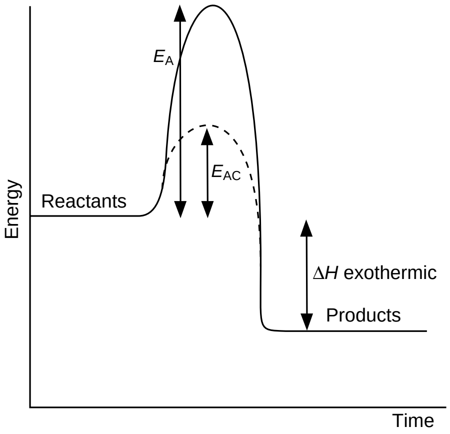


Fig. 2.7 *Effect of a catalyst on* E_A

Categories and Mechanisms of Catalysed Reactions

There are two major divisions of catalysed reactions.

Homogeneous[6]

These are reactions in which the reactants and catalyst are in the same phase. The general mechanism here is that an intermediate compound is formed between the catalyst and one of the reagents. The intermediate compound subsequently decomposes, rearranges or reacts with another reagent to form the product or products of the reaction and the catalyst is regenerated. This stepwise mechanism involving the catalyst is faster than the reaction between the reagents in the absence of the catalyst.

Sulphuric acid is a common catalyst in homogeneous systems. Sulphuric acid may be used in the acid-catalysed hydrolysis of an ester. Sulphuric acid is also used as a catalyst in the dehydration of alcohols to form alkenes.

Other homogeneous catalysts are soluble transition metal complexes. Here the abilty of the transition metal atom to bond using some of its vacant, or partially filled, d-orbitals accounts for the formation of the intermediate compound. An industrial example of homogeneous transition metal catalysis is the rhodium salt catalysed reaction of methanol with carbon monoxide to produce ethanoic acid. (See Experiment 2.8, p. 50.)

Heterogeneous[7,8]

In this type of catalysis there is a definite physical boundary between the catalyst and the reactants; commonly the catalyst is a solid and the reactants are liquids or gases. The surface area of a solid catalyst is typically 1 - 500 $m^2\ g^{-1}$. Metals from the d-block or their oxides are often good catalysts in heterogeneous reactions, the vacant d-orbitals being used to adsorb molecules on the solid surface. However, this type of catalytic activity is not exclusive to the d-block metals. Main group metals and their oxides can also catalyse reactions because the atoms on the surface of a solid have the ability to form additional bonds and so adsorb reactant molecules onto the solid surface. This adsorption has the two-fold effect of locally increasing the concentration of reactant molecules and additionally weakening the bonds within the reactant molecules. Bonding interactions between the reactant molecules and the catalyst can vary from weak to strong and therefore the internal bonding of the reactant molecules can be weakened to different extents. Both the effects of concentrating the reactant on a surface and weakening its internal bonding structure accelerate the rate of reaction.

There are five distinct phases in the mechanism of heterogeneous catalysis. These steps were first proposed and investigated by the American chemist **Irving Langmuir** (1881-1957) in 1919.

a) Diffusion of reactants to the catalyst surface.

b) Adsorption of reagent molecules onto the surface.

c) Reaction between two molecules on the catalyst surface or between one molecule on the catalyst surface and another in the gas or liquid phase.

d) Desorption of products from the catalyst surface.

e) Diffusion of products away from the surface.

The first and last steps are not considered to be rate-determining since molecules diffuse rather quickly through liquids and gases. Any one of, or any combination of, the three middle steps could be rate-determining.

These steps are illustrated in Fig. 2.8 for the reaction between hydrogen and deuterium.

$$H_{2(g)} + D_{2(g)} \longrightarrow 2HD_{(g)}$$

A similar sequence of events is believed to occur in all heterogeneous catalysed systems, i.e. the weakening of the bonds holding the atoms of the reactants together as the reactants bind to the surface and the formation of new bonds between the reactants while held in close proximity upon the catalyst surface. These steps all have a lower activation energy than the formation of an intermediate complex involving the reactants only.

This mechanism is somtimes called the rack mechanism of catalysis because the reactant internal bonds are stretched to breaking point on the catalyst surface. (See Experiment 2.9, p. 51.)

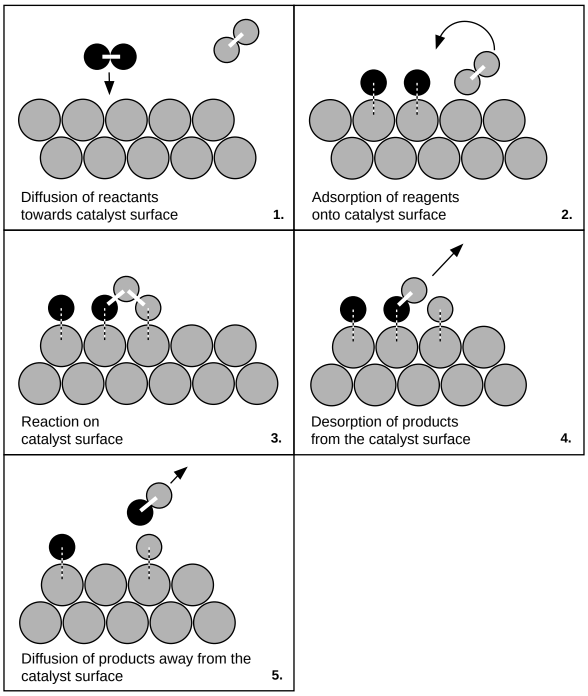


Fig. 2.8 *Mechanism of heterogeneous catalysis*

Catalyst Preparation

In a reaction system, the catalyst must be in an active state. This active state is sometimes unstable and difficult to maintain in storage. In these situations, a catalyst precursor is placed in the reaction vessel and activated *in situ*. An example of a catalyst which has been activated is the iron oxide (Fe_3O_4) catalyst used in the synthesis of ammonia from nitrogen and hydrogen. This catalyst must be in a finely divided condition of large surface area for effective catalytic activity and is consequently very susceptible to air oxidation. To avoid the difficulties of transporting, storing and handling the catalyst in its activated state, the catalyst is purchased, transported, stored and filled into the reaction vessel as iron(III) oxide, Fe_2O_3, and reduced with hydrogen gas immediately prior to start-up.

$$3Fe_2O_{3(s)} + H_{2(g)} \longrightarrow 2Fe_3O_{4(s)} + H_2O_{(g)}$$

Pelleting is another preparation stage for heterogeneous catalysts. In industrial processes pellets, often with hollow centres, permit good freedom of movement of gases or liquids through the catalyst beds.

Support

In some cases the mass of catalyst required to catalyse a process is quite small. It is technically difficult to make a sufficiently large surface area of a small mass of catalyst. It is undesirable to use a large mass as modern industrial catalysts are very expensive. One way of maximising the surface area of a small mass is to disperse it in a thin layer on a solid support. Porous solids such as carbon, alumina or silica are suitable for this purpose. The advantages are that the supported catalyst is more easily handled, is readily recovered by filtration and, since the particles of catalyst are highly dispersed on the support, the catalyst is less prone to sintering.

Promoters

A promoter is a substance which is added to the catalyst in 5-10% abundance and which enhances the catalytic activity and also perhaps extends the lifetime of the catalyst. An example of a promoter is the aluminium oxide added to the iron oxide (Fe_3O_4) catalyst used in the conversion of nitrogen and hydrogen to ammonia. The aluminium oxide prevents sintering of the iron oxide catalyst. Sintering is associated with decreasing total catalyst surface area, consequently decreasing the catalytic activity and reducing its lifetime.

Catalyst Poisons

A catalyst poison is a substance which interferes in an undesirable way with the action of a catalyst. Small quantities of strongly adsorbed substances, such as sulphur and phosphorus compounds, or mercury and arsenic are very effective in reducing the potency of a catalyst. They irreversibly bind to the surface. The raw materials must be pretreated to eliminate potential catalyst poisons from industrial processes.

Lead compounds are poisons of the catalysts used in the catalytic converters of cars. Hence leaded fuel should not be used if a car is fitted with a ‘cat’. Mercurial poisoning and other forms of cumulative poisoning by metals is attributed to the irreversible bonding of these metals or their compounds with enzymes in the body.

Catalyst Lifetime

An industrial catalyst would be expected to have a lifetime of about ten years. While the catalyst does not become chemically consumed by the reaction it catalyses, its effectiveness can be reduced by other physical and chemical processes occurring in the reaction vessel. Physical processes which could be responsible for reduction in catalyst activity are flushing of the catalyst out of the system or sintering. Sintering is the fusion of small crystals, forming more massive crystals, as a result of heating below the melting point of the substance, with simultaneous compacting. Sintering results in a reduced surface area of catalytic activity and thus a reduced effectiveness. Chemical processes which could reduce the activity of the catalyst are poisoning or a change in oxidation state.

Catalyst Regeneration

This is the treatment of the catalyst to restore its efficiency. The procedure can be expensive because it involves shut down of the operation and perhaps removal of the catalyst from its reactor so that it can be subjected to high temperature heat treatment to burn off surface contaminants.

Autocatalysis

When one of the products of a chemical reaction is itself a catalyst for the reaction, the reaction is described as being autocatalysed. The reaction is initially slow but then speeds up when the catalyst is formed but slows down again as the concentration of the reactants decreases. These autocatalysed reactions have characteristic S-shaped rate of reaction curves for rate versus time.

An example of an autocatalysed reaction is the reaction in which ethanedioate is oxidised by potassium manganate(VII), the Mn^{2+} ion product catalysing the reaction.

$$2MnO_4^-{}_{(aq)} + 5C_2O_4^{2-}{}_{(aq)} + 16H^+{}_{(aq)} \xrightarrow{Mn^{2+}} 2Mn^{2+}{}_{(aq)} + 10CO_{2(g)} + 8H_2O_{(l)}$$

(See Experiment 2.10, p. 52.)

Negative Catalysis or Inhibition

Negative catalysis or inhibition is the use of a catalyst to reduce the speed of a chemical process. An example is the use 2-*tert*-butyl-4-methoxyphenol (BHA), Fig. 2.9, as an anti-oxidant used to increase the shelf life of margarine and other oils and fats. It slows down the air oxidation of the C-C bonds in fats and oils by interfering with the mechanism of the oxidation reaction[9].

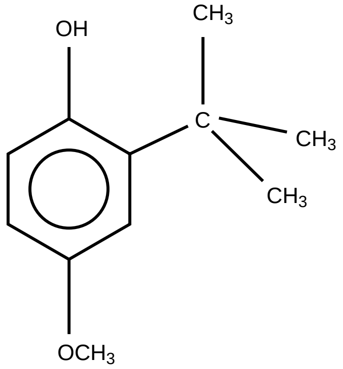


Fig. 2.9 *2-tert-butyl-4-methoxyphenol (BHA)*

Enzymes

Enzymes are biological catalysts which control all the metabolic activity of an organism, from the essential biochemical steps of respiration and digestion in animals and photosynthesis in plants, to determining the colour of an eye or petal. Their activities can prevent or cause metabolic disorder. For example, the absence of the enzyme lactase causes the disorder lactose intolerance, which afflicts 90% of the African American population and approximately 15% of the United States population of Western European descent[10].

Enzymes are increasingly used as catalysts for industrial processes. Indeed the world's oldest chemical process, brewing, uses enzymes in yeast to convert sugars in fruit to alcohol. Nowadays, biological chemicals and drugs are manufactured using enzymes.

Enzymes are highly successful catalysts for biological systems where high temperatures and pressures are not available to overcome high activation energies. For example, a single catalase molecule can catalyse the breakdown of up to ten million hydrogen peroxide molecules per minute at 0 ˚C in a biological system. Like inorganic catalysts, enzymes are not consumed by the reactions they speed up and consequently only small amounts of them are required.

Enzymes are highly specific in their activity. They are protein molecules, often of complex structure, which operate by forming a complex with the substrate (reactant). To do this some enzymes require certain metal ions or certain small organic molecules, which include the minerals and vitamins of a balanced diet. The substrate molecule undergoes a chemical change during the brief time it is attached to the enzyme and then the products are released, regenerating the free enzyme. Specificity is guaranteed because the bonding which attaches the enzyme active site to the substrate molecule will only occur if the substrate molecule has a particular complementary bonding ability, e.g. having a certain functional group present and possessing the correct overall size and shape, i.e. having good steric fit. The precise fit between enzyme and substrate which makes enzyme action specific was first described by **Emil Fischer** (1852-1919), the distinguished German carbohydrate chemist. He said that the substrate and enzyme must fit each other like a lock and key[11].

Some laundry detergents contain enzymes which exhibit good practical specificity. They can break down the protein in stains on clothing, e.g. blood and food, and not digest the protein fibres of certain textiles, e.g. silk, wool. They can survive the harsh conditions encountered during laundering. Occasionally the specificity of enzymes can be interfered with by a reactant which has a similar but not identical type of bonding, size and shape to the correct reactant. Then the enzyme might form a complex with the wrong substrate. No reaction to form products occurs and the enzyme molecule remains temporarily or permanently occupied - these processes being called competitive inhibition and irreversible inhibition, respectively. Some nerve gases are irreversible inhibitors of the enzyme acetylcholinesterase, which is essential for nerve impulse conduction. The victim's nerve impulses cease, breathing and heartbeat cease, and death occurs. Heavy metal atoms may also deactivate an enzyme in this way. Several examples of poisoning are attributed to enzyme deactivation by heavy metals, e.g. lead, mercury, etc., or non-metals, e.g. arsenic.

Enzymes usually have a very narrow range of conditions within which they give optimum performance. They operate across narrow temperature and pH ranges similar to the conditions found in the biological environment in which they occur. If the enzyme is placed outside the optimum range of temperature or pH it may become deactivated or denatured. For example, enzyme activity is reduced upon cooling but can be destroyed upon heating.

Some enzymes have trivial names which give no information, e.g. trypsin acts on protein. Other enzymes, discovered more recently, have been given systematic names ending with the suffix *-ase*, according to the substrate they act upon, e.g. lipase acts on lipids. Alternatively, the name gives the substrate the enzyme acts upon and the action carried out on the substrate, e.g. triose phosphate dehydrogenase is an enzyme which acts on a triose phosphate by removing two hydrogen atoms.

2.5 Quenching

It is sometimes necessary to bring a reaction to a stop, e.g. if it was becoming too vigorous and unsafe. This procedure is called quenching. Using our knowledge of controlling chemical reactions we could plan to quench reactions in a number of different ways or by using a combination of these ways. Some methods are more suitable than others in a given case.

(i) Reduce the temperature by removing any heat source and place the reaction vessel in an ice bath.

(ii) Greatly dilute the reaction mixture with a liquid solvent to reduce significantly the number of collisions between the reacting species per unit time.

(iii) Filter off any solid catalyst or solid reactant.

(iv) Add a substance which reacts quickly with one of the reactants.

2.6 Experiments

Experiment 2.1

The Reaction Between Household Bleach and Food Dyes[10]

Student experiment or teacher demonstration (which can be adapted for OHP)

Materials

Green, blue and red commercially available food dyes
Household bleach
Water - deionised
Dropping pipettes
Beakers - 250 ml and 50 ml
Sticky labels or marker suitable for labelling glass
Stopwatch or watch with seconds-hand

Safety

Wear safety spectacles.

These household chemicals and their reaction products may be washed down the sink. Bleach is an irritant and may release chlorine gas upon reaction with some substances. Tartrazine should not be allowed to make contact with the skin as it may cause sensitisation.

Procedure

1. Prepare dilute solutions of the food dye solutions by adding 5 drops of each dye to approximately 100 ml of water in 250 ml beakers.

2. Prepare a solution of dilute bleach by adding 20 ml of commercial bleach using a dropping pipette to 100 ml of water in a 250 ml beaker.

3. Transfer two 20 ml portions of each of the dye solutions to each of two beakers, one labelled ‘reference’.

4. Add 10 ml of the bleach solution to the samples not labelled ‘reference’, simultaneously starting a stopwatch or noting the time.

5. Observe the colour changes and the corresponding times.

Conclusion

Reactions between chemicals occur at different rates which may be measured by monitoring some property of the system, in this case, by monitoring the disappearance of the colour of one of the reactants.

Discussion

Yellow food dye is a dilute ethanoic acid solution of tartrazine, blue food dye is a dilute ethanoic acid solution of brilliant blue and green food colouring is a mixture of the two. This simple, colourful experiment demonstrates fast and slow reaction rates and can be modified to illustrate effects of concentration, temperature, etc.

Experiment 2.2

To Plot a Rate Curve for a Reaction

Student experiment

Materials

Hydrogen peroxide solution, 100 ml, 6% (w/v). This can be prepared from 30% (w/v) hydrogen peroxide (sold as 100 volume hydrogen peroxide) by diluting 200 ml to 1 l in a volumetric flask.

Manganese dioxide
Delivery tubing, rubber or plastic
Cork bored to accommodate delivery tube
Conical flask
Beehive shelf
Graduated cylinder, 250 ml
Large water trough
Spatula
Long-stemmed funnel
Stopwatch

Procedure

1. Place the hydrogen peroxide in the conical flask. Avoid wetting the neck of the flask by using a long-stemmed funnel.

2. Clamp the flask on its side, Fig. 2.10, and using a spatula, place 2 g manganese dioxide carefully in the neck of the flask. Do not allow any of the powder to fall into the flask itself.

3. Fit the delivery tube to the cork and fit the cork to the conical flask.

4. Arrange the delivery tube, water trough, beehive shelf and graduated cylinder as shown in the diagram. The graduated cylinder must be filled with water before being positioned on top of the beehive shelf and clamped.

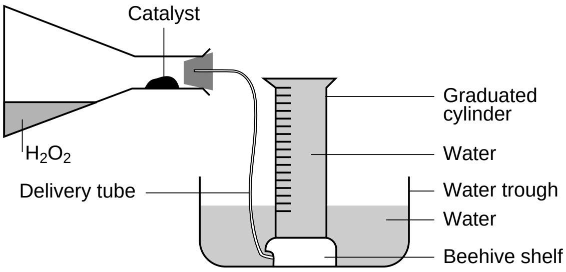


Fig. 2.10 *Catalytic decomposition of hydrogen peroxide*

5. Rearrange the flask to a vertical position, allowing the catalyst to fall into the hydrogen peroxide and start the reaction. Start a stopwatch at the same time. The reaction which occurs is

$$2H_2O_{2(aq)} \longrightarrow 2H_2O_{(l)} + O_{2(g)}$$

6. Take readings of volume of gas collected and the time elapsed, frequently at first, e.g. every thirty seconds for the first five minutes, and then less frequently, e.g. every minute for the following five minutes and every three minutes thereafter.

7. Plot a graph of volume of gas liberated versus time.

Conclusion

Data about the rate of progress of a reaction are collected and can be displayed graphically.

Discussion

The effects of changes in hydrogen peroxide concentration on the initial rate and the total volume of oxygen gas produced should be considered. The effects of changes in temperature and quantity of catalyst used should also be considered again in terms of initial rate and total yield. This reaction could also be carried out by connecting the delivery tube to a gas syringe or by placing the flask, with a piece of cotton wool acting as a spray trap in its mouth, on a balance and monitoring the loss in mass of the contents with time.

If a rate curve for a reaction where a water soluble gas is evolved is to be drawn, the gas can be collected using a gas syringe or the loss in mass of the gas can be monitored using a top-pan balance.

Experiment 2.3

To Demonstrate the Effect of Surface Area on the Rate of Reaction

Student experiment

Materials

Cube of wood, paint, saw
Powdered calcium carbonate, $CaCO_3$
Medium and small marble chips or seashells, $CaCO_3$
Hydrochloric acid solution, approximately 6 M
Spatula
Mortar and pestle
Beakers - 400 ml
Graduated cylinder, 100 ml
Clock glasses
Electronic balance

Safety

Wear safety spectacles.
Hydrochloric acid is corrosive and its fumes are irritating.

Procedure

1. Calculate the effect on the overall surface area of cutting a cube of side 1 cm into small pieces. Summarise findings in a table.

2. Paint the outside of a cube of wood and allow to dry before cutting it into a number of smaller cubes, e.g. twenty seven or sixty four cubes, depending on the size of the original cube.

3. Using the balance take 30 g each of the medium marble chips, small marble chips and powdered calcium carbonate on separate clock glasses.

4. Measure 200 ml of hydrochloric acid solution into each beaker using the graduated cylinder.

5. Transfer the contents of the clock glasses to the beakers and at the same time start a stopwatch. Note the appearance of the mixtures and record observations. The reaction which takes place is:

$$CaCO_{3(s)} + 2HCl_{(aq)} \longrightarrow CaCl_{2(aq)} + H_2O_{(l)} + CO_{2(g)}$$

Conclusion

The greater the available surface area of a solid reactant, the greater the rate of reaction.

Discussion

Table 2.1 shows how finely dividing a solid cubic particle into pieces approximately the size of table salt crystals increases the surface area available for reaction.

No. of equal cubic portions *n*	Length one side of one cubic portion/cm	Surface area of one face of one cubic portion/cm^2	Total surface area of one cubic portion/cm^2	Total surface area of *n* cubic portion/cm^2
1	1.00	1.00	6.0	6
8	0.50	0.25	1.5	12
64	0.25	0.0625	0.375	24
8000	0.05	0.0025	0.015	120

Table 2.1

Experiment 2.4

The Rapid Reactions Between Ionic Compounds in Solution

Student experiment or teacher demonstration (which can be adapted for OHP)

Materials

Sodium chloride
Silver nitrate
Barium chloride, $BaCl_2{\bullet}2H_2O$
Sodium sulphate, $Na_2SO_4{\bullet}10H_2O$
Water - deionised
Balance
Beakers - 250 ml
Test-tubes
Stopwatch or watch with seconds-hand

Safety

Wear safety spectacles.
Silver nitrate solution is corrosive. It should not be poured down the sink as it is a heavy metal salt; also it is valuable and should be recycled. Barium chloride and sodium sulphate are harmful.

Procedure

1. Prepare approximately 0.1 M solutions of sodium chloride and silver nitrate by dissolving 0.59 g sodium chloride and 1.7 g of silver nitrate, respectively, in water to produce 100 ml of aqueous solution.

2. Measure out 5 ml portions of each solution into separate test-tubes. Note the appearance of the solutions.

3. Transfer the contents of one test-tube to the other. Note appearance of the mixture. The reaction which occurs is

$$NaCl_{(aq)} + AgNO_{3(aq)} \longrightarrow AgCl_{(s)} + NaNO_{3(aq)}$$

4. Prepare approximately 0.1 M solutions of sodium sulphate and barium chloride by dissolving 3.2 g of sodium sulphate and 2.4 g of barium chloride, respectively, in water to produce 100 ml of aqueous solution.

5. Measure out 5 ml portions of each solution into separate test-tubes. Note the appearance of the solutions.

6. Transfer the contents of one test-tube to the other. Note the appearance of the mixture. The reaction which occurs is

$$BaCl_{2(aq)} + Na_2SO_{4(aq)} \longrightarrow BaSO_{4(s)} + 2NaCl_{(aq)}$$

Conclusion

Rapid reactions occur when solutions of ionic substances are mixed. The reaction time is too fast to measure using a stopwatch.

Discussion

If solutions of two ionic substances which do not form an insoluble product are mixed, their ions remain dissociated in solution.

Experiment 2.5

The Relatively Slow Reactions in Solution of Compounds with Covalent Bonds

Student experiment or teacher demonstration (which can be adapted for OHP)

Materials

2.5 g sodium thiosulphate ($Na_2S_2O_3{\bullet}5H_2O$) in water to produce 100 ml of approximately 0.1 M solution
Hydrochloric acid, 9 ml of conc. HCl in water to produce 1000 ml of dilute aqueous solution
Water - deionised
Balance
Graduated cylinders - 25 ml
Beakers - 250 ml
Test-tubes
Petri dishes
Stopwatch or watch with seconds-hand
Newspaper

Safety

Wear safety spectacles.
Sodium thiosulphate solution is harmful and in this experiment produces sulphur dioxide gas which is toxic by inhalation. The experiment should be carried out in a fume cupboard. Hydrochloric acid is corrosive and its fumes are irritating.

Procedure

1. Measure out 20 ml portions of the sodium thiosulphate and hydrochloric acid solutions into separate test-tubes. Note the appearance of the solutions.

2. Transfer the contents of the two test-tubes to a petri dish standing on a printed page. Start a stopwatch. Note the appearance of the mixture and the print through the solution until the print is obscured. Note the time. For safety it is necessary to observe the newsprint from outside the fume cuboard. The reaction which occurs is

$$Na_2S_2O_{3(aq)} + 2HCl_{(aq)} \longrightarrow 2NaCl_{(aq)} + H_2O_{(l)} + S_{(s)} + SO_{2(g)}$$

Conclusion

A reaction where covalent bonds are broken and formed is slower than reactions where only ionic substances react and form.

Discussion

What is the reaction time? What covalent bonds are broken in this experiment? What covalent bonds are formed? Is the rate of reaction equally dependent on the concentrations of hydrochloric acid and of sodium thiosulphate? How could this be confirmed?

Experiment 2.6

To Demonstrate the Effect of Temperature on a Reaction

Student experiment or teacher demonstration

Materials

Two *Alka Seltzer* tablets
Ice
Cold water
Hot water
Graduated cylinder - 100 ml
Beakers - 250 ml
Stopwatch or watch with seconds-hand

Safety

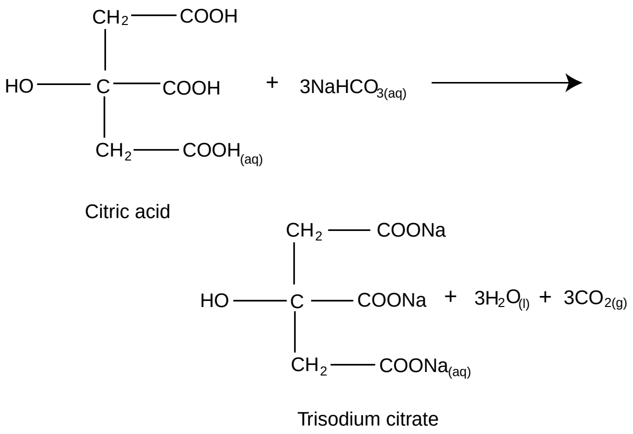
Wear safety spectacles.

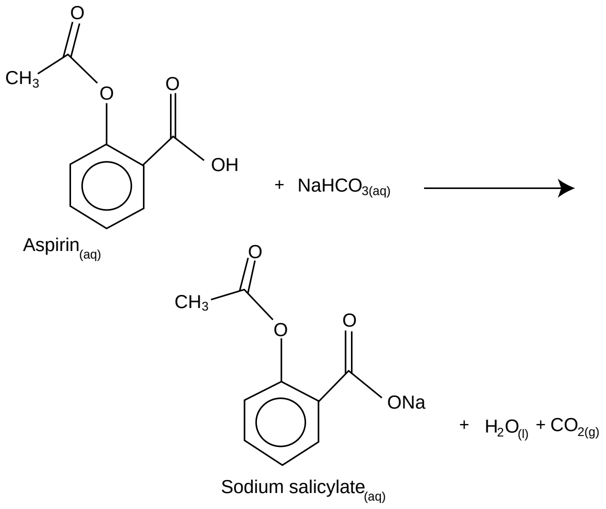
Procedure

1. Cool cold water to freezing point by adding ice cubes to it and allowing it to stand for a few minutes.

2. Measure out, using the graduated cylinder, 150 ml portions of hot water (about 60 ˚C) and iced water (no ice cubes) into separate 250 ml beakers.

3. Add an *Alka Seltzer* tablet to each beaker, starting a stopwatch at the same time. Note the appearance of the contents of each beaker. Note the time for complete reaction in each case. The reactions which occur are





Conclusion

A reaction occurs more rapidly when it is carried out at a higher temperature.

Discussion

Why do the substances not react before adding them to water? How could it be established whether or not a slow reaction was taking place in the solid tablet? How do the reaction times differ? Data for a graph of temperature versus rate of reaction could be obtained by carrying out similar experiments at a number of temperatures between 0 ˚C and 70 ˚C. In each case the inverse of reaction time is a measure of the rate.

Experiment 2.7

To Demonstrate the Effect of Concentration on a Reaction Rate

Student experiment

Materials

Sodium thiosulphate solution, 0.2 M, 25 g $Na_2S_2O_3•5H_2O$ in 500 ml deionised water
Hydrochloric acid solution, approximately 3 M
Water - deionised
Graduated cylinder - 10 ml
Burettes
Petri dishes
Sheets of newsprint with similar density of type
Stopwatch or watch with seconds-hand

Safety

Wear safety spectacles.
Sodium thiosulphate solution is harmful and in this experiment produces sulphur dioxide gas which is toxic by inhalation. The experiment should be carried out in a fume cupboard. Hydrochloric acid is corrosive and its fumes are irritating.

Procedure

1. Prepare solutions of sodium thiosulphate from the given 0.2 M solution as follows. Use a burette to measure out the required volume of 0.2 M sodium thiosulphate solution into 100 ml beakers and add the correct volume of

deionised water from a second burette. Label each beaker with the concentration of sodium thiosulphate solution it contains.

To 40 ml of the stock solution add 10 ml deionised water; solution diluted to 4/5 (40 ml to 50 ml) of its original concentration - 0.16 M.

To 35 ml of the stock solution add 15 ml deionised water; solution diluted to 7/10 (35 ml to 50 ml) of its original concentration - 0.14 M.

To 30 ml of the stock solution add 20 ml deionised water; solution diluted to 3/5 original concentration - 0.12 M.

To 25 ml of the stock solution add 25 ml deionised water; solution diluted to 1/2 original concentration - 0.10 M.

To 20 ml of the stock solution add 30 ml deionised water; solution diluted to 2/5 original concentration - 0.08 M.

To 15 ml of the stock solution add 35 ml deionised water; solution diluted to 3/10 original concentration - 0.06 M.

To 10 ml of the stock solution add 40 ml deionised water; solution diluted to 1/5 original concentration - 0.04 M.

2. Measure out 20 ml portions of each sodium thiosulphate solution into separate labelled petri dishes standing on newsprint.

3. Add 2 ml of the hydrochloric acid solution, measured using a 10 ml graduated cylinder, to the petri dish containing the 0.04 M sodium thiosulphate solution, starting a stopwatch at the same time.

4. Note the appearance of the mixture and the print through the solution until the print is obscured. Note the time. The reaction which occurs is:

$$Na_2S_2O_{3(aq)} + 2HCl_{(aq)} \longrightarrow 2NaCl_{(aq)} + H_2O_{(l)} + S_{(s)} + SO_{2(g)}$$

5. Repeat steps 3 and 4 with each petri dish in turn.

6. Plot a graph of rate of reaction (inverse of time) versus concentration of sodium thiosulphate.

Conclusion

The rate of reaction increases as the concentration of one of the reactants increases.

Discussion

In this experiment the reacting volume is kept constant and the concentration of the reacting solution is constant with respect to HCl but the sodium thiosulphate concentration is varied. The time for reaction decreases as the concentration of the solution increases. The rate of reaction is inversely proportional to the time for reaction. For practice, the students should carry out the dilutions and calculate the concentrations of the diluted solutions themselves.

Experiment 2.8

To Investigate Homogeneous Catalysis

Student experiment or teacher demonstration. The quantities should be scaled down five-fold for the student version.

Materials

Beakers, 600 ml
Volumetric flasks, 250 ml and 1 litre
Sodium potassium tartrate solution, 15 g $KNaC_4H_4O_6{\bullet}4H_2O$ made up to 250 ml with deionised water
Hydrogen peroxide solution, 100 ml, 6% weight by volume. This can be prepared from 30% weight by volume hydrogen peroxide (sold as 100 volume hydrogen peroxide) by diluting 200 ml to 1 litre in a volumetric flask.
Cobalt(II) chloride solution, 5 g $CoCl_2{\bullet}6H_2O$ in 10 ml water
Hotplate
Thermometer

Safety

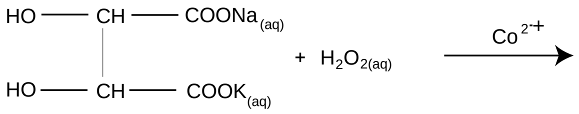
Wear safety spectacles. Cobalt chloride is toxic. Sodium potassium tartrate is harmful. Hydrogen peroxide is corrosive and oxidising. The contents of the beaker will froth and may overflow during the experiment, especially if the sodium potassium tartrate solution is heated in advance.

Procedure

1. Add 100 ml of the sodium potassium tartrate solution to the beaker. If desired, warm to a temperature not exceeding 70 °C.

2. Add 50 ml of the hydrogen peroxide solution. Record any observations.

3. Repeat steps 1 and 2 but, immediately after adding the hydrogen peroxide, add the cobalt chloride solution. Record any observations.



$$\begin{matrix} HO - CH - COONa_{(aq)} \\ | \\ HO - CH - COOK_{(aq)} \end{matrix} + H_2O_{2(aq)} \xrightarrow{Co^{2+}}$$

Products include water, carbon dioxide, oxygen and sodium and potassium salts of ethanedioic acid.

Conclusion

A reaction in solution occurs more rapidly upon adding a solution of a substance which participated in the reaction but which was not consumed by it.

Discussion

The catalyst is in the same phase as the other reagents, i.e. in aqueous solution. This is therefore an example of homogeneous catalysis. The rate of reaction before the catalyst is added is undetectable. There is a temporary complex formed during the reaction between the catalyst and a reagent. The change of the cobalt colour from pink to blue-green to pink again is evidence of this. If the temperature is high the rate of reaction is too fast for the colour changes to be clearly seen. This procedure can be adapted to investigate the change in rate of reaction with temperature. In each case the inverse of reaction time is a measure of the rate. Reaction time is measured from the addition of the catalyst to the reappearance of the pink colour of Co^{2+} ions.

Experiment 2.9

To Investigate Heterogeneous Catalysis

Teacher demonstration

Materials

Conical flask, 250 ml
Ethanol
Cardboard chimney in the shape of a T which fits neck of conical flask
Platinum wire (or copper wire)
Hotplate
Tongs

Safety

Wear safety spectacles. Ethanol and ethanal are flammable. The chimney may ignite as the reaction is exothermic. Ethanal vapours are very irritating and this experiment should be carried out using a fume hood.

Procedure

1. Add 15 - 20 ml of ethanol to the flask. Hook the wire onto the neck of the flask with most of its length inside the flask. Insert the cardboard chimney.

2. Warm the flask gently on the hotplate.

3. Remove from the hotplate and observe carefully. The reaction which occurs is

$$C_2H_5OH_{(g)} \longrightarrow CH_3CHO_{(g)} + H_{2(g)}$$

4. Remove the wire with a tongs and observe whether the reaction proceeds without the catalyst.

Conclusion

A reaction of a vapour occurs readily at a metal surface but not in the absence of the metal. The metal is not a reactant.

Discussion

The solid metal is a heterogeneous catalyst for the oxidation of ethanol to ethanal. The reaction is exothermic and does not need to have heat supplied once it has commenced. Indications that the reaction is exothermic are the glow of the metal and the popping sounds as the hydrogen gas produced ignites.

Experiment 2.10

To Demonstrate Autocatalysis

Student experiment or teacher demonstration

Materials

Potassium manganate(VII), approximately 0.02 M, 3.16 g potassium manganate(VII) crystals made up to a litre with deionised water
Ethanedioic acid solution, 0.05 M, 6.3 g $H_2C_2O_4{\bullet}2H_2O$ made up to a litre with deionised water
Manganese(II) sulphate
Sulphuric acid, approximately 2 M
Water - deionised
Burette
Conical flasks, 250 ml
Graduated cylinder
Stopwatch or watch with seconds-hand

Safety

Wear safety spectacles.
Potassium manganate(VII) is an oxidising agent and is harmful. Ethanedioic acid is harmful. Manganese(II) sulphate is harmful.

Procedure

1. Fill a burette with potassium manganate(VII).

2. Measure out 20 ml of ethanedioic acid into each of two conical flasks using a graduated cylinder. Add 10 ml dilute sulphuric acid to each flask.

3. Add one drop of the potassium manganate(VII) solution to the ethanedioic acid solution in one of the flasks, starting the stopwatch simultaneously.

4. Record the time for the pink colour of the potassium manganate(VII) to disappear.

5. Repeat Steps 3 and 4 for a second drop of potassium manganate(VII).

6. Add one crystal of manganese(II) sulphate to the second flask of acidified ethanedioic acid solution.

7. Add one drop of the potassium manganate(VII) solution to this second ethanedioic acid solution, starting the stopwatch simultaneously.

8. Record the time for the pink colour of the potassium manganate(VII) to disappear.

Conclusion

A reaction product, the Mn^{2+} ion, has a noticeable catalytic effect on the reaction.

$$2MnO^{-}_{4(aq)} + 5C_2O^{2-}_{4(aq)} + 16H^{+}_{(aq)} \xrightarrow{Mn^{2+}} 2Mn^{2+}_{(aq)} + 10CO_{2(g)} + 8H_2O_{(l)}$$

Discussion

That there is a catalytic effect from one of the products is established by comparing the rates of reaction for the first and second drop of potassium manganate(VII) solution added to the first ethanedioic acid solution. It can be deduced that the catalytic effect is from the Mn^{2+} ion because there is sulphate ion present in both flasks throughout. Note when these substances are titrated the ethanedioic acid solution is usually heated to increase the initial rate of reaction.

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CHAPTER 3 CHEMICAL EQUILIBRIUM

3.1 Reversible Reactions and Equilibrium

Introduction

A chemical equilibrium is associated with a reversible reaction. A reversible reaction is one in which the products, once formed, begin to change back into the reactants again. This means that a system consisting of two opposing processes is generated. The rate of the forward reaction is initially high because the concentration of the reactants is initially high and there is no reverse reaction because the concentration of the products is zero. As the reaction progresses, the rate of the forward reaction decreases as the reactant concentration decreases and the rate of the reverse reaction increases as the product concentration increases. After some time, the rate of the forward reaction will be exactly equal to the rate of the reverse reaction and no further change in the composition of the reaction mixture can then occur. Chemical equilibrium has now been established in the reversible chemical reaction. However, both forward and reverse reactions continue to occur indefinitely and the term **dynamic** equilibrium is applied to convey the idea of continuous activity occurring in the reaction mixture although the overall composition is unchanging.

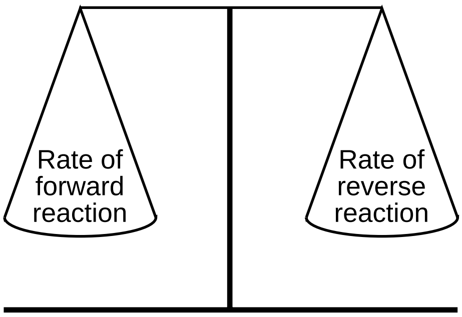

Fig. 3.1 *Chemical equilibrium*

The formation of an equilibrium can be illustrated in two different ways as the diagrams on the following page show. Fig. 3.2 shows the changes in concentration of the reactants and products with time when sulphur dioxide and oxygen gases reach equilibrium with sulphur trioxide gas at high temperature, catalysed by vanadium(V) oxide.

$$2SO_{2(g)} + O_{2(g)} \xrightleftharpoons{V_2O_5} 2SO_{3(g)},\ \Delta H = -196\text{ kJ}$$

After a certain time, *t*, there is no further change in the concentrations of any of the substances. The mixture has constant composition and equilibrium has been reached. Note however that the concentrations of the three substances at equilibrium are not the same (see section 3.4).

Note the double arrow indicating a reversible reaction. The reaction as read from left to right is referred to as the forward reaction and the reaction as read from right to left is the reverse reaction. If an enthalpy of reaction is stated, it refers to the forward reaction. The enthalpy of the reverse reaction is the additive inverse of the enthalpy of the forward reaction[1]. For example, in the equilibrium reaction above established at 298 K, the conversion of sulphur dioxide and oxygen to sulphur trioxide is exothermic with a ΔH of –196 kJ, while the reverse reaction is endothermic with a ΔH of 196 kJ. If a catalyst is mentioned, e.g. vanadium(V) oxide in the example above, it is written above the double arrow and it catalyses both reactions, equally (see section 3.3.) The state of each of the chemicals at equilibrium, whether solid, liquid, gaseous or in dilute aqueous solution is indicated in equations by the subscripts (s), (l), (g) or (aq).

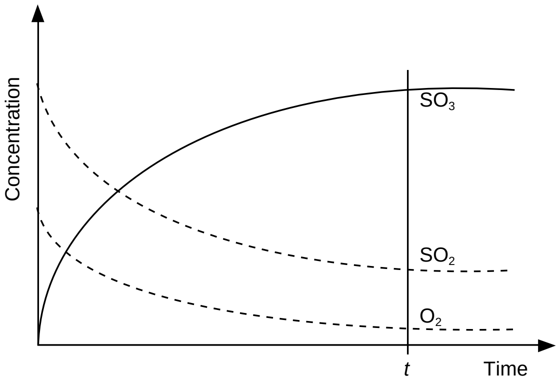

Fig. 3.2 *Equilibrium corresponds to reaction mixture of constant composition*

In Fig. 3.3 the same equilibrium is illustrated, this time by plotting rate of reaction versus time. Initially the forward reaction is rapid but decreasing and the reverse reaction has zero rate initially but increases. At time *t* both reactions have the same rate and equilibrium is established.

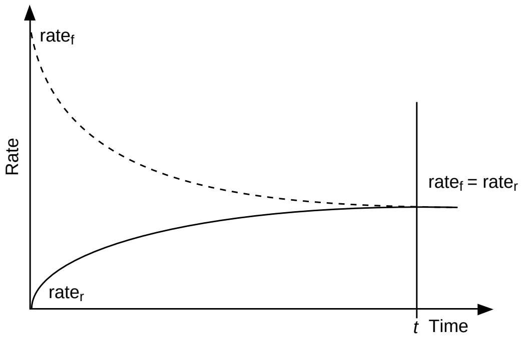

Fig. 3.3 *Equilibrium occurs when the rates of the forward and reverse reactions are equal*

From a practical point of view, reversible reactions present problems because, when equilibrium is established, the products must be separated from the reactants and other products and the unreacted reactants recycled back into the process. These problems do not occur to the same extent when a reaction goes to completion; there are no unused reactants and the required product must only be separated from a less complex mixture of products. In both cases the physical properties of the substances involved are employed to design separation methods. For example, in a gaseous mixture, one gas might more easily condense than the others at low temperature. One product in an organic reaction might precipitate if the reaction mixture was added to brine. Solvent-solvent extraction based on different solubilities of different components of a mixture is another technique used to separate organic mixtures. Another separation technique is distillation of one of the products from the reaction mixture.

Another practical consideration with reversible reactions can be utilised to drive a reversible reaction to completion. It is obvious that a chemical equilibrium cannot exist if the reactants and products escape from one another. In a lime kiln, for example, the following reaction takes place

$$CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}$$

The carbon dioxide produced is allowed to escape from the reaction vessel as it is formed. Therefore the reverse reaction, which is industrially undesirable, can never commence and equilibrium can never be established. However, if the same chemicals were mixed in a sealed container at high temperature an equilibrium could be established between the forward and reverse reactions.

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

An analogy for chemical equilibrium

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'One of the inhabitants of Paintersland decides to paint a line down the middle of a 100-meter road connecting his town with Nonpaintersland, the town of experts on paint-removing. The awkward painter starts the line but the paint bucket is left in town at the point where the line begins. Therefore, each time the brush is dry he must walk back to the bucket to re-wet it. Then he walks once again to the line end and continues his painting. Meanwhile, a nonpainter of the other town takes a sponge with paint remover in it, walks to the freshly painted line and begins to remove it thus partially undoing the painter's action. Each time his sponge is dry he too has to walk back to his town to the bucket of paint remover, re-wet his sponge, return once again to the line and continue to remove it. What is the end of the story? How does the line distance change with time?'

Disturbing a Reaction System which has Reached Equilibrium

If additional reactants are added to the equilibrium mixture this will temporarily disturb the equilibrium by increasing the rate of the forward reaction. This in turn will produce more products but then the rate of the reverse reaction increases also. After some time the rate of the forward reaction diminishes further, but the rate of the reverse reaction increases further until they are again equal and equilibrium is restored.

If additional products are added to the equilibrium this too will temporarily disturb the equilibrium by increasing the rate of the reverse reaction. This in turn will use up products and produce more reactants and then the rate of the forward reaction increases also. After some time the rate of the reverse reaction diminishes further, the rate of the forward reaction increases further until they are again equal and equilibrium is restored.

So a temporary imbalance occurs between the two activities of the equilibrium situation if the rate of one activity is changed relative to the other. Equilibrium is restored when the rate of the opposing activity also changes in response to the first.

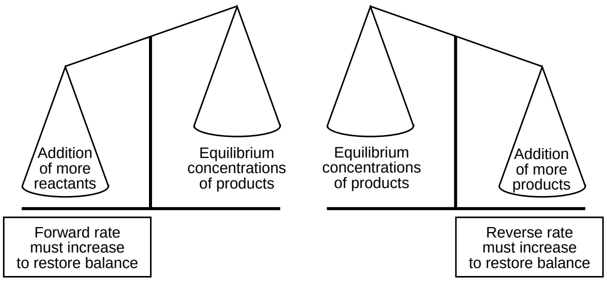

Fig. 3.4 *Equilibrium disturbed*

Disturbances can also be created by changing the temperature of the reaction mixture or by increasing or decreasing the overall pressure. (See section 3.6 on Le Châtelier's principle.)

3.2 Examples of Reversible Reactions and Equilibria

Example 1

A very simple example of an equilibrium process can be set up with liquid bromine in a stoppered glass bottle, Fig. 3.5.

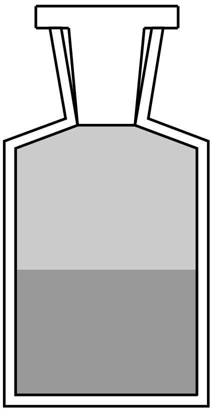

Fig. 3.5 *Bromine liquid and bromine vapour in equilibrium at room temperature*

The red-brown bromine liquid exists in equilibrium with its vapour. The space above the liquid is coloured by the presence of bromine vapour. Molecules in the vapour phase are continuously being condensed to liquid while molecules of the liquid are evaporating off the liquid surface into the vapour phase.

$$Br_{2(l)} \rightleftharpoons Br_{2(g)}$$

Both processes, which are physical changes, rather than chemical changes, occur at the same rate and continue indefinitely.

Example 2

An equilibrium can be set up if equal numbers of moles of hydrogen gas and iodine gas are mixed in a closed container at a temperature of about 450 °C. The initial colour of the mixture is deep purple due to the high concentration of iodine gas. After some time it is noticeable that the deep purple colour has faded to a lighter shade but has not disappeared completely. After another period of time no further fading is noticed. The reaction *appears* to have stopped. These observations are consistent with a reaction occurring between the gases to produce hydrogen iodide, a colourless product. This accounts for the fading. The reaction is represented by the equation

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

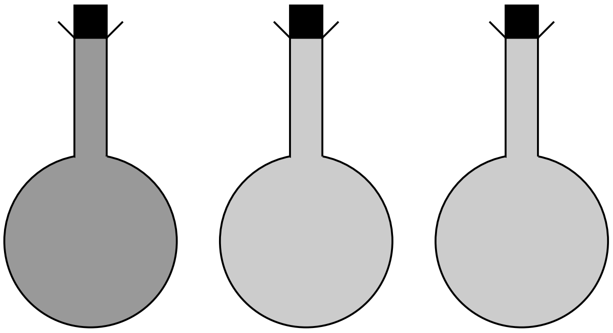

***Fig. 3.6** Iodine, hydrogen, hydrogen iodide equilibrium*

However, there is still some iodine in the container. This accounts for some of the purple colour persisting. The fact that the colour fades to a certain intensity and does not fade further could be accounted for in two ways: either chemical reaction in the flask stopped completely when it reached a certain point or the conversion of hydrogen and iodine to hydrogen iodide continues but produces no colour change because the hydrogen iodide decomposes equally rapidly to form hydrogen and iodine gases again, thus maintaining a constant concentration of the purple iodine in the flask. Observers can see colour, a macroscopic property of the mixture but cannot see the activities of the individual molecules. Observation alone cannot determine whether only the forward reaction occurs or whether the forward and reverse reactions both occur and continue indefinitely at equal rates. So how can we say that the system has reached a *dynamic* equilibrium?

Experiments involving isotopically labelled reagents can be used to show that these systems at equilibrium are not static but are dynamic systems where the forward and reverse reactions both continue at equal rates. Mass spectrometry can be used to confirm the presence of the tracer isotope in the different components of the equilibrium mixture.

Example 3

There are several important industrial equilibrium reactions; most noteworthy are the reactions between steam and methane to form hydrogen and carbon monoxide and between hydrogen and nitrogen to form ammonia in the fertiliser industry, the reaction between sulphur dioxide and oxygen to form sulphur trioxide in sulphuric acid manufacture, and in organic chemistry, the formation of esters from alcohols and carboxylic acids.

$$CH_{4(g)} + H_2O_{(g)} \overset{Ni}{\rightleftharpoons} 3H_{2(g)} + CO_{(g)}$$

$$N_{2(g)} + 3H_{2(g)} \overset{Fe}{\rightleftharpoons} 2NH_{3(g)}$$

$$2SO_{2(g)} + O_{2(g)} \overset{V_2O_5}{\rightleftharpoons} 2SO_{3(g)}$$

$$CH_3COOH_{(l)} + C_2H_5OH_{(l)} \overset{H^+}{\rightleftharpoons} CH_3COOC_2H_{5(l)} + H_2O_{(l)}$$

In each of these industrial examples, a simple equilibrium, based on a single reversible chemical reaction, is established. In the following examples more complex equilibria are described, involving a number of physical and chemical changes.

Example 4

In the atmosphere, a number of gases exist in equilibrium concentrations as a result of the processes adding those gases to the atmosphere occurring at the same rate as the processes removing those gases from the atmosphere. For example, measurements of carbon dioxide gas concentration in air have shown a constant concentration of the gas of approximately 0.03% by volume since the end of the last ice age (approximately 10 000 years ago) to the middle of the nineteenth century[2]. Carbon dioxide is added to the atmosphere by combustion of carbon compounds, respiration, roasting limestone, etc. These processes are called sources of carbon dioxide. It is removed by photosynthesis and by dissolving in water. These processes are called sinks for carbon dioxide. These processes occurred at equal rates maintaining a steady atmospheric carbon dioxide concentration. However, since the middle of the nineteenth century the concentration of carbon dioxide in the atmosphere has increased by approximately 25% of its early nineteenth century value. This increase occurred because of the increased rates of combustion of fossil fuels and the increased deforestation of the planet. This example illustrates a system, which was in equilibrium, experiencing a disturbance.

Example 5

Another atmospheric example of a gas in an equilibrium concentration as a result of sources and sinks balancing, is stratospheric ozone[3]. The formation mechanism of ozone is principally the photodissociation of oxygen gas into single atoms followed by the reaction between atoms of oxygen and molecules of oxygen to form ozone.

$$O_{2(g)} \xrightarrow{hf} 2O_{(g)}$$

$$O_{2(g)} + O_{(g)} \longrightarrow O_{3(g)}$$

The removal mechanisms for ozone include the reaction between ozone and atoms of oxygen, the photodissociation of ozone and the catalytic destruction of ozone by atmospheric NO.

$$O_{3(g)} + O_{(g)} \longrightarrow 2O_{2(g)}$$

$$O_{3(g)} \xrightarrow{hf} O_{(g)} + O_{2(g)}$$

$$2O_{3(g)} \xrightarrow{NO} 3O_{2(g)}$$

Until recently, the formation reactions and destruction reactions occurred at equal rates to keep a thin layer of ozone at approximately 50 km above the earth's surface. However, an additional destruction reaction arose when CFC gases, not found in nature, were released into the atmosphere. These gases give rise to chlorine atoms in the stratosphere as a result of photodissociation of the CFC molecules. The chlorine atoms remove many ozone molecules by the following chain reaction steps.

$$Cl_{(g)} + O_{3(g)} \xrightarrow{hf} ClO_{(g)} + O_{2(g)}$$

$$ClO_{(g)} + O_{(g)} \longrightarrow Cl_{(g)} + O_{2(g)}$$

Thus, like the carbon dioxide case, recent times have witnessed a disturbance in the equilibrium concentration of ozone, and a thinning of the ozone above the Antarctic has been measured and is often described as the 'hole in the ozone layer'.

Example 6

Insulin, a hormone produced in the pancreas, controls the rate of sugar metabolism in the body. *Diabetes mellitus* is the medical condition where the pancreas cannot manufacture sufficient insulin to maintain blood sugar levels within the normal range. Many diabetics take injections of insulin to relieve their symptoms.

The balance is maintained by two opposing actions, consumption of sugar in the diet and metabolism of sugar to avoid glucose accumulation. If the rate of sugar intake is equal to the rate of sugar metabolism by insulin, neither hypoglycaemia (blood sugar level too low) nor hyperglycaemia (blood sugar level too high) occurs. This situation persists indefinitely provided the insulin supply is regular and the consumption of sugar in the diet is maintained at a steady level. If, however, there is a disturbance in the system, e.g. a larger than normal sugar intake upon eating a bar of chocolate or an increased rate of metabolism of sugar following vigorous exercise, the balance is disturbed.

If the extra sugar intake is not matched by an additional insulin dose and/or preferably additional exercise, there will be an accumulation of sugar in the blood. If there is increased exercise but there is no additional sugar intake, or preferably no reduction in insulin supply, the result is a reduction in blood sugar levels. To maintain equilibrium following an intake of sugar or performing vigorous exercise, a diabetic understands that additional sugar consumption must be balanced by additional insulin and extra exercise must be balanced by additional sugar or a reduction in insulin.

The stable diabetic is in a dynamic biomedical equilibrium - once the stable blood sugar range is achieved neither sugar intake nor sugar metabolism ceases. The individual's food intake is continual and metabolism of sugar is ongoing also and the stable blood sugar range is maintained.

Unfortunately, while reversible reactions are common in the chemical industry and several quite complicated equilibrium systems exist in nature, there are very few examples of simple reversible reactions occurring with everyday chemicals in the home or garden.

3.3 Equilibrium Constant Expressions

Equilibrium Constant Expression, K_c

Consider a general reversible chemical reaction, where A, B, C, D are chemicals and *a, b, c*, and *d* are the corresponding numbers of moles of each in the balanced chemical equation (stoichiometry factors or coeffcients) which has established the following equilibrium.

$$a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D}$$

It is possible to show experimentally that at equilibrium

$$K_c = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b} \qquad (1)$$

where square brackets are used to denote that the concentrations of the reactants and products are expressed in moles per litre. K_c is a constant known as the equilibrium constant in terms of molar concentrations. This mathematical expression is known as the Equilibrium Law.

In heterogeneous reaction systems, the actual molar concentration of a substance might not be appropriate. If a reactant is a solid present in excess in a mixture with gases or solutions, it is usually assigned a molar concentration of 1. In aqueous solution, water is also assigned a molar concentration of 1 (see section 2.2).

Equilibrium Constant Expression, K_p

The equilibrium constant was discussed above in terms of equilibrium concentrations of the reactants and products in moles per litre. However, any other quantity related to concentration in moles per litre could be used to express an equilibrium constant. For example, in a mixture of gases the molar concentration of an individual gas is related to the partial pressure of that gas in the mixture. The partial pressure of a gas in a mixture is the same as the pressure the gas would exert if it alone occupied the container, i.e. the other gases present have no influence on the pressure exerted by any particular gas and the partial pressure of that gas is related only to the number of molecules of the gas present. Thus partial pressure is another way of expressing concentration or activity of a gas. It can be a more practical measure than molar concentration for gaseous systems since pressures in industrial processes may often be easily read from gauges and partial pressures may be deduced from apparent molecular masses in systems where one gaseous molecule dissociates into gaseous products.

Therefore, an alternative form of an equilibrium law can be written, where activities of gases are expressed in terms of partial pressures. This alternative is the equilibrium constant expression in terms of partial pressures and is denoted K_p. For the reaction

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

the equilibrium constant expression for K_p, where the partial pressures are usually measured in industry in either atmospheres or bars, is

$$K_p = \frac{(p_{HI})^2}{(p_{H_2})^2\,(p_{I_2})^2} \qquad (2)$$

Most textbooks treat the equilibrium law in terms of partial pressures as above, giving expressions like equation (2) which may or may not have units depending on the numbers of moles of reactants and products. From theory, however, it is known that K_p is dimensionless and a more rigorously theoretical treatment does lead to an expression for the equilibrium law in terms of partial pressures where K_p is always dimensionless[4,5].

The relationship between the two equilibrium constant expressions, where Δn is the difference between the number of gaseous moles of products and reactants, is

$$K_p = K_c(RT)^{\Delta n} \qquad (3)$$

This relationship in turn is based on the relationship between molar concentrations and gaseous pressures given by the ideal gas equation, $pV = nRT$, where p, V, T are the pressure, volume and temperature of n moles of a gas and R is the gas constant. (See sections 4.2 and 4.4, in the module Stoichiometry I).

$$\Delta n = n_{(products)} - n_{(reactants)}$$

In this example $\Delta n = 2 - (1 + 1) = 0$. Therefore $K_p = K_c$ in this case.

For Leaving Certificate, students are no longer required to perform calculations using this alternative K_p expression.

3.4 Notes on K_c

Units for K_c

The units for K_c depend on the particular chemical reaction for which the equilibrium constant expression is written. Examining equations (1) and (2) shows that in a chemical reaction where there are equal numbers of molecules of reactants and products in the equation, the units cancel leaving a dimensionless value of K_c. Applying equation (1) to the reaction

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

gives the following expression for K_c

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

The units partly cancel leaving $(moles/l)^{-1}$ or $l\ mol^{-1}$ as the unit for K_c.

Magnitude of K_c

The value of K_c indicates whether the reaction has proceeded very much towards products or whether there has been little conversion. The expression for K_c shows that its value will be large, that is significantly greater than one, when the concentrations (or partial pressures) of products are large - this is sometimes phrased ‘the equilibrium lies on the right’. Small values of K_c, that is significantly less than one, with the ‘equilibrium lying on the left’ have relatively small product concentrations and large reactant concentrations when equilibrium is established. If the value of K_c is close to one, the equilibrium concentrations of reactants and products are of the same order of magnitude.

How constant is K_c?

The value of K_c is constant for a particular reaction at a fixed temperature. As stated above, the equilibrium constant is the ratio of the rate constants for the forward and reverse reactions and these terms are temperature dependent.

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

The rate constants of both forward and reverse reactions increase with temperature but not at the same rate. (See section 2.2.) Hence, the ratio of rate constants varies with temperature and therefore the value of K_c changes with temperature also.

However, a change in the molar concentration of any substance in the equilibrium mixture results in no change in the value of K_c for a particular reaction. If the concentration of one of the reactants is increased, for example by adding more of that reactant into the reaction vessel and closing it again, the rate of the forward reaction is temporarily increased and more products are formed. This in turn produces an increase in the rate of the reverse reaction and equilibrium is restored. Quantitative experiments have shown that the new concentrations of reactants and products still give the same value for K_c when substituted into equation (1).

Effect of a Catalyst on K_c

If a catalyst is added to a reversible reaction and K_c values for the catalysed and uncatalysed reactions are compared there is no difference. The catalyst catalyses the forward and reverse reactions to equal extents by lowering the activation energy for the reaction pathway between reactants and products. (See section 2.4, Fig. 2.7.) Its only effect is that the equilibrium condition will be reached more quickly (or more slowly in the case of a negative catalyst).

Balanced Equation for the Equilibrium Reaction

Do the reactions

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \quad (1)$$

and

$${}^{1}/_{2}N_{2(g)} + {}^{3}/_{2}H_{2(g)} \rightleftharpoons NH_{3(g)} \quad (2)$$

have the same K_c values? If not, why not ?

They do not have the same value for K_c. The equilibrium constant expressions for the two reactions as given are

$$K_{c(1)} = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

and

$$K_{c(2)} = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}}$$

Clearly the first expression is the square of the second and the equilibrium constant calculated using the first expression is the square of the equilibrium constant from the second.

$$K_{c(1)} = (K_{c(2)})^2$$

Why should the same reaction have two different values for K_c ? Which one is correct?

In most chemical calculations, only the ratio of moles of reactants and products is important and so the two reactions as written would be equivalent. However, in the case of equilibrium calculations or thermochemical calculations the exact form in which the reaction is written is significant. For example, the reactions given above also have different enthalpy of reaction, Δ*H*, values.

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$, $\Delta H = -92.4$ kJ

and

${}^{1}/{}_{2}N_{2(g)} + {}^{3}/{}_{2}H_{2(g)} \rightleftharpoons NH_{3(g)}$, $\Delta H = -46.2$ kJ

The value for an equilibrium constant, K_c, like the enthalpy of reaction value, Δ*H,* is meaningless unless it is referred to a specific balanced equation. Equilibrium constants generated from experimental data and an equilibrium constant expression consistent with any correctly balanced version of the equation are all valid provided the exact form of the equation is specified along with the K_c, value. The equilibrium constant value is thus independent of the mechanism of the reaction.

3.5 Equilibrium and Spontaneity

An example of a reversible reaction is

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

which we assume takes place in a sealed vessel at high temperature.

This reaction is not a reversible reaction at room temperature. Indeed, marble, chalk or limestone, all minerals with a high calcium carbonate content, have no tendency to decompose to form calcium oxide and carbon dioxide at room temperature. At room temperature the forward reaction is not spontaneous (ΔG^o = 130.7 kJ mol^{-1}, see section 1.8). Although it has a large increase in entropy associated with it (ΔS^o = 152.1 J K^{-1} mol^{-1}) one of the products being gaseous, the reaction is highly endothermic (ΔH^o = 176.0 kJ mol^{-1}). The reaction between calcium oxide and carbon dioxide is spontaneous at room temperature - the reaction is sufficiently exothermic to overcome the unfavourable change in entropy. When the reaction conditions are changed to a significantly higher temperature, the energy change associated with entropy change is increased also. This is because at higher temperatures there is a greater degree of freedom of movement and hence greater disorder than at lower temperatures. Thus the forward reaction tends to have a greater release of energy due to increasing entropy associated with it as temperature increases while the entropy change associated with the reverse reaction means that this reaction becomes less spontaneous as temperature rises. At equilibrium both reactions occur, both reactions are therefore spontaneous and neither can therefore be associated with absorption of energy. The energy change for the forward reaction must be the additive inverse of the energy change for the reverse reaction according to the principle of conservation of energy. Thus, when equilibrium is reached the total energy change for both forward and reverse reactions is zero, i.e. ΔG for both reactions is zero.

3.6 Le Châtelier’s Principle

This principle applies to systems in dynamic equilibrium and states that when subjected to a stress, the system in equilibrium will react in such a way as to relieve the stress. A stress is constituted by changing the temperature of the system, changing the pressure of a system which contains gases or changing the concentration of any of the substances in the system. Le Châtelier’s principle is useful in predicting the outcome of disturbances of a system in equilibrium in terms of yields of any one of the reactants or products and in terms of changes in the value of K_c.

Henri Le Châtelier (1850-1936) was a French chemist with a special interest in mining. He studied flame bahaviour to try to prevent explosions in mines. He then went on to study heat and the measurement of high temperatures. This work with thermodynamics led him to state in 1888 his rule for the response of chemicals in equilibrium to changes in temperature, pressure and concentration. This rule has since then helped industrial chemists select conditions to optimise yields. Haber, for example, used Le Châtelier’s principle when designing an industrial process for the conversion of nitrogen and hydrogen to ammonia.

Temperature Changes

If the equilibrium is disturbed by changing the temperature, the result is determined by the thermodynamics of the forward and reverse reactions. If the temperature of the system in equilibrium is raised, then a reaction which can absorb heat will be observed to occur. Thus, whichever reaction is endothermic, the forward or reverse, its rate will be increased.

Suppose the forward reaction is endothermic and the temperature is raised, then equilibrium will be disturbed because the rate of the forward reaction is now greater than the rate of the reverse and more products on the right hand side of the equation accumulate. Equilibrium is re-established only when sufficient extra products have accumulated to increase the reverse reaction again until it is equal to the rate of the forward reaction. The second equilibrium lies to the right of the first, i.e. more products, less reactants and K_c has a bigger numerical value. See Fig. 3.7.

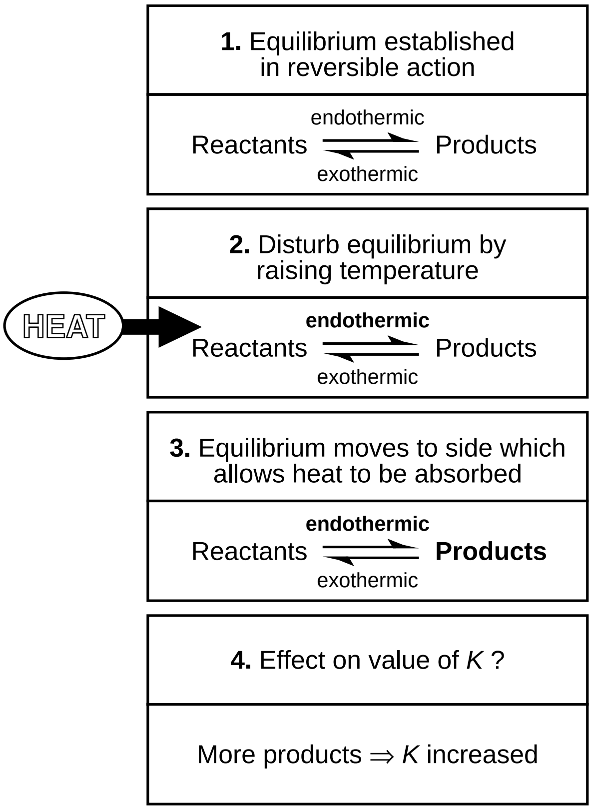

Fig. 3.7 *Effect of increasing the temperature on equilibrium where the forward reaction is endothermic*

Conversely, a reversible reaction where the forward reaction is endothermic, responds to a lowering of temperature by releasing heat, i.e. the reverse exothermic reaction is observed. Consequently, some of the products are consumed and the value of K_c is decreased, (see Fig. 3.8). It is clear that, in equilibrium systems where the forward reaction is endothermic, increasing the temperature favours the forward reaction whereas decreasing the temperature promotes the reverse reaction.

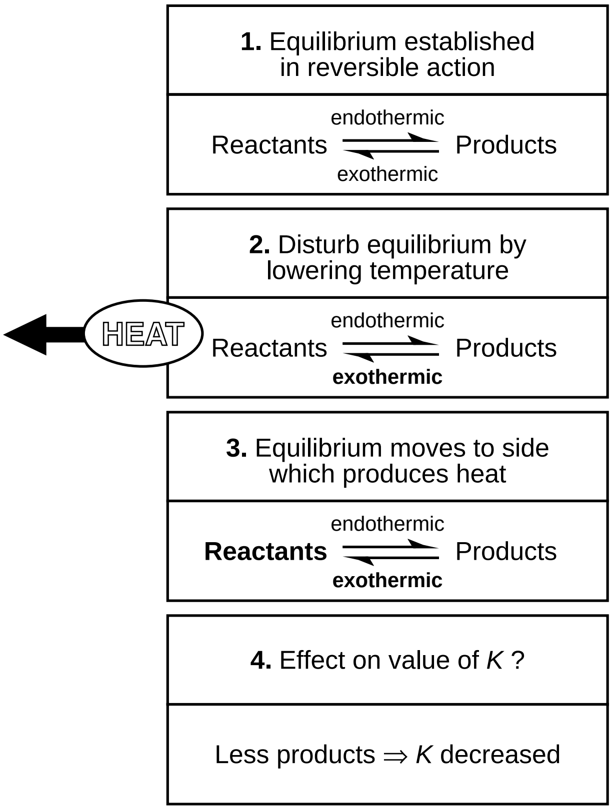

Fig. 3.8 *Effect of lowering the temperature on equilibrium where the forward reaction is endothermic*

Suppose then that the forward reaction is exothermic and the temperature is lowered, then equilibrium will be disturbed because the rate of the forward reaction is now greater than the rate of the reverse reaction and more products accumulate. Equilibrium is re-established only when sufficient extra products have accumulated to increase the reverse reaction again until it is equal to the rate of the forward reaction. The second equilibrium lies to the right of the first, i.e. more products, less reactants, and K_c has a larger numerical value.

Conversely, a reversible reaction where the forward reaction is exothermic, responds to an increase of temperature by absorbing heat, i.e. the reverse endothermic reaction is observed. Consequently, some of the products are consumed and the value of K_c is decreased. It is clear that, in equilibrium systems where the forward reaction is exothermic, decreasing the temperature promotes the forward reaction and increasing the temperature favours the reverse reaction.

Changes in Pressure

If the pressure is increased on a gaseous system in equilibrium, according to Le Châtelier's principle chemical changes will occur in the system to relieve the stress of the pressure change, i.e. the pressure will fall if possible. Assuming the temperature of the system does not change as the pressure is increased, the volume of the system decreases. This increases the molar concentration of each of the substances present at equilibrium. The rates of both the forward and reverse reactions are therefore increased but the reaction which involves the bigger number of gaseous moles will be increased to a greater extent than the other. Therefore, equilibrium moves to the side of the balanced equation which uses up most gaseous molecules and lies on the side with the least number of gaseous molecules. For example in the hydrogen, nitrogen, ammonia equilibrium,

$$N_{2(g)} + 3H_{2(g)} \overset{Fe}{\rightleftharpoons} 2NH_{3(g)}$$

the rate of the forward reaction, which is fourfold dependent on molar concentrations of substances in the equilibrium mixture, will be increased to a greater extent than the rate of the reverse reaction which is twofold dependent on the molar concentration of a substance in the equilibrium mixture. Eventually equilibrium is re-established and the value of the equilibrium constant is unchanged, although the individual equilibrium concentrations of all the reactants and products have changed.

If pressure is reduced, at constant temperature, the volume of the system increases. The concentration of each substance present at equilibrium decreases and the reaction which favours the formation of more gaseous molecules is favoured according to Le Châtelier's principle.

If there is no change in the number of gaseous moles as a reaction proceeds, then it is unaffected by changes in pressure.

Changes in Concentration

If, when equilibrium is established in a reversible reaction, some of any product or reactant is added or removed from the system, according to Le Châtelier's principle reaction will occur to oppose the change in concentration made. This is exactly what is expected if the chemical equilibrium is considered as a balance between the rates of the forward and reverse reactions. If additional reactant is added, for example, the rate of the forward reaction is initially increased resulting in more products being formed and the reactant added is thus consumed. Similarly, if one of the products is removed, the rate of the reverse reaction is initially decreased and more of the products, including the one removed, accumulate. Eventually equilibrium is re-established and the value of the equilibrium constant is unchanged although the individual equilibrium concentrations of all the reactants and products have changed.

How substances are added to or removed from a system in equilibrium depends on the chemical or physical properties of the reactants and products. In a gaseous system it is easy to add gases to the system *via* taps. In an equilibrium system established in solution, any reactant may be added to the solution. Some reactants or products in solution may be removed by adding a reagent which will absorb the substance, e.g. H_3O^+ ion or OH^- ion concentration can be lowered by adding a suitable base or acid, respectively. An ion may be removed as a precipitate by the addition of a suitable reagent, e.g. chloride ions may be removed from solution as a silver chloride precipitate upon addition of silver nitrate.

Effects of changes in concentration may be illustrated and explained as follows. Fig. 3.9 shows equilibrium established at t_1 in the reaction

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

which occurs in the Contact Process for sulphuric acid manufacture. After equilibrium is established, more SO_3 is admitted to the system, at t_2 in the diagram. The concentration of SO_3 is immediately increased. The diagram shows that this is followed by a decrease in the concentration of SO_3 because of an increase in its rate of reaction. This causes an increase in the concentration of SO_2 and O_2 which in turn react. Equilibrium is re-established at t_3.

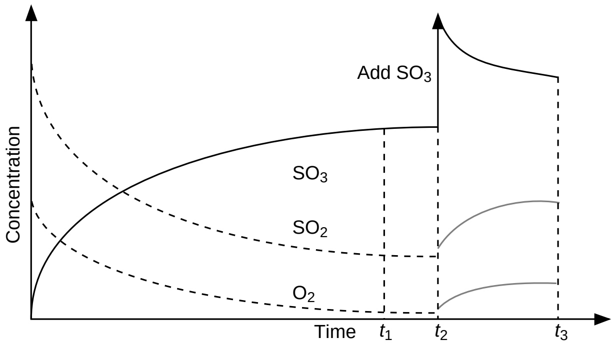

Fig. 3.9 *Disturbing a system which has reached equilibrium by adding more product*

Fig. 3.10 shows equilibrium established at t_1 in the reaction

$$Cr_2O_{7(aq)}^{2-} + 3H_2O_{(l)} \rightleftharpoons 2CrO_{4(aq)}^{2-} + 2H_3O_{(aq)}^{+}$$

which occurs in aqueous solution. After equilibrium is established some of the hydronium ions formed are removed from the system by adding a solution of sodium hydroxide at t_2 in the diagram. The concentration of hydronium ion is immediately decreased. The diagram shows that this is followed by an increase in the concentration of hydronium ion because of a decrease in its rate of reaction compared to its rate of formation. Similarly chromate ion, CrO_4^{2-}, also accumulates. The concentration of dichromate ion, $Cr_2O_7{}^{2-}$, decreases. The concentration of water is not considered to change in aqueous solution. Its concentration is taken as unity as it is always present in such an excess that it does not in any way limit the rate of any reaction. Equilibrium is re-established at t_3.

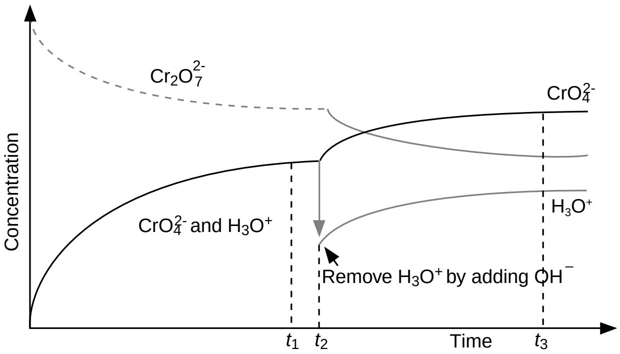

Fig. 3.10 *Disturbing a system in equilibrium by removing some product*

Le Châtelier's Principle in Industry

Le Châtelier's principle is very useful in predicting the outcome of various conditions of temperature, pressure and concentration on the equilibrium concentrations in a reversible chemical reaction. Thus the principle can be used to predict the optimum conditions to move the equilibrium to the far right and thus increase the yield of the forward reaction in a reversible system. However, in industry, if production is based on an equilibrium reaction, maximum yield is not the only consideration of importance. The time required for equilibrium to be reached is an important factor, as are any special equipment and conditions which might be required to drive the equilibrium to the right. For example, if high temperature is required to favour an endothermic forward reaction, the cost of operating at high temperature is a consideration. If high pressure is required in the case of a forward reaction leading to a reduction in the number of gaseous moles, then compressors must be provided and operated. Reaction vessels and pipe work must be strengthened to withstand high pressure and safety considerations associated with pressurised plant is an additional factor. In industry, a compromise is made between safety, economy and chemistry to operate the plant at the optimal conditions.

3.7 Experiments

Experiment 3.1

To Establish a Chemical Equilibrium and Disturb the Equilibrium Concentrations

Student experiment

Materials

Potassium dichromate crystals, $K_2Cr_2O_7$
Potassium chromate crystals, K_2CrO_4
Nitric acid, 1.5 M
Sodium hydroxide, 3 M
Barium nitrate
Beakers
Glass rod
Balance

Safety

Wear safety spectacles.
Potassium dichromate and potassium chromate are irritants. Sodium hydroxide and sulphuric acid are corrosive. Concentrated sulphuric acid should be used with extreme caution. Barium nitrate is harmful and contact with combustible material may cause fire.

Procedure

1. Prepare a solution of potassium dichromate in a beaker by dissolving approximately 3.7 g in 50 ml of water. Observe the orange colour.

2. Prepare a solution of potassium chromate in a beaker by dissolving approximately 2.5 g in 50 ml of water. Observe the yellow colour.

3. Add sodium hydroxide solution dropwise until the orange colour of the potassium dichromate solution changes to a bright yellow colour, indicating the presence of potassium chromate. The following equilibrium is now established.

$$2CrO^{2-}_{4(aq)} + 2H_3O^{+}_{(aq)} \rightleftharpoons Cr_2O^{2-}_{7(aq)} + 3H_2O_{(l)}$$

4. Add some 1.5 M nitric acid, dropwise, and note that the orange colour is again observed.

5. Add sodium hydroxide solution dropwise until a distinct yellow colour is observed again.

6. Add more 1.5 M nitric acid dropwise until the orange colour is obtained again and then add water until the yellow colour reappears.

7. Dissolve approximately 3.3 g of barium nitrate in 50 ml of water. In a fume cupboard, add the barium nitrate solution to the equilibrium mixture. A yellow precipitate is formed.

Conclusion

A chemical equilibrium is established between the two ions, chromate and dichromate, in aqueous solution.

Discussion

The position of the equilibrium can be controlled by adding H^+ ions (or removing them by adding OH^- ions). The effect of barium nitrate is to remove chromate ion as a barium chromate precipitate. Is this likely to increase or decrease the dichromate ion concentration?

Experiment 3.2

To Demonstrate the Effect of Temperature on a Chemical Equilibrium

Teacher demonstration

Materials

Ampoule containing dinitrogen tetroxide/nitrogen dioxide mixture

Water/ice bath
Water bath (large beaker of water) heated above 50 ˚C.

Safety

Wear safety spectacles.
Handle the glass ampoule with care.

Procedure

1. Observe the colour of the gases contained in the ampoule.

2. Place the ampoule in a water/ice bath for a few minutes. Observe the colour of the gases contained in the ampoule.

3. Place the ampoule in a water bath for a few minutes. Observe the colour of the gases contained in the ampoule.

Conclusion

Chemical reactions occur when the ampoule is placed in different temperature environments. A pale yellow gas is formed at low temperature and a dark brown gas at high temperature. At room temperature, an intermediate colour is observed indicating a mixture of the gases in similar proportions.

$$N_2O_{4(g)} \underset{\text{exothermic}}{\overset{\text{endothermic}}{\rightleftharpoons}} 2NO_{2(g)}$$

Discussion

The observations are in keeping with the existence of an equilibrium mixture of gases at room temperature. Lowering the temperature favours an exothermic reaction and a greater proportion of dinitrogen tetroxide is present and a pale yellow colour is observed. Pure dinitrogen tetroxide is actually colourless. Raising the temperature favours the endothermic reaction and dark brown nitrogen dioxide is formed by the dissociation of the dinitrogen tetroxide. Is there any nitrogen dioxide present at the low temperature or any dinitrogen tetroxide at the higher temperature?

3.8 References

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CHAPTER 4 CALCULATIONS

4.1 Thermochemistry

Enthalpies of Combustion and Kilogram Calorific Values

Questions on enthalpies of combustion and kilogram calorific values can be easily solved if the definitions for both quantities are borne in mind. Some questions also require a knowledge of the definition of the mole.

Worked Example 1

The standard enthalpy of combustion of propane is –2220 kJ mol^{-1}. How much energy is released when 4 g of propane are burned?

This question may be solved by setting up a ratio, using the definition of enthalpy of combustion to supply some of the information in the ratio. The student must know the formula of propane, C_3H_8, and how to find its molar mass, 44 g. Since the question is about mass and energy, the ratio must involve mass and energy.

4 g : x kJ
44 g : 2220 kJ

$$\frac{4}{44} = \frac{x}{2220}$$

$$x = \frac{2220 \text{ x } 4}{44}$$

$$= 201.82$$

Energy released on burning 4 g propane = 202 kJ

Worked Example 2

What is the standard enthalpy of combustion of benzene if its kilogram calorific value is 41.96 MJ ?

This question may also be solved by setting up a ratio, using the definitions of enthalpy of combustion and kilogram calorific value to supply some of the information in the ratio. The ratio must involve energy and either moles or mass. The student must know the formula for benzene, C_6H_6, and find its molar mass, 78 g.

78 g : x MJ
1000 g : 41.96 MJ

$$x = \frac{78 \text{ x } 41.96}{1000}$$

$$= 3.273$$

Note that this energy is released and therefore by convention the corresponding enthalpy change has a negative sign. Enthalpies of combustion are usually given in kJ rather than MJ and since the question is about the standard enthalpy of combustion and therefore refers to a mole of benzene, the unit is the kJ mol^{-1}.

Standard enthalpy of combustion of benzene = –3273 kJ mol^{-1}

Worked Example 3

How much energy is released when 200 ml of methanol are burned? The density of methanol is 0.778 g ml^{-1} and its standard enthalpy of combustion is –715 kJ mol^{-1}.

This question must be solved in two stages. The information given about volume and density of methanol must first be used to find the mass of methanol. The standard enthalpy of combustion refers to a mole or to the molar mass of a substance. Then a ratio involving mass and energy can be constructed. The student must know the formula for methanol and find its molar mass.

$$\text{Density} = \frac{\text{mass}}{\text{volume}}$$

$\Rightarrow$ Mass = density x volume

Density and volume units must be consistent: 778 kg m^{-3} = 0.778 kg l^{-1} = 0.000778 kg ml^{-1} = 0.778 g ml^{-1}.

$\Rightarrow$ Mass = 0.778 x 200 = 155.6 g

(ii) 155.6 g : x kJ
32 g : 715 kJ

$$\frac{155.6}{32} = \frac{x}{715}$$

$$x = \frac{155.6 \times 715}{32}$$

$$= 3476.69$$

Energy released upon burning 200 ml methanol = 3477 kJ

Exercise 4.1

Q.1. The standard enthalpy of combustion of methane is – 890.4 kJ mol^{-1}. What is the enthalpy change when 4 g of methane are burned?

Q.2. Using the data in Table 1.1, p. 7, calculate the standard enthalpies of combustion of hydrogen and methane.

Q.3. Given the densities of ethanol and petrol as 790 kg m^{-3} and 700 kg m^{-3} respectively, using Table 1.1 calculate the heat content of each of these fuels in terms of megajoules per litre.

Q.4. Calculate the kilogram calorific value of glucose, $C_6H_{12}O_6$, from its enthalpy of combustion which is –2816 kJ mol^{-1}.

Q.5. Calculate the kilogram calorific value of ethanol, C_2H_5OH, from its enthalpy of combustion which is –1371 kJ mol^{-1}. Which is a better source of energy, glucose or ethanol?

Q.6. According to nutritional data, diet *Coca-Cola* contains 1.9 kJ/100 ml and traditional *Coca-Cola* contains 168 kJ/100 ml. What is the energy content (in kJ) of a 330 ml can of each?

Assuming that all the energy in the diet *Coca-Cola* is carbohydrate energy, what mass of carbohydrate is present in 100 ml of diet *Coca-Cola*? Carbohydrate contains on average 17 kJ g^{-1}.

Q.7. *Lucozade* contains 321 kJ/100 ml and *Mars* bars contain 1889 kJ/100 g. How much *Lucozade* would one have to drink to have the energy equivalent to one standard *Mars* bar of mass 65 g? Remember there are important nutritional considerations other than energy content when comparing foods.

Q.8. Kellogg’s *Coco Pops* contain 1600 kJ/100 g and Kellogg’s *Frosties* contain 480 kJ per 30 g serving. Which would be recommended for a more energetic breakfast?

Q.9. Estimate how much energy is lost in the process of losing 500 g of water by sweating if the enthalpy of evaporation of water is 43.46 kJ mol^{-1} at body temperature (37 ˚C).

Answers

Q.1. –222.6 kJ.
Q.2. –285.8 kJ mol^{-1}, –891.2 kJ mol^{-1}.
Q.3. 23.5 MJ l^{-1}, 33.8 MJ l^{-1}.
Q.4. 15.64 MJ kg^{-1}.
Q.5. 29.8 MJ kg^{-1}, ethanol.
Q.6. 6.3 kJ, 554 kJ, 0.11 g.
Q.7. 383 ml.
Q.8. They contain equal energy in equal size servings.
Q.9. 1207 kJ.

Calorimetry: Enthalpies of Combustion, Solution and Neutralisation

Worked Example 1

Calculate the heat of combustion of ethanol from the following information. A 10 ml sample of ethanol was burned in excess oxygen in a bomb calorimeter. The density of ethanol is 0.785 g ml^{-1}. The heat capacity of the bomb and the water in which it is immersed can be taken as 44.7 kJ K^{-1} and the temperature of the water rose from 24.5 ˚C to 29.7 ˚C.

All questions based on calorimetry have a common part to their solution. The formula $E = mc\Delta\theta$ (where m is the mass of the substance heated, c is the specific heat capacity of that substance and $\Delta\theta$ is the temperature increase) gives the energy required to heat a substance. When more than one substance is being heated there may be more than one $mc\Delta\theta$ term in the calculation. Alternatively, the heat capacity, C, of an apparatus may be given. (See section 1.5.)

$$E = mc\Delta\theta = C\Delta\theta$$

$$E = 44.7 \text{ x } 5.2 = 232.44$$

The energy released upon burning 10 ml of ethanol is 232 kJ.

The temperature rise is the same whether the Kelvin scale or Celsius scale is used. The unit of energy is consistent with the unit in which heat capacity or specific heat capacity is given.

$$\text{Density} = \frac{\text{mass}}{\text{volume}}$$

Mass = density x volume

= 10 x 0.785

= 7.85 g (units are consistent)

A ratio is constructed to finish the calculation.

46 g : x kJ

7.85 g : 232.44 kJ

$$x = \frac{46 \text{ x } 232.44}{7.85}$$

= 1362.07

The result is in kJ mol^{-1} because it refers to a mole of ethanol and a negative sign must be supplied because heat is evolved.

Standard enthalpy of combustion of ethanol is estimated to be –1362 kJ mol^{-1}.

Worked Example 2

Calculate the heat of solution of ammonium nitrate from the following information. A 5 g sample of ammonium nitrate was dissolved in 100 ml of water in a polystyrene container of negligible heat capacity. The density of water is 1.0 g ml^{-1}. The specific heat capacity of water can be taken as 4200 J kg^{-1} K^{-1} and the temperature of the water fell from 23.2 ˚C to 19.4 ˚C.

Solution: The formula $E = mc\Delta\theta$ (where m is the mass of the substance cooled, c is the specific heat capacity of that substance and $\Delta\theta$ is the temperature decrease) gives the energy required to cool a substance. In this example only one substance is being cooled so there is one $mc\Delta\theta$ term in the calculation. Note that in this calculation the mass of the substance losing heat must be in kilograms. This is so that the unit for mass is consistent with that for specific heat capacity which is J kg^{-1} K^{-1}.

$$\text{Density} = \frac{\text{mass}}{\text{volume}}$$

Mass = density x volume

= 1.0 x 100

= 100 g (units are consistent).

100 g = 0.1 kg

$E = mc\Delta\theta$

$E = 0.1 \text{ x } 4200 \text{ x } 3.8$

= 1596 J

Note that it is the mass of the substance losing heat which is required in this formula and not the mass of the substance whose heat of solution is required.

Note the unit of energy is consistent with the unit in which specific heat capacity was given.

This is the energy absorbed upon dissolving 5 g of ammonium nitrate.

The temperature <u>fall</u> is the same whether the Kelvin scale or the Celsius scale is used.

A ratio is constructed to finish the calculation.

80 g : x J
5 g : 1596 J

$$x = \frac{80 \times 1596}{5}$$

$$= 25536$$

The result is in J mol^{-1} because it refers to a mole of ammonium nitrate and a positive sign must be assigned because heat is absorbed.

Standard enthalpy of solution of ammonium nitrate is estimated to be 26 kJ mol^{-1}.

Worked Example 3

Calculate the heat of neutralisation of sodium hydroxide by ethanoic acid from the following information. A 50 ml solution of 1.0 M sodium hydroxide is mixed with 50 ml of 1.1 M ethanoic acid solution in a polystyrene container of negligible heat capacity. The density of the solution formed may be assumed to be 1.0 g ml^{-1}. The specific heat capacity of the solution may be assumed to be the same as water and can be taken as 4200 J kg^{-1} K^{-1}. The initial temperature of the sodium hydroxide was 27.0 ˚C and that of the acid was 26.2 ˚C and the final temperature of the solution formed was 33.1 ˚C.

In this example only one substance is being heated so there is one $mc\Delta\theta$ term in the calculation. Note that in this calculation the mass of the substance absorbing heat must be in kilograms. The average temperature of the acid and base solutions may be used to find the initial temperature and therefore the rise in temperature during the reaction since equal volumes of both solutions are used.

$$\text{Averge initial temperature} = \frac{26.2 + 27.0}{2} = 26.6\ ˚\text{C}$$

Rise in temperature = 33.1 – 26.6 = 6.5 K

The temperature <u>rise</u> is the same whether the Kelvin scale or Celsius scale is used.

$$\text{Density} = \frac{\text{mass}}{\text{volume}}$$

Mass = density x volume.

= 1.0 x 100

= 100 g (units are consistent)

100 g = 0.1 kg

Note that the mixture of the two solutions absorbs energy in the reaction.

$$E = mc\Delta\theta$$

$$E = 0.1 \times 4200 \times 6.5$$

$$= 2730\ \text{J}$$

This is the energy released upon neutralising 50 ml 1.1 M ethanoic acid with 50 ml of 1.0 M sodium hydroxide. Note the unit is consistent with the unit in which specific heat capacity was given.

Next the number of moles of H^+ or OH^- ion neutralised must be calculated. Consider whether the acid or base is in excess. 50 ml 1.1 M ethanoic acid is reacted with 50 ml 1.0 M sodium hydroxide. The acid is in excess. The base is the limiting reagent. There is enough acid to neutralise all the base.

$$\text{No. moles of base neutralied} = \frac{50}{1000} \times 1$$

$$= 0.05\ \text{mol}\ OH^-$$

A ratio is constructed to finish the calculation.

1 mole : x J
0.05 mole : 2730 J

$$x = \frac{2730 \text{ x } 1}{0.05}$$

$$= 54600$$

The result is in J mol^{-1} because it refers to a mole of water formed and a negative sign must be assigned because heat is released.

Standard enthalpy of neutralisation of sodium hydroxide by ethanoic acid is estimated to be –54.6 kJ mol^{-1}.

Exercise 4.2

Q.1. A sample of naphthalene, $C_{10}H_8$, an aromatic chemical sometimes used in mothballs, was burned in excess oxygen in a bomb calorimeter. The heat capacity of the bomb and its auxiliary apparatus was 3.78 kJ K^{-1}. The temperature increase recorded upon burning 0.48 g of naphthalene was 5.12 K. Estimate the standard enthalpy of combustion of naphthalene from these figures.

Q.2. A 5 g sample of a chemical was burned completely in a bomb calorimeter apparatus of heat capacity 44.7 kJ K^{-1}. A temperature rise of 4.0 K was recorded. If the standard enthalpy of combustion of the substance is –2673 kJ mol^{-1}, calculate its relative molecular mass.

Q.3. A sample of potassium hydroxide of mass 2 g was dissolved in 200 ml of water in a copper calorimeter of mass 62 g. A temperature rise of 2.27 K was observed. Given the specific heat capacities of copper and water as 385 J kg^{-1} K^{-1} and 4200 J kg^{-1} K^{-1}, respectively, and the density of water as 1 g ml^{-1}, calculate the enthalpy of solution of potassium hydroxide.

Q.4. Two salts were dissolved simultaneously in water. One salt, ammonium chloride, dissolves endothermically with an enthalpy of solution of 15.2 kJ mol^{-1}. The second salt, lithium chloride, dissolves exothermically with an enthalpy of solution of -37.2 kJ mol^{-1}. If 2.0 g of ammonium chloride are used, what mass of lithium chloride is required if no change in temperature is permitted?

Q.5. An experiment to measure the enthalpy of neutralisation of sulphuric acid by sodium hydroxide was carried out by mixing a 50 ml sample of 1.5 M sulphuric acid with 100 ml of 1.6 M sodium hydroxide in a polystyrene cup of negligible heat capacity. The temperature rise recorded was 13.6 K. Assume the specific heat capacity and the density of the solution are close to the water values of 4200 J kg^{-1} K^{-1} and 1 g ml^{-1}, respectively. What is the standard enthalpy of neutralisation for the reaction?

Q.6. Calculate the temperature rise you would expect to record in an experiment to measure the heat of neutralisation of sulphuric acid with potassium hydroxide if 50 ml of a 1.1 M solution of sulphuric acid are mixed with 50 ml of 2 M potassium hydroxide in a polystyrene cup of negligible heat capacity. The specific heat capacity and the density of the solution may be asumed to be equal to the specific heat capacity and the density of water, 4200 J kg^{-1} K^{-1} and 1 g ml^{-1}, respectively. Take the standard enthalpy of neutralisation of sulphuric acid by potassium hydroxide as -57.2 kJ mol^{-1}.

Answers

Q.1.	–5161 kJ mol^{-1}.
Q.2.	75.
Q.3.	–55 kJ mol^{-1}.
Q.4.	0.65 g.
Q.5.	–57.12 kJ mol^{-1}.
Q.6.	13.6 K.

Hess's Law

Worked Example 1

Calculate the standard enthalpy change for the reaction

$$Zn_{(s)} + S_{(s)} + 2O_{2(g)} \longrightarrow ZnSO_{4(s)}$$

from the following information

$$Zn_{(s)} + S_{(s)} \longrightarrow ZnS_{(s)},\ \Delta H = -206.0 \text{ kJ mol}^{-1}$$

$$ZnS_{(s)} + 2O_{2(g)} \longrightarrow ZnSO_{4(s)},\ \Delta H = -776.8\ \text{kJ mol}^{-1}$$

The two equations for which thermochemical data are given are rearranged to give a stepwise route equivalent to the formation of zinc sulphate from its elements. Choose or rearrange the given equations so that zinc and sulphur are reactants in the correct quantities and zinc sulphate is the product. Take the first equation as written to have the correct quantities of zinc and sulphur as reactants. Take the second reaction as written so that one mole of zinc sulphate is formed. Finally check oxygen; if all the other substances are balanced it will balance also - if not, an error has been made.

Add the two reactions to show that any substances which appear on the left and right in equal quantities cancel and that the zinc sulphide generated in the first reaction is used up in the second. Add the enthalpies for each process. The sum of these equations where zinc sulphate is formed via zinc sulphide is equivalent to the formation of zinc sulphate from its elements.

$$Zn_{(s)} + S_{(s)} \longrightarrow ZnS_{(s)},\ \Delta H = -206.0\ \text{kJ mol}^{-1}$$

$$ZnS_{(s)} + 2O_{2(s)} \longrightarrow ZnSO_{4(s)},\ \Delta H = -776.8\ \text{kJ mol}^{-1}$$

$$Zn_{(s)} + S_{(s)} + 2O_{2(g)} \longrightarrow ZnSO_{4(s)},\ \Delta H = -982.8\ \text{kJ mol}^{-1}$$

The standard enthalpy of formation of zinc sulphate is therefore –982.8 kJ mol^{-1}.

Worked Example 2

Taking the enthalpy of formation of methane and the standard enthalpies of combustion of hydrogen and carbon as –74.9 kJ mol^{-1}, –285.8 kJ mol^{-1} and –393.5 kJ mol^{-1}, respectively, calculate the standard enthalpy of combustion of methane.

Balanced equations must first be written corresponding to the question posed and the three pieces of thermochemical information supplied.

$$\boxed{CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)},\ \Delta H = ?}$$

$$C_{(s)} + 2H_{2(g)} \longrightarrow CH_{4(g)},\ \Delta H = -74.9\ \text{kJ mol}^{-1}$$

$$H_{2(g)} + {}^{1}/_{2}O_{2(g)} \longrightarrow H_2O_{(l)},\ \Delta H = -285.8\ \text{kJ mol}^{-1}$$

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)},\ \Delta H = -393.5\ \text{kJ mol}^{-1}$$

The three equations for which thermochemical data are given are now rearranged to give a stepwise route equivalent to the direct combustion of methane. Choose or rearrange the given equations so that methane is a reactant and carbon dioxide and water are products in the correct quantities. Reverse the first equation to make methane a reactant. Reverse its enthalpy change also. Double the second reaction so that two moles of water are formed. Double its enthalpy change also. Take the third reaction as it is. Check oxygen - it is usually involved in several equations in combustion processes and excesses on one side cancel with excesses on the other leaving the correct amount if all the other substances are balanced - it should balance automatically - if not, an error has been made.

$$CH_{4(g)} \longrightarrow C_{(s)} + 2H_{2(g)},\ \Delta H = 74.9\ \text{kJ mol}^{-1}$$

$$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)},\ \Delta H = -571.6\ \text{kJ mol}^{-1}$$

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)},\ \Delta H = -393.5\ \text{kJ mol}^{-1}$$

$$CH_{4(s)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)},\ \Delta H = -890.2\ \text{kJ mol}^{-1}$$

Add these equations, ensuring that any substances which appear on the left and right in equal quantities cancel; hydrogen and carbon are generated in some reactions and consumed in others. Add the enthalpies for each process. The sum of these equations is equivalent to the direct combustion of methane. According to Hess's law the enthalpy for burning methane completely in oxygen to form carbon dioxide and water is the same as first changing methane into its elements, then burning the elements in oxygen, making carbon dioxide and water. The standard enthalpy of combustion of methane is therefore the sum of the enthalpies, i.e. –890.2 kJ mol^{-1}.

Exercise 4.3

Q.1. Data tables give the standard enthalpy of combustion of carbon as

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)},\ \Delta H = -393.5\ \text{kJ mol}^{-1}$$

In the conversion of graphite to diamond

$$C_{(s,\ graphite)} \longrightarrow C_{(s,\ diamond)},\ \Delta H = -1.90\ \text{kJ mol}^{-1}$$

What is the enthalpy of combustion for each of the following reactions?

$$C_{(s,\ graphite)} + O_{2(g)} \longrightarrow CO_{2(g)}$$

$$C_{(s,\ diamond)} + O_{2(g)} \longrightarrow CO_{2(g)}$$

Q.2. Is the standard enthalpy of formation of ozone zero? Explain.

Q.3. Given the standard enthalpies of formation of iron(III) oxide and aluminium(III) oxide as –822 kJ mol^{-1} and –1669 kJ mol^{-1}, calculate the standard enthalpy change for the reaction

$$Fe_2O_{3(s)} + 2Al_{(s)} \longrightarrow Al_2O_{3(s)} + 2Fe_{(s)}$$

Is the reaction exothermic?

Q.4. The standard enthalpies of formation of carbon dioxide, water and benzene are –393.5 kJ mol^{-1}, –285.8 kJ mol^{-1} and 82.9 kJ mol^{-1}, respectively. The standard enthalpy of combustion of ethyne is –1299 kJ mol^{-1}. Calculate the enthalpy of formation of ethyne and the enthalpy of polymerisation of ethyne to benzene.

Q.5. Apply Hess's law to calculate the enthalpy change in the following reaction.

$$CO_{2(g)} + H_{2(s)} \longrightarrow CO_{(g)} + H_2O_{(g)}$$

given that

$$2CO_{(g)} + O_{2(g)} \longrightarrow 2CO_{2(g)},\ \Delta H = -565.5\ \text{kJ mol}^{-1}$$

$$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)},\ \Delta H = -571.6\ \text{kJ mol}^{-1}$$

$$H_2O_{(g)} \longrightarrow H_2O_{(l)},\ \Delta H = -43.9\ \text{kJ mol}^{-1}$$

Q.6. Calculate the enthalpy of formation of liquid hydrazine, N_2H_4, from the data below.
The products of hydrazine combustion in oxygen are nitrogen and liquid water. What is the enthalpy of combustion of liquid hydrazine?

$$2NH_{3(g)} + 3N_2O_{(g)} \longrightarrow 4N_{2(l)} + 3H_2O_{(l)},\ \Delta H = -1009.8\ \text{kJ mol}^{-1}$$

$$N_2O_{(g)} + 3H_{2(g)} \longrightarrow N_2H_{4(l)} + H_2O_{(l)},\ \Delta H = -317.0\ \text{kJ mol}^{-1}$$

$$2NH_{3(g)} + {}^1\!/_2O_{2(g)} \longrightarrow N_2H_{4(l)} + H_2O_{(l)},\ \Delta H = -143.0\ \text{kJ mol}^{-1}$$

$$H_{2(g)} + {}^1\!/_2O_{2(g)} \longrightarrow H_2O_{(l)},\ \Delta H = -285.8\ \text{kJ mol}^{-1}$$

Given the following thermodynamic data, calculate the heat of formation of dinitrogen tetroxide.

$$N_2O_{4(g)} \longrightarrow 2NO_{2(g)},\ \Delta H = 24.0\ \text{kJ mol}^{-1}$$

$${}^1\!/_2N_{2(g)} + O_2 \longrightarrow NO_{2(g)},\ \Delta H = -33.9\ \text{kJ mol}^{-1}$$

The lunar module of the Apollo moon missions used liquid hydrazine fuel but the oxidant was N_2O_4. The combustion reaction is

$$N_2H_{4(l)} + {}^1\!/_2N_2O_{4(g)} \longrightarrow {}^3\!/_2N_{2(g)} + 2H_2O_{(l)}$$

What is the heat of combustion of hydrazine in this case?

Q.7. Use the following enthalpy changes

$$2B_{(s)} + 3H_{2(g)} + 3O_{2(g)} \longrightarrow B_2O_{3(s)} + 3H_2O_{(l)},\ \Delta H = -2135.6\ \text{kJ mol}^{-1}$$

$$B_2O_{3(s)} + 3H_2O_{(l)} \longrightarrow 2H_3BO_{3(aq)},\ \Delta H = -17.4\ \text{kJ mol}^{-1}$$

$$H_{2(g)} + {}^1\!/_2O_{2(g)} \longrightarrow H_2O_{(l)},\ \Delta H = -285.8\ \text{kJ mol}^{-1}$$

to estimate the enthalpy of formation of B_2O_3 and the enthalpy change for the reaction

$$2B_{(s)} + 3O_{2(g)} + 3H_{2(g)} \longrightarrow 2H_3BO_{3(aq)}$$

Answers

Q.1. –393.5 kJ mol^{-1}, –395.4 kJ mol^{-1}.

Q.2. The standard enthalpy of formation of ozone is not zero because ozone is not the most common allotrope of oxygen at standard conditions. The energy released or required to convert dioxygen to one mole of ozone at standard conditions is the standard enthalpy of formation of ozone.

$$O_{2(g)} + {}^{1}/{}_{2}O_{2(g)} \longrightarrow O_{3(g)},\ \Delta H = 142 \text{ kJ mol}^{-1}$$

Q.3. –847 kJ mol^{-1}, yes.

Q.4. 226.2 kJ mol^{-1}, –595.7 kJ mol^{-1}.

Q.5. 40.9 kJ.

Q.6. 50.4 kJ mol^{-1}, –622.0 kJ mol^{-1}, –91.8 kJ mol^{-1}, –576.1 kJ mol^{-1}.

Q.7. –1278.2 kJ mol^{-1}, –2153.0 kJ mol^{-1}.

Enthalpies of Reaction from Enthalpies of Formation

Worked Example 1

Using the standard enthalpy of formation data given, calculate the standard enthalpy change for the following reaction.

$$Fe_2O_{3(s)} + 3H_{2(g)} \longrightarrow 2Fe_{(s)} + 3H_2O_{(l)}$$

The standard enthalpies of formation of iron(III) oxide and water are –822 kJ mol^{-1} and –286 kJ mol^{-1}, respectively.

Heat of reaction =

Σ(Enthalpies of formation of products) – Σ (Enthalpies of formation of reactants)

Heat of reaction =

$$\Sigma\Delta H_f \text{ (products)} - \Sigma\Delta H_f \text{ (reactants)}$$

$$= \{3 \times (-286)\} - \{-822\} = -36 \text{ kJ mol}^{-1}$$

Exercise 4.4

Q.1. The white pigment, titanium oxide, used in paints and correcting fluids, is prepared by the following reaction

$$TiCl_{4(g)} + 2H_2O_{(g)} \longrightarrow TiO_{2(s)} + 4HCl_{(g)}$$

Calculate the enthalpy of this reaction, given that the standard enthalpies of formation of titanium(IV) chloride, steam, titanium(IV) oxide and hydrogen chloride are, respectively,

–750 kJ mol^{-1}, –242 kJ mol^{-1}, –912 kJ mol^{-1} and –92.3 kJ mol^{-1}.

Q.2. Calculate the enthalpy change for the reaction

$$4NH_{3(g)} + 5O_{2(g)} \longrightarrow 4NO_{(g)} + 6H_2O_{(g)}$$

given the standard enthalpies of formation of ammonia, nitrogen(II) oxide and steam are, respectively, –46.2 kJ mol^{-1}, 90.4 kJ mol^{-1} and –242 kJ mol^{-1}.

Q.3. The enthalpy change for the following reaction is -34.5 kJ.

$$FeS_{(s)} + H_2SO_{4(l)} \longrightarrow FeSO_{4(s)} + H_2S_{(g)}$$

Given the standard enthalpies of formation of iron(II) sulphide, iron(II) sulphate and hydrogen sulphide are, respectively, -95.1 kJ mol^{-1}, –923 kJ mol^{-1} and –20.6 kJ mol^{-1}, calculate the standard enthalpy of formation of sulphuric acid.

Answers

Q.1. –47.2 kJ.

Q.2. –905.6 kJ.

Q.3. –814 kJ mol^{-1}.

Bond Energies

Bond energy calculations are not examinable at Leaving Certificate but the following worked example would not be beyond the students' understanding and it illustrates several points from different parts of the syllabus.

Worked Example 1

Calculate the energy required to break a single Cl-Cl bond. The Cl-Cl bond energy is 242 kJ mol^{-1}. If the bond is broken by absorbing a photon of sunlight what is the minimum energy the photon must possess? What is the corresponding frequency? Give an example of where breaking the Cl-Cl bond in this way occurs in an organic reaction.

The first question is based on the definition of bond energy. The energy required to break a single bond is Avogadro's number times smaller than the bond energy in kJ mol^{-1}.

$$E = \frac{242}{6 \text{ x } 10^{23}}$$

$$= 4.03 \text{ x } 10^{-22} \text{ kJ}$$

$$= 4.03 \text{ x } 10^{-19} \text{ J}$$

$$= 4 \text{ x } 10^{-19} \text{ J}$$

A single photon must possess enough energy to break a single bond. The corresponding minimum photon energy is therefore 4 x 10^{-19} J.

The energy of a photon is given by $E = hf$, where h is the Planck constant, 6.6 x 10^{-34} J s, and f is the frequency of the light.

$$f = \frac{E}{h}$$

$$= \frac{4 \ x \ 10^{-19}}{6.6 \ x \ 10^{-34}}$$

$$= 6.06 \text{ x } 10^{14} \text{ Hz}$$

$$= 6 \text{ x } 10^{14} \text{ Hz}$$

This frequency falls within the uv range which extends approximately from 5.5 x 10^{16} Hz to 7.5 x 10^{14} Hz. This homolytic fission occurs in the initiation step of the free radical substitution of alkanes.

Exercise 4.5

Q.1. Calculate the energy required to break one N≡N triple bond. The N≡N bond energy is 944 kJ mol^{-1}. If the bond is broken by absorbing electricity during a lightning storm what is the minimum energy absorbed by breaking the bond? State the economic importance of breaking the N≡N bond in this way. Could this bond be broken by uv radiation of frequency in the range 5.5 x 10^{16} Hz to 7.5 x 10^{14} Hz ?

Answer

Q.1. 1.57 x 10^{-21} kJ, 1.57 x 10^{-21} kJ, natural fixation of nitrogen, yes, f = 2.38 x 10^{15} Hz is within the range given.

4.2 Chemical Kinetics

Guide to Graph Drawing

The ability to draw and interpret a graph is an important skill demanded in all of the Science disciplines. In Chemistry, graphs are often used in the area of kinetics, and examination questions on this topic can be designed around graph drawing and graph interpretation. Graph drawing and interpretation may also be required in thermochemistry, to illustrate trends in the periodic table, trends in properties of covalent molecules, for the gas laws, for pH curves, etc. A general approach to drawing graphs is not usually covered in the textbooks and so a guide to practising this skill is given below.

What is a graph?

In its simplest form a graph is a drawing showing the relationship between two quantities by means of a set of points, plotted with respect to two coordinate axes and joined by a curve or line.

The graph is drawn on graph paper, printed with equally spaced, intersecting, horizontal and vertical lines. The sheet of paper represents the plane of two-dimensional space containing two axes, mutually perpendicular, which intersect at a point called the origin. The axes represent the two quantities, between which a relationship is to be shown by the graph. A point, (x_1,y_1), in the plane is located by measuring, from the origin, x_1 units along the horizontal x-axis and y_1 units along the vertical y-axis.

During an experiment, if all but two variable quantities are kept constant, and data are collected on the two variables, the data may be represented on a graph and often a relationship is shown to exist between the two variables. For example, in a thermochemistry experiment, the variables may be temperature and time. To show the relationship between temperature and time as a reaction proceeds, a stopwatch is started by the experimenter a few minutes before the start of a reaction and read at 30 second intervals before, during and for a few minutes after the reaction is complete; the corresponding temperatures are measured. See Figs 1.5 and 1.7, p. 4. Here time is the independent variable and temperature is the dependent variable. The graph will show the relationship between time and temperature before, during and after reaction. All other variables must be kept constant, e.g. temperature of the surroundings, quantities of reactants, etc.

The usefulness of the graph lies in its accuracy and its ease of use. To ensure accuracy, the data must be recorded with care, the points must be plotted with care and the curve which best represents them drawn with care. To ensure ease of use, the graph must be neat and free of clutter, e.g. unnecessary figures, unerased errors, etc. Compare a graph to any measuring instrument used in the laboratory, a ruler, a protractor, a balance, etc. The scales of the ruler, the protractor, the balance, etc., are accurately marked, neat, the scale is marked for the convenience of the user not the instrument maker, and no marks from any previous experiments are left on the instrument. Students should be encouraged to understand the purpose of drawing graphs and should have an appreciation of the need for accuracy and of neatness for the sake of accuracy.

What is the function of a graph?

A graph is a measuring instrument prepared from data recorded with care during an experiment.

It displays the data pictorially, e.g. the relationship between temperature and time in a thermochemistry experiment, first ionisation energies of the elements *versus* atomic number, etc.

It allows data within the range of the graph to be read from the graph accurately, e.g. a pH curve for an acid-base neutralisation reaction can be used to read the volume of base added to bring the pH to a certain value or to give the volume of base added for neutralisation, etc.

It allows predictions to be made about experimental results outside the range of the data recorded during an experiment, e.g. a graph of molecular masses versus boiling points for a homologous series can be extended to predict the boiling point of a high molecular mass member of the series; this is called extrapolation.

It allows a mathematical relationship to be established between two variables in an experiment, e.g. the shape of a graph of change in concentration of a reactant *versus* time can establish the order of that reaction with respect to that reactant.

Accuracy

In principle, a graph is more accurate than any of the individual points used to draw it. Every point on a graph represents two pieces of recorded data. Each of these pieces of recorded data contains an experimental error. Experimental errors include human errors associated with taking readings, e.g. from a burette scale. Experimental errors also include instrumental errors, e.g. in the digital readout of a pH meter there should be no error in reading the pH but the degree of accuracy of the instrument itself may have introduced an error into the reading. Thirdly, experimental errors include errors associated with rounding off a figure, e.g. most molecular masses are rounded off to whole numbers and so molarities contain small errors associated with rounding off in this way. Most errors are random in the sense that in an experiment it is usually equally probable to introduce an error which makes a reading too large and one which makes a reading too small. Therefore each point on the graph is to some extent unreliable and perhaps should be displaced a little to the left or right and/or above or below where it is actually plotted. Experimental errors in data can be reduced by taking a number of readings and averaging. The errors tend to cancel since the readings which are too large compensate for those which are too small. The greater the number of points averaged the more reliable the result. Experimental errors in data can also be reduced by drawing a straight line or smooth curve so that the line or curve passes through or as close as possible to as many points as possible. Since the line or curve contains an infinite set of points the line or curve represents a result with errors eliminated even more effectively than averaging a finite number of pieces of data.

Similarly, any datum read from the graph is more accurate than recording the information in isolation, e.g. a graph of Boyle's law can be used to give the volume of a gas at a particular pressure more accurately than simply reading the volume of the gas at the pressure in question.

Guidelines for drawing graphs

1. Use only A4 graph paper for practice as this is the size supplied for State examinations. Use graph paper with pale blue or pale green print rather than grey print as pencil marks show more clearly. Standard A4 graph paper has 90 x 2 mm or 180 x 1 mm spaces along the short side and 140 x 2 mm or 280 x 1 mm spaces along the long side.

2. Use a sharpened HB pencil and resharpen as necessary. Blunt pencils make inaccurate thick lines. A transparent ruler and an eraser are required. Allow for the thickness of the pencil when drawing lines, curves and points. Do not use a biro or a felt-tip. In most hands, a pencil is the most controllable drawing instrument and errors can be erased. If the eraser is used, the error should be removed completely.

3. For graphs of experimental work, it is normally the practice to plot the independent variable along the *x*-axis and the dependent variable along the *y*-axis. For examination questions, instructions are often given as to how to plot the variables; the quantity mentioned first in the instructions is plotted along the *y*-axis.

4. There are three important things to bear in mind when choosing scales.

   a) Choose the scales so that the points fill the page, i.e. the first point is near the top left and the last is near the bottom right or the first point is near the bottom left and the last is near the top right. If most of the page is used there is a smaller degree of error in plotting each point and consequently in reading information from the graph.

   b) Make sure that the scale chosen makes it quick and easy to plot the data and read the graph.

   c) Sometimes the data for one variable make a scale which conveniently fits the short side of the graph sheet, 90 or 180 boxes, better than the long side, 140 or 280 boxes, so try plotting the data both ways.

   A good compromise must be made between these three considerations and practice is required to become skilful in making a good compromise quickly.

5. It is not advisable to break the scale, i.e. start at the origin and then interrupt the scale and proceed with a different scale. This can lead to errors.

6. Draw solid pencil lines to mark the axes. Use the ruler carefully to ensure the pencil lines coincide exactly with printed lines on the graph paper and are perfectly vertical and horizontal. Label each axis with the quantity it represents divided by the units used to measure that quantity, e.g. time/minutes or volume/ml or concentration/mol l^{-1}, etc.

Label the axes with a *few* numbers to indicate the progression of the scales.

7. Should the origin appear on the graph or not?

If data are supplied, or implied, corresponding to (0,0), clearly the origin itself is a point on the graph. For example, the volume of gas produced is 0 ml at zero time in many rates of reaction questions and it would be incorrect not to show the origin on the graph.

If, however, the data supplied do not refer to the origin and if the other data are greatly above zero values for the variables in question it is appropriate to omit the origin. For example, if data were given for reaction times for a particular chemical change at different temperatures in a school laboratory, and all the times were well above zero seconds and of course all the temperatures would be well above zero kelvin, it could be safely assumed that the reaction time at zero kelvin is not of interest. Here it would be inappropriate to show the origin on the graph as this would result in all the data being compressed in a very small space and lowered in significance on the graph sheet. This would result in greater inaccuracy in plotting the data, drawing the curve and reading the graph.

However, it is sometimes necessary to extrapolate a graph, that is, to extend the curve beyond the data points and estimate the relationship between the two variables outside the experimental range shown on the graph. Since temperatures near zero kelvin are inaccessible in practice, extrapolation of the data for reaction times at different temperatures could give the expected reaction time at a very low temperature, e.g. 10 K. In this case the origin should be shown on the graph since the point to which one must extrapolate lies so near the origin. Note, however, that in order to extrapolate safely, one must consider whether the relationship between the two quantities shown on the graph applies to the conditions where we want to predict data. For example, at very low temperatures, substances may have frozen and may not react at all.

If it is necessary to prove that the variables under consideration are proportional to each other, a graph which is a straight line through the origin is required and the origin must appear on the graph.

8. The points should be located accurately with reference to the scales and marked neatly with a dot surrounded with a small circle, the centre of the dot itself marking the **exact** position of the point. Remember points are dimensionless and therefore should not appear on paper as blobs. Do not clutter up the scales with the coordinates of the points plotted. This may be convenient when plotting the graph but it makes it very untidy and more difficult to read and use subsequently. In general, a minimum of six points are required to draw an acceptable graph.

9. A random scatter of points indicates two unrelated quantities, e.g. the cost of the label on a chemical versus the density of the chemical are obviously unrelated and would give a scatter of data.

Points falling in a pattern, a straight line or a clear curve, indicate a mathematical relationship between the two variables.

A horizontal line indicates that the variable represented by the y-axis is a constant with respect to changes in the variable represented by the x-axis.

A vertical line indicates that the variable represented by the x-axis is a constant with respect to changes in the variable represented by the y-axis.

A straight line graph through the origin indicates that the two quantities are proportional to each other, e.g. pressure of a fixed mass of gas versus inverse of its volume.

A straight line, with slope m, which does not pass through the origin indicates that the quantities are related by the formula

$$y = mx + c$$

where c is the intercept on the y-axis.

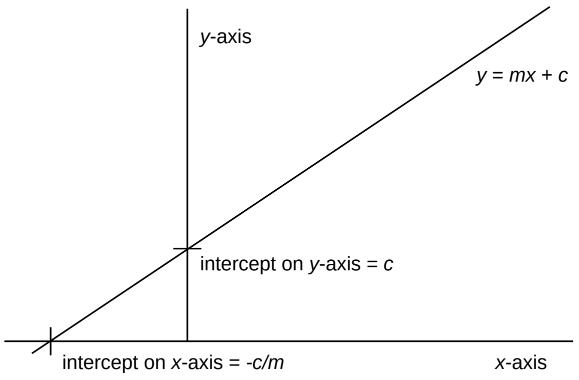

Fig. 4.1 *Graph of quantities x and y related by* $y = mx + c$

An example of this type of graph is obtained when the volume of a fixed mass of gas is measured at various temperatures on the Celsius scale. The graph of volume versus temperature (˚C) is a straight line with an intercept on the positive part of the volume axis. If this graph is extrapolated until the line cuts the x-axis, the corresponding temperature is -273 ˚C. The volume of the gas at this temperature is zero. Data for this situation cannot be obtained from experiment since all real gases liquefy at low temperatures but the graph provides a good discussion of the volume of a gas at -273 ˚C, the definition of absolute zero, etc.

If the points are arranged in a line, use a transparent ruler to find the best line through them. This line does not necessarily touch every single point, or indeed any point at all, but should pass through or as close as possible to as many points as possible.

If the points may be represented by a smooth curve, then a definite mathematical relationship between the two variables shown on the graph is indicated. Possibilities are

$$y \propto x^2,\ y \propto 1/x,\ y \propto \ln x,\ y \propto \sqrt{x}, \text{ etc.}$$

The actual relationship is verified by plotting graphs of respectively

y versus x^2, y versus $1/x$, y versus ln x, y versus $\sqrt{x}$, etc.

The graph should be a straight line if the relationship holds.

If the points represent a curve, they should be joined by a smooth curve, drawn freehand or using a French curve or a flexicurve. The curve does not necessarily touch every single point but should pass through or as close as possible to as many points as possible, i.e. give a smooth curve and remain faithful to the data. Note that there are various mathematical methods and computer programmes for finding the best fit between points on a graph and a line or curve.

10. The graph should be titled. In an examination paper, it is quite probable that only one question requires information to be displayed graphically and it is unambiguous what the graph represents. But for general school work, a graph produced might be one of a number of graphs for a series of related experiments, or one of several graphs drawn during a year for different experiments, or a graph drawn in answer to part of a question. Therefore, since a graph is seldom drawn in isolation from an experiment or an exercise, every graph should be labelled.

An example of how a graph could be titled is ‘Volume of gas produced *versus* time’ or ‘Volume of gas produced against time’, both of which titles mean that the graph represents the relationship between the volume of gas produced, which is displayed on the y-axis and time, which is displayed on the x-axis. Alternatively, the graph could be given a title corresponding to the experiment it was associated with, e.g. ‘Temperature change during exothermic neutralisation reaction of sodium hydroxide (0.1 M) and hydrochloric acid (0.1 M)’. The graph could be given a title corresponding to the question it was associated with in an examination or an exercise, e.g. Question 6 (b).

11. To draw a tangent to a curve, the student should remember that a tangent makes contact with the curve at a single point. Place the transparent ruler above the curve so that, allowing for the thickness of the pencil, it just touches the curve. The two angles marked α should be equal.

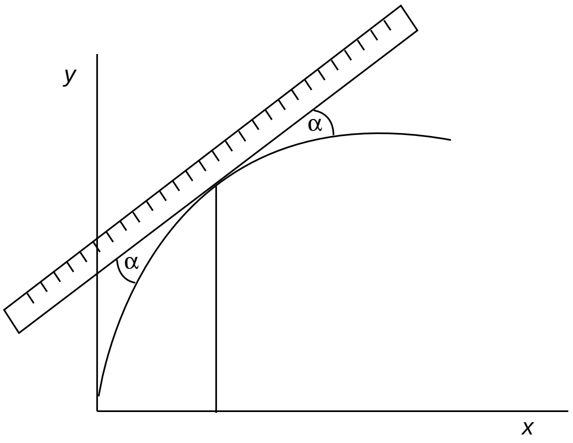

Fig. 4.2 *Drawing the tangent to a curve*

Another method is to place a small plane mirror at the point where the tangent is to be drawn and rotate it until there is no break between the curve and its image in the mirror. The mirror is then perpendicular to the curve at that point.

12. To find the slope, m, of a straight line graph or the slope of the tangent to a curve, there are two methods.

Method A

Choose two points on the line as far apart as possible, preferably points which coincide with the grid of the graph paper. Read the coordinates of these points from the scales, (x_1,y_1) and (x_2,y_2). Use the coordinate geometry formula for the slope of the line joining two points:

$$m = \frac{\Delta y}{\Delta x} = \frac{y_2 - y_1}{x_2 - x_1}$$

There will be the least error in the value of the slope when there is least error in Δy and Δx. Hence the two points chosen to calculate the slope should be as far apart as possible so that percentage errors in reading their coordinates are minimised. The units for the slope are the units of the quantity on the y-axis/ the units of the quantity on the x-axis.

The points used to calculate the slope and their coordinates should be marked on the graph but the calculation of the slope should not be carried out on the graph paper.

Method B

It is possible to find the slope of a line from the angle, θ, the line makes with the positive direction of the x-axis.

However, there is a serious complication in using this method to find the slope: the choice of scales will determine the size of the angle θ, hence tan θ, and hence the value for the slope of the graph. The method is valid only where the scales are chosen such that the same scale is used to represent 1 unit of each of the two quantities represented on the graph.

13. To read information from a graph, one usually has one piece of data for reference and is asked to find the corresponding value of the second variable. Find the position corresponding to this piece of data on the x-axis (or y-axis). Draw a perfectly vertical (or horizontal) line to meet the line or curve of the graph. Then from this point of intersection, draw a perfectly horizontal (or vertical) line to the y-axis (or x-axis). Read the corresponding data from this axis.

14. The instruction ‘draw’ means plot points accurately on graph paper. The instruction ‘sketch’ means give an outline of the shape of the graph; it need not appear on graph paper although it often makes the task easier to use graph paper. The axes should be labelled with the quantities they represent in each case but the unit for each quantity need be only included in the case of ‘sketch’ if suitable information is provided.

Drawing and Interpreting Trends in Kinetics Graphs

Worked Example 1

Oxygen gas can be prepared in the laboratory by the catalytic decomposition of hydrogen peroxide. In an experiment, 2.5 g of a manganese dioxide catalyst were added to 15 ml of 3% (w/v) hydrogen peroxide and the volume of oxygen liberated was measured at regular time intervals at room temperature and pressure. Molar volume at room temperature and pressure is 24 l. The results were as follows

Time/min	0	2	4	6	9	13	18	22	26
Volume/ml	0	32	56	76	105	126	137	140	140

Table 4.1

(a) Using graph paper, plot a graph of volume of oxygen evolved *versus* time.

(b) Calculate the instantaneous rate of the reaction at 7 minutes in ml/minute. Express this rate in moles per second.

(c) How many moles of oxygen had been produced after 5 minutes? After what time had 1.25×10^{-3} moles of oxygen been evolved?

(d) Write a balanced equation for the reaction. Calculate the number of moles of hydrogen peroxide used in the reaction and hence the number of moles and the volume of oxygen expected to be produced at room temperature and pressure. Compare with the volume of oxygen actually produced.

(a) See Fig. 4.3 on graph paper (p. 85).

(b) Taking the coordinates of two points on the tangent drawn to the curve at seven minutes, calculate the slope of the tangent as follows.

$$m = \frac{\Delta y}{\Delta x}$$

$$= \frac{y_2 - y_1}{x_2 - x_1}$$

$$m = \frac{150 - 46}{14.8 - 1.6}$$

$$= \frac{104}{13.2}$$

$$= 7.88$$

Slope of tangent to curve at 7 minutes = 7.88 ml min^{-1}

Instantaneous rate of reaction at 7 minutes = 7.9 ml min^{-1}

Molar volume at room temperature and pressure is 24 l or 24 000 ml. Therefore, using a ratio:

7.9 ml	:	x mol
24000 ml	:	1 mol

$$x = \frac{7.9}{24000}$$

$$= 3.29 \times 10^{-4}$$

In one second one sixtieth of the quantity of gas evolved in one minute is produced.

$$\frac{3.29 \times 10^{-4}}{60} = 5.48 \times 10^{-6} \text{ mole oxygen/second}$$

Instantaneous rate of reaction at 7 minutes = 5.5×10^{-6} mol s^{-1}

(c) A vertical line at time = 5 minutes to intercept the graph and then a horizontal line to the *y*-axis gives the volume of oxygen produced after 5 minutes as 66 ml.

Molar volume at room temperature and pressure is 24 l. Therefore, using a ratio

66 ml	:	x moles
24000 ml	:	1 mole

$$x = \frac{66}{24000}$$

$$= 2.75 \times 10^{-3} \text{ mol}$$

The quantity of oxygen produced after 5 minutes is 2.8×10^{-3} mol

Use another ratio to convert 1.25×10^{-3} mole to the corresponding volume at room temperature and pressure.

1.25×10^{-3} mole	:	x ml
1 mole	:	24000 ml

$$x = \frac{1.25 \times 10^{-3} \times 24000}{1}$$

$$= 30$$

A horizontal line at volume = 30 ml to intercept the graph and then a vertical line to the *x*-axis gives the time at which 30 ml (or 1.25 x 10^{-3} mol) of oxygen is produced as 1.8 minutes.

(d) $H_2O_2 \longrightarrow H_2O + {}^1\!/_2O_2$

In the reaction 15 ml of 3% (w/v) hydrogen peroxide were consumed. The expression *x*% weight by volume means that there are *x* grams of a substance in 100 ml of solution. The mass of hydrogen peroxide used therefore was

$$\frac{15 \times 3}{100} = 0.45 \text{ g}$$

The number of moles of hydrogen peroxide used is calculated using the formula:

$$n = \frac{m}{m_r}$$

$$n = \frac{0.45}{34}$$

$$= 0.013 \text{ mol } H_2O_2$$

The ratio of hydrogen peroxide to oxygen in the balanced equation is consulted.

H_2O_2	:	O_2
1	:	0.5
0.013	:	0.0065

Therefore 6.5 x 10^{-3} mol of oxygen gas are expected to be produced in the reaction. Using a ratio to give the corresponding volume:

6.5 x 10^{-3} mole	:	*x* ml
1 mole	:	24000 ml

$$x = \frac{6.5 \times 10^{-3} \times 24000}{1}$$

$$= 156$$

In the experiment the volume of gas expected to be produced was 156 ml but the observed volume was only 140 ml. A possible explanation is that hydrogen peroxide is unstable and it could have partially decomposed upon storage. The concentration could have been below the 3% (w/v) on which the calculated yield of oxygen was based.

Worked Example 2

Carbon dioxide gas is produced by the action of an acid on a carbonate or hydrogencarbonate. In an experiment, 2.5 g of calcium carbonate chips were added to 35 ml of 0.6 M hydrochloric acid in a conical flask and the quantity of carbon dioxide liberated was measured at regular time intervals at room temperature and pressure by measuring the loss in mass of the conical flask and contents. A cotton wool plug was used to allow gas, but not spatters of liquid, to escape from the flask. Molar volume at room temperature and pressure is 24 l. The results are given in Table 4.2.

Time/min	0	1	2	3	4	5	7	9	11	13	14
Mass/g	156.64	156.48	156.40	156.34	156.31	156.28	156.25	156.23	156.22	156.21	156.21

Table 4.2

Click here to view Figure 4.3
Volume O2 Versus Time

(a) Explain how the first reading of mass was obtained.

(b) Using graph paper, plot a graph of loss in mass *versus* time.

(c) Calculate the instantaneous rate of the reaction at 3 minutes in g min^{-1}. Express this rate in moles s^{-1}.

(d) Calculate the average rate over the first 3 minutes. Express this rate in mol s^{-1}.

(e) What is the rate of reaction at 14 minutes?

(f) At what time is the reaction half complete?

(a) The first reading was obtained by adding the mass of the calcium carbonate, weighed separately, to the mass of the hydrochloric acid and flask.

(b) First calculate loss in mass at each time interval. See Table 4.3, p. 87 and Fig. 4.4, p. 88.

(c) Taking the coordinates of two points on the tangent drawn to the curve at three minutes, calculate the slope of the tangent as follows

$$m = \frac{\Delta y}{\Delta x}$$

$$= \frac{y_2 - y_1}{x_2 - x_1}$$

$$m = \frac{0.43 - 0.20}{6.0 - 0.8}$$

$$= \frac{0.23}{5.2}$$

$$= 0.044 \text{ g min}^{-1}$$

Slope of tangent to curve at 3 minutes = 0.044 g min^{-1}

Instantaneous rate of reaction at 3 minutes = 0.044 g min^{-1}

Relative molecular mass of carbon doxide is 44. Therefore, using a ratio

0.044 g	:	*x* moles
44 g	:	1 mole

$$x = \frac{0.044}{44}$$

$$= 1.0 \times 10^{-3}$$

In one second one sixtieth of the quantity of gas evolved in one minute is produced.

$$\frac{1 \times 10^{-3}}{60} = 1.67 \times 10^{-5} \text{ mole } CO_2\text{/second}$$

Instantaneous rate of reaction at 3 minutes = 1.7 x 10^{-5} mol s^{-1}

(d) The average rate of reaction is the total mass of carbon dioxide evolved divided by the corresponding time.

$$\text{Average rate at 3 minutes} = \frac{0.3}{3}$$

$$= 0.1 \text{ g } CO_2\text{/min}$$

Relative molecular mass of carbon dioxide is 44. Therefore, using a ratio

0.1 g	:	*x* moles
44 g	:	1 mole

$$x = \frac{0.1}{44}$$

$$= 2.27 \times 10^{-3}$$

In one second one sixtieth of the quantity of gas evolved in one minute is produced.

$$\frac{2.27 \times 10^{-3}}{60} = 3.79 \times 10^{-5} \text{ mole } CO_2\text{/second}$$

Average rate of reaction over the first 3 minutes = 3.8 x 10^{-5} mol s^{-1}

Time/min	0	1	2	3	4	5	7	9	11	13	14
Mass/g	156.64	156.48	156.40	156.34	156.31	156.28	156.25	156.23	156.22	156.21	156.21
Loss in mass/g	0.00	0.16	0.24	0.30	0.33	0.36	0.39	0.41	0.42	0.43	0.43

Table 4.3

(e) The rate of reaction at 14 minutes is zero. The tangent to the curve is parallel to the *x*-axis and therefore has zero slope. No further gas is evolved; the reaction is complete.

(f) The reaction is complete when 0.43 g of carbon dioxide are lost. Therefore the reaction is half complete when 0.215 g of carbon dioxide are evolved. A horizontal line at mass lost = 0.215 g to intercept the graph and then a vertical line to the *x*-axis gives the time at which 0.215 g of carbon dioxide is produced as 1.6 minutes.

Worked Example 3

The rate of reaction of sodium thiosulphate with hydrochloric acid is proportional to the sodium thiosulphate concentration, all other variables kept constant. Use the following results to draw a graph of concentration versus rate to confirm this statement.

$Na_2S_2O_3$ conc./mol l^{-1}	0.20	0.16	0.14	0.12	0.10	0.08	0.06	0.04
Time, *t*/s	31	37	44	52	60	78	100	160

Table 4.4

The rate of a reaction is inversely proportional to the reaction time, *t*. A graph of concentration of sodium thiosulphate versus 1/*t* should be a straight line through the origin if the quantities are proportional. Extend the table to show the reciprocals of reaction times.

$Na_2S_2O_3$ conc./mol l^{-1}	0.20	0.16	0.14	0.12	0.10	0.08	0.06	0.04
Time, *t*/s	31	37	44	52	60	78	100	160
t^{-1}/s^{-1}	0.032	0.027	0.023	0.019	0.017	0.013	0.010	0.006

Table 4.5

See Fig. 4.5 on graph paper, p. 89.

Note that the points form a straight line through the origin confirming that rate of reaction of sodium thiosulphate and hydrochloric acid is proportional to the sodium thiosulphate concentration.

Worked Example 4

The effect of temperature on a reaction time, *t*, all other variables kept constant, was investigated. The results are shown in Table 4.6. Draw a graph of rate of reaction versus temperature. What is the time for reaction at 65 ˚C and the estimated reaction time at 110 ˚C ?

Temperature/˚C	10	20	40	60	80	90
Time, *t*/s	250	141	100	51	33	24

Table 4.6

A graph of 1/*t* versus temperature is required. Extend the table to show the reciprocals of reaction times. When planning the graph make allowance on the scales for extrapolating the graph.

Temperature/˚C	10	20	40	60	80	90
Time, *t*/s	250	141	100	51	33	24
t^{-1}/s^{-1}	0.004	0.007	0.010	0.020	0.030	0.042

Table 4.7

See Fig. 4.6 on graph paper p. 90.

The reaction time at 65 ˚C can be deduced from the graph. Draw a vertical line from 65 ˚C to intercept the graph. Draw a horizontal line to the

Click here to view Figure 4.4
Loss in mass of CO2 versus time

Click here to view Figure 4.5
NaS2O3 concentration versus
reciprocal of reaction time

Click here to view Figure 4.6
Reciprocal of reaction time versus
temperature

y-axis. The corresponding rate is 0.022 s^{-1}. Thus the corresponding reaction time is 1/ 0.022 = 45 s.

The reaction time at 110 ˚C can be deduced from the graph by first extrapolating the curve and then drawing a vertical line from 110 ˚C to intercept the graph. Draw a horizontal line to the y-axis. The corresponding rate is 0.071 s^{-1}. Thus the corresponding estimated reaction time is 1/ 0.071 = 14 s.

Worked Example 5

Sketch a graph a similar to that shown in Fig. 2.2 to represent a reaction which has an equation of the form

$$2A \rightarrow C + 3D$$

and where the initial concentration of A is 2 moles per litre and the reaction is complete after 3 minutes. Mark the half-life on the graph and estimate its value.

There is no need for graph paper since the instruction was 'sketch'. With a ruler, draw a horizontal line marked off in three approximately equal sized portions to represent time in minutes. Label it time/minutes and mark the scale. Having consulted the balanced equation draw, with a ruler, a vertical line marked off in three approximately equal sized portions to represent concentration in moles per litre. Label it concentration/mol l^{-1} and mark the scale. Sketch smooth curves to represent reactant A decreasing from an initial concentration of 2 mol l^{-1} to zero at three minutes and products C and D increasing from zero to final concentrations of 1 mol l^{-1} and 3 mol^{-1}, respectively. The half-life is the time corresponding to 1 mol of A consumed. Start with 1 mol on the vertical axis, draw a horizontal line to intercept the curve for A, then a vertical line to the y-axis. Estimate this time from the scale.

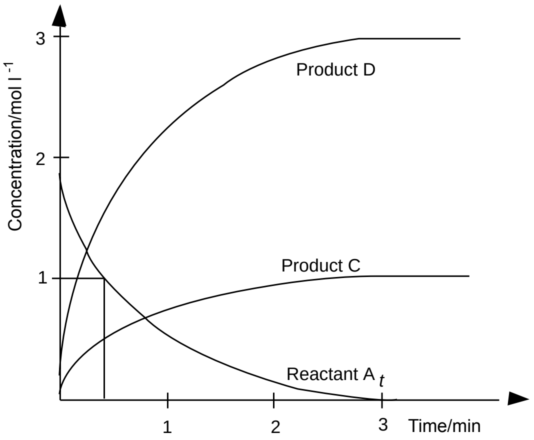

Fig. 4.7 *Change in reactant and product concentrations with time*

$t_{1/2}$ is 0.4 minutes approximately.

Worked Example 6

The rates of change of mass of ethanol in the body fluids for a woman and a man are shown in Fig. 4.8. Each has consumed a certain amount of alcohol and in each case a five-hour period has elapsed before the alcohol consumed has been decomposed completely. (a) How many units of alcohol did each person consume? (b) Assuming the alcohol was consumed as wine, how many glasses of wine did each person drink? (c) How much alcohol was decomposed in each case in the first hour immediately after drinking? (d) How much alcohol was decomposed in each case in the fifth hour after drinking? (e) Was either or both at any stage 'over the limit' for driving? If so calculate the maximum body fluid alcohol content in mg/100 ml.

The rates of alcohol decomposition in the body are 5.3 g per hour for women and 7.3 g per hour for men. One alcohol unit is 8 g ethanol. A glass of wine is equivalent to one unit. The current legal maximum permitted alcohol concentration in blood to be in charge of a motor vehicle in Ireland is 80 mg per 100 ml. The average body fluid distribution volumes for women and men are, respectively, 28 l and 40 l.

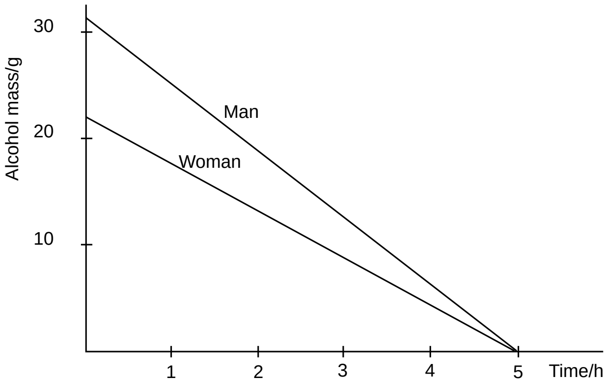

Fig.4.8 *Rates of change of ethanol in body fluids*

(a) From the *y*-axis, the initial alcohol masses for the man and woman were, respectively, 36.5 g and 24.0 g. The man therefore consumed 36.5/8 = 4.56 units and the woman 24.0/8 = 3.0 units of alcohol.

(b) A glass of wine is one unit and therefore the man drank a little over 4.5 glasses of wine and the woman drank 3.0 glasses of wine.

(c) In one hour 7.3 g of alcohol are decomposed in the man's body. In one hour 5.3 g of alcohol are decomposed in the woman's body.

(d) In the fifth hour 7.3 g of alcohol are decomposed in the man's body. In the fifth hour 5.3 g of alcohol are decomposed in the woman's body. The rate is constant.

(e) The current legal maximum permitted alcohol concentration in blood to be in charge of a motor vehicle in Ireland is 80 mg per 100 ml. The body fluid distribution volumes for women and men are, respectively, 28 l and 40 l.

A person over the limit has a minimum of 80 mg alcohol per 100 ml blood, i.e 0.08 g per 100 ml or 0.8 g per l.

In the case of a man with body fluids of 40 l this gives a total alcohol 'content' of

0.8 x 40 = 32 g alcohol

This puts the man over the limit. The man had 36.5 g of alcohol. Per litre of body fluids this is 36.5/40 = 0.9125 g l^{-1}. In 100 ml of body fluids this is 0.9125 g/10 = 0.09125 g/100 ml. Expressed in mg/100 ml the man's blood alcohol reading was at a maximum of 91.25 mg/100 ml.

In the case of a woman with body fluids of 28 l at the 'limit' she would have a total alcohol 'content' of

0.8 x 28 = 22.4 g alcohol.

This puts the woman over the limit as she has consumed 24 g alcohol.

Exercise 4.6

Q. 1. When manganese dioxide catalyst is added to hydrogen peroxide solution, oxygen gas is produced. The gas was collected over water in a graduated cylinder over a 30 minute period. The volume of gas collected was noted at intervals over the duration of the experiment and the results are given in Table 4.8 below.

Time/min	0	2	4	6	9	12	18	24	30	36
Volume/ml	0	57	78	95	107	113	117	119	120	120

Table 4.8

(a) Plot a graph of volume of oxygen produced *versus* time.

(b) Calculate the average rate and the instantaneous rate of reaction after 8 minutes.

(c) Calculate, from the graph, the total number of moles of oxygen gas produced during the experiment, assuming that molar volume at room temperature and pressure is 24 l.

(d) At what time is the reaction half complete?

Q. 2. When sulphuric acid is added to excess zinc turnings, hydrogen gas is produced. The rate of production of hydrogen gas was monitored by collecting the gas over water in a graduated cylinder over a period of 18 minutes. The following results were obtained.

Time/min	0	2	4	6	8	10	12	15	18
Volume/ml	0	100	152	190	218	234	241	245	245

Table 4.9

(a) Plot a graph of the volume of hydrogen produced *versus* time.

(b) Calculate the insantaneous rate in moles per second at 7 minutes.

(c) Write a balanced equation for the reaction. Calculate the number of moles of hydrogen gas produced when the reaction is complete and hence the molarity of the sulphuric acid used, if the volume of acid used was 50 ml.

(d) Sketch on the graph the curve which would be expected if the same volume of sulphuric acid of half the original concentration were used.

Q. 3. Draw a diagram similar to that shown in Fig. 2.2 to represent the rates of reaction of sodium thiosulphate and hydrochloric acid and the rate of formation of sodium chloride according to the equation:

$$Na_2S_2O_{3(aq)} + 2HCl_{(aq)} \longrightarrow 2NaCl_{(aq)} + SO_{2(g)} + S_{(s)} + H_2O_{(l)}$$

Let the initial concentration of sodium thiosulphate be x and the time taken for the reaction to go to completion under the given conditions be t. Let the initial concentration of hydrochloric acid be $2x$. Show $t_{1/2}$ on the diagram.

Q. 4 The graph, A, in Fig. 4.9 shows the variation in the volume of oxygen collected with time as hydrogen peroxide is catalytically decomposed over manganese dioxide.

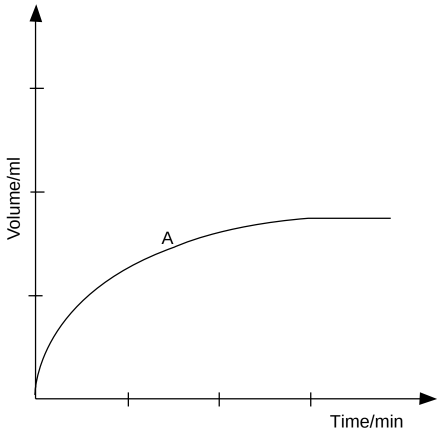

Fig. 4.9 *Variation in the volume of oxygen collected with time*

Sketch on the graph other curves to show how the graph would appear if (i) the temperature were increased, (ii) the temperature were decreased, (iii) the same volume of hydrogen peroxide were used but the concentration were halved, (iv) the same volume of hydrogen peroxide were used but the concentration were doubled and (v) less catalyst were used.

Q. 5. The rates of change of mass of ethanol in the body fluids for a woman and a man are shown in the diagram, Fig. 4.10. The average rates of alcohol decomposition in the body are 5.3 g per hour for women and 7.3 g per hour for men. One alcohol unit is 8 g ethanol. A pint of beer is equivalent to two units. The current legal maximum permitted alcohol concentration in blood to be in charge of a motor vehicle in Ireland is 80 mg per 100 ml. The body fluid distribution volumes for women and men are, respectively, 28 l and 40 l.

Both persons in this case have consumed the same amount of alcohol at time zero and in each case data for the alcohol decomposition over a five-hour period are given.

(a) How many units of alcohol did each person consume?

(b) Assuming the alcohol was consumed as beer, how many pints of beer did each person drink?

(c) How long in each case before all the alcohol consumed is decomposed?

(d) Calculate how long after time zero before each person is at the legal maximum level of alcohol in body fluids for taking charge of a motor vehicle.

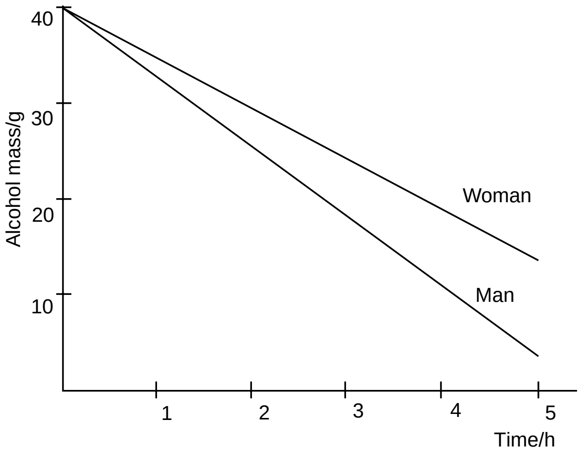

Fig. 4.10 *Rates of change of ethanol concentration in body fluids*

Answers

Q. 1. (a) See Fig. 4.11 on graph paper (p. 95), (b) average rate = 13 ml min^{-1}; instantaneous rate = 3.4 ml min^{-1}, (c) 5 x 10^{-3} mol (d) 2.1 min.

Q. 2. (a) See Fig. 4.12 on graph paper (p. 96), (b) instantaneous rate = 13.14 ml min^{-1} = 9 x 10^{-6} mol s^{-1}, (c)

$$H_2SO_{4(aq)} + Zn_{(s)} \longrightarrow ZnSO_{4(aq)} + H_{2(g)}$$

0.01 mol hydrogen gas produced, 0.2 M sulphuric acid.

Q. 3.

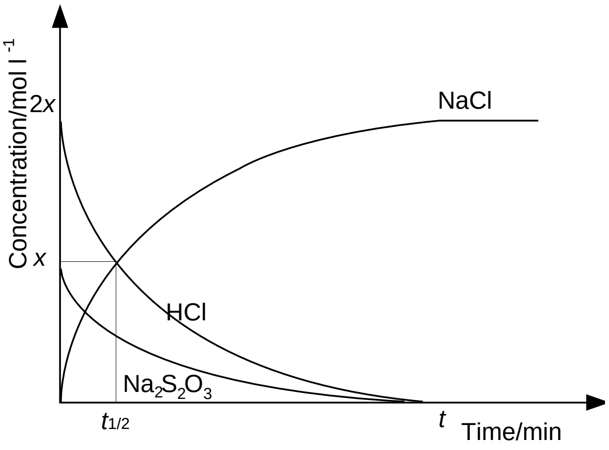

Fig. 4.13 *Change of concentrations as reaction proceeds* Q. 4.

Q. 4.

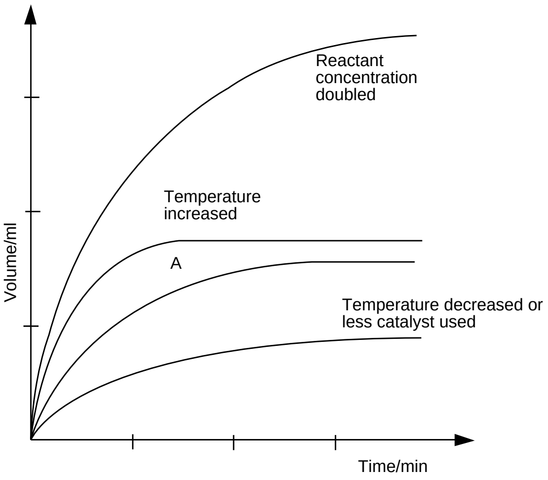

Fig. 4.14 *Effect on rate of reaction of a catalyst or change of temperature or concentration*

Q 5. (a) 5 units of alcohol each, (b) 2.5 pints of beer each, (c) 7.55 hours for the woman and 5.48 hours for the man, (d) From Fig. 4.15 (p. 97) and/or by calculation 3.3 hours for the woman and 1.1 hours for the man.

Click here to view Figure 4.11
Volume of O2 versus time

Click here to view Figure 4.12
Volume of H2 versus time

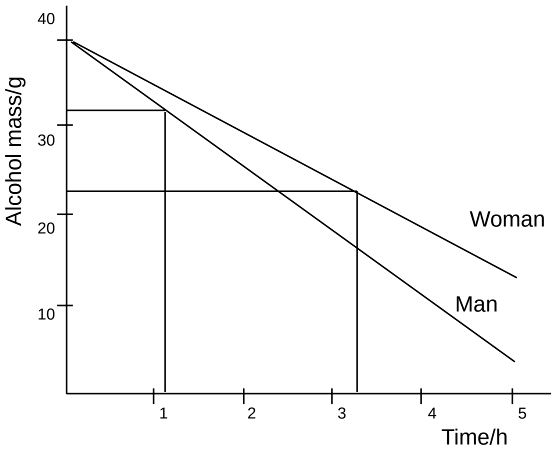

Fig. 4.15 *Times elapsed until legal limit is reached after alcohol consumption*

4.3 Chemical Equilibrium

Calculating K_c from Experimental Data

Worked Example 1

Two moles of dinitrogen tetroxide were sealed into a 2 litre vessel. The dinitrogen tetroxide decomposes into nitrogen dioxide which in turn dimerises to give dinitrogen tetroxide again and an equilibrium is set up between the two reactions.

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

Calculate the equilibrium constant for the reaction at 293 K if the vessel was found to contain 0.76 moles of dinitrogen tetroxide at that temperature.

A table is often used to lay out the solution to this type of equilibrium problem. The balanced equation is written at the top of the table and entries are made in columns under each substance in the balanced equation for the number of moles of the substance present initially, the change in this number of moles as equilibrium is established, the number of moles at equilibrium and the molar concentration at equilibrium. In Table 4.10 the information given in the question is entered, i.e. the number of moles of dinitrogen tetroxide and nitrogen dioxide present initially and the number of moles of dinitrogen tetroxide present at equilibrium are filled in.

Balanced equation	$N_2O_{4(g)}$ $\rightleftharpoons$	$2NO_{2(g)}$
No. moles present initially	2	0
Change in no. moles as equilibrium is established		
No. moles present at equilibrium	0.76	
Molar concentration at equilibrium		

Table 4.10

When equilibrium is reached there will have been a net decrease in the number of moles of dinitrogen tetroxide and a net increase in the number of moles of nitrogen dioxide present. In the third row of the table the number of moles of dinitrogen tetroxide consumed is designated $-x$. Using the *balanced* equation at the top of the table as a guide, the increase in the number of moles of nitrogen dioxide is therefore $2x$. The entries in the second and third rows are added to give the number of moles of each substance present at equilibrium. See Table 4.11.

Balanced equation	$N_2O_4(g)$ $\rightleftharpoons$	$2NO_2(g)$
No. moles present initially	2	0
Change in no. moles as equilibrium is established	$-x$	$+2x$
No. moles present at equilibrium	$2 - x = 0.76$	$2x$
Molar concentration		

Table 4.11

There are now two entries for the number of moles of dinitrogen tetroxide present at equilibrium and they must be equal. Therefore

$$2 - x = 0.76$$

$$\Rightarrow x = 2 - 0.76$$

$$= 1.24$$

$$\text{and } 2x = 2.48$$

Numerical values for all expressions of x in the fourth line of the table are filled in. The molar concentrations at equilibrium, i.e. the number of moles per litre, are calculated by dividing the total number of moles of each substance present by the total volume of the vessel. The original table is now complete and looks like Table 4.12.

Balanced equation	$N_2O_{4(g)} \rightleftharpoons$	$2NO_{2(g)}$
No. moles present initially	2	0
Change in no. moles as equilibrium is established	$-x$	$+2x$
No. moles present at equilibrium	$2 - x = 0.76$	$2x = 2.48$
Molar concentration at equilibrium	$\frac{0.76}{2} = 0.38$	$\frac{2.48}{2} = 1.24$

Table 4.12

The equilibrium constant expression, K_c, for the reaction is now written and the molar concentrations at equilibrium entered and the value of K_c is calculated.

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

$$K_c = \frac{(1.24)^2}{0.38}$$

$$= 4.046$$

$$= 4.0 \text{ mol l}^{-1}$$

Worked Example 2

Calculate the equilibrium constant at 500 K for the reaction

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

from the following information. A mass of 625.5 g of phosphorus(V) chloride was sealed with 1 mole of chlorine gas into a flask of volume 2.5 l at 500 K. When equilibrium was established, there were 0.14 moles of phosphorus(III) chloride in the flask.

A table is constructed as before and the data given are entered. The mass of phosphorus(V) chloride is converted to moles.

$$n = \frac{m}{m_r}$$

$$n = \frac{625.5}{208.5}$$

$$= 3 \text{ mol}$$

The number of moles of phosphorus(V) chloride consumed as equilibrium is established is entered as $-x$. The balanced equation is consulted to write expressions in terms of x for the amounts of phosphorus(III) chloride and chlorine formed before equilibrium is established. The entries of the second and third lines of the table are added to give the number of moles of each substance present at equilibrium. See Table 4.13.

Balanced equation	$PCl_{5(g)} \rightleftharpoons$	$PCl_{3(g)}$ +	$Cl_{2(g)}$
No. moles present initially	$\frac{625.5}{208.5} = 3$	0	1
Change in no. moles as equilibrium is established	$-x$	$+x$	$+x$
No. moles present at equilibrium	$3 - x$	$0 + x = 0.14$	$1 + x$
Molar concentration at equilibrium			

Table 4.13

The number of moles of phosphorus(III) chloride at equilibrium is given as 0.14. Therefore

$$x = 0.14$$

$$\Rightarrow 3 - x = 2.86 \text{ and}$$

$$1 + x = 1.14$$

Numerical values for all expressions of x in the fourth line of the table are filled in. The molar concentrations at equilibrium, i.e. the number of moles per litre are obtained by dividing the total number of moles of each substance present by the total volume of the vessel. The table is now complete and looks like Table 4.14.

Balanced equation	$PCl_{5(g)} \rightleftharpoons$	$PCl_{3(g)}$ +	$Cl_{2(g)}$
No. moles present initially	$\frac{625.5}{208.5} = 3$	0	1
Change in no. moles as equilibrium is established	$-x$	$+x$	$+x$
No. moles present at equilibrium	$3 - x = 2.86$	$x = 0.14$	$1 + x = 1.14$
Molar concentration at equilibrium	$\frac{2.86}{2.5} = 1.144$	$\frac{0.14}{2.5} = 0.056$	$\frac{1.14}{2.5} = 0.456$

Table 4.14

The equilibrium constant expression, K_c, for the reaction is now written and the molar concentrations at equilibrium entered and the value of K_c is calculated.

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$K_c = \frac{(0.056)(0.456)}{(1.144)}$$

$$= 0.022$$

$$= 0.02 \text{ mol l}^{-1}$$

Worked Example 3

The equilibrium constant for the reaction between carbon monoxide and water vapour to form carbon dioxide and hydrogen at 1173 K is required.

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$$

If two moles each of carbon dioxide and hydrogen are sealed into a vessel at 1173 K and allowed to equilibrate, calculate the value of K_c for the reaction if 15.93 g of water vapour were present in the equilibrium mixture.

A table is constructed as before and the data given are entered. Although the substances which initially react are actually the products of the forward reaction, the question asks for the equilibrium constant for this forward reaction forming carbon dioxide and hydrogen. Therefore these substances should be considered products and kept on the right of the table and in the numerator of the equilibrium constant expression. Otherwise, the answer obtained will be the multiplicative inverse of the one required.

The mass of water vapour given is converted to moles.

$$n = \frac{m}{m_r}$$

$$n = \frac{15.93}{18}$$

$$= 0.885 \text{ mol}$$

The number of moles of carbon dioxide consumed before equilibrium is established is entered as $-x$ as its concentration has to decrease. The balanced equation is consulted to write expressions in terms of x for the number of moles of hydrogen used and the numbers of moles of water vapour and carbon monoxide formed before equilibrium is established. The entries of the second and third lines of the table are added to give the number of moles of each substance present at equilibrium. See Table 4.15.

Balanced equation	$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$			
No. moles initially	0	0	2	2
Change in no. moles	$+x$	$+x$	$-x$	$-x$
No. moles at equilibrium	$+x$	$x = \frac{15.93}{18} = 0.885$	$2-x$	$2-x$
Molar concentration at equilibrium				

Table 4.15

There are two entries for the number of moles of water vapour at equilibrium. Therefore

$$x = 0.885$$

$$\Rightarrow 2 - x = 2 - 0.885$$

$$= 1.115$$

Numerical values for all expressions of x in the fourth line of the table are filled in. The molar concentrations at equilibrium, i.e. the number of moles per litre are obtained by dividing the total number of moles of each substance present by the total volume of the vessel. This volume is unknown and designated V in Table 4.16.

Balanced equation	$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$			
No. moles initially	0	0	2	2
Change in no. moles	$+x$	$+x$	$-x$	$-x$
No. moles at equilibrium	$x = 0.885$	$x = \frac{15.93}{18} = 0.885$	$2-x = 1.115$	$2-x = 1.115$
Molar concentration at equilibrium	$\frac{0.885}{V}$	$\frac{0.885}{V}$	$\frac{1.115}{V}$	$\frac{1.115}{V}$

Table 4.16

The equilibrium constant expression, K_c, for the reaction is now written and the molar concentrations at equilibrium entered and the value of K_c is calculated.

$$K_c = \frac{[CO_2][H_2]}{[H_2O][CO]}$$

$$K_c = \frac{\left(\frac{1.115}{V}\right)\left(\frac{1.115}{V}\right)}{\left(\frac{0.885}{V}\right)\left(\frac{0.885}{V}\right)} = 1.59$$

Note that the volume of the vessel cancels in this calculation as it would in any other calculation where there are the same number of moles of reactants as products in the equation. It is not necessary to know the volume of the vessel in such cases.

$$K_c = 1.59$$

Exercise 4.7

Q. 1. Find the value of K_c at 673 K for the reaction

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

if 1 mol of nitrogen and three mol of hydrogen produce an equilibrium mixture containing 0.92 mol of ammonia in a 1 litre flask.

Answer

Q. 1. $0.37\ l^2\ mol^{-2}$.

Calculating Equilibrium Concentrations from K_c

Worked Example 1

The value for K_c for the reaction of hydrogen and iodine vapour to form hydrogen iodide is 50.54 at a temperature of 721 K.

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

Calculate the number of moles of each substance at equilibrium when 1 mol of hydrogen is initially mixed with 1 mol of iodine.

A table is once more constructed and the given data are entered.

The number of moles of hydrogen consumed before equilibrium is established is entered as $-x$; its concentration has to decrease. The balanced equation is consulted to write expressions in terms of x for the number of moles of iodine used and the number of moles of hydrogen iodide formed before equilibrium is established. The entries of the second and third lines of the table are added to give the number of moles of each substance present at equilibrium. See Table 4.17.

Balanced equation	$H_{2(g)}$ +	$I_{2(g)}$ $\rightleftharpoons$	$2HI_{(g)}$
No. moles present initially	1	1	0
Change in no. moles as equilibrium is established	$-x$	$-x$	$+2x$
No. moles present at equilibrium	$1-x$	$1-x$	$2x$
Molar concentration at equilibrium			

Table 4.17

Note that there are no double entries for the number of moles of any substance in terms of x. Therefore the value for x cannot be found at this stage.

Expressions for the molar concentrations at equilibrium, i.e. the number of moles per litre are obtained by dividing the total number of moles of each substance present by the total volume of the vessel. In this example, no volume was given. Therefore the symbol V is introduced to represent volume. The table is now as complete as possible and looks like Table 4.18.

Balanced equation	$H_{2(g)}$ +	$I_{2(g)}$ $\rightleftharpoons$	$2HI_{(g)}$
No. moles present initially	1	1	0
Change in no. moles as equilibrium is established	$-x$	$-x$	$+2x$
No. moles present at equilibrium	$1-x$	$1-x$	$2x$
Molar concentration at equilibrium	$\frac{1-x}{V}$	$\frac{1-x}{V}$	$\frac{2x}{V}$

Table 4.18

The equilibrium constant expression, K_c, for the reaction is now written and the molar concentrations at equilibrium entered and the value of K_c is used to solve for x.

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

$$K_c = 50.54$$

$$K_c = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{1-x}{V}\right)\left(\frac{1-x}{V}\right)}$$

Note that the V terms cancel. This will always occur if there are equal numbers of moles of reactants and products in the balanced equation.

$$K_c = 50.54$$

$$K_c = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{1-x}{V}\right)\left(\frac{1-x}{V}\right)}$$

Next note that the square root of the part of the expression on the right is very easily written.

$$\sqrt{50.54} = \frac{2x}{1 - x}$$

Solve for x.

$$7.11(1 - x) = 2x$$

$$7.11 - 7.11x = 2x$$

$$7.11 = 9.11x$$

$$x = 0.78$$

Therefore there are $(1 - x) = 0.22$ moles of hydrogen and iodine and $2x = 1.56$ moles of hydrogen iodide at equilibrium.

Worked Example 2

The value for K_c for the reaction of ethanoic acid and ethanol to form ethyl ethanoate is 4 at a temperature of 373 K.

$$CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_{5(l)} + H_2O_{(l)}$$

Calculate the number of moles of each substance present at equilibrium when 180 g of ethanoic acid are initially mixed with 115 g of ethanol. The volume of the reaction mixture is 316 cm^3.

A table is once more constructed and the given data are entered. The masses of ethanoic acid and ethanol must be expressed in moles.

$$n = \frac{m}{m_r}$$

$$n = \frac{180}{60} = 3 \text{ moles ethanoic acid}$$

$$n = \frac{115}{46} = 2.5 \text{ moles ethanol}$$

The change in the number of moles of hydrogen when equilibrium is established is entered as $-x$; its concentration has to decrease. The balanced equation is consulted to write expressions in terms of x for the number of moles of ethanoic acid and ethanol used and the numbers of moles of ethyl ethanoate and water formed before equilibrium is established. The entries of the second and third lines of the table are added to give the number of moles of each substance present at equilibrium. See Table 4.19.

Balanced equation $CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_{5(l)} + H_2O_{(l)}$				
No. moles initially	$\frac{180}{60} = 3$	$\frac{115}{46} = 2.5$	0	0
Change in no. moles	$-x$	$-x$	$+x$	$+x$
No. moles at equilibrium	$3 - x$	$2.5 - x$	x	x
Molar concentration at equilibrium				

Table 4.19

Note that there are no double entries for the number of moles of any substance in terms of x. Therefore the value for x cannot be found at this stage.

Expressions for the molar concentrations at equilibrium, i.e. the number of moles per litre are obtained by dividing the total number of moles of each substance present by the total volume of the reaction mixture. In this example, the volume is 0.316 l. The table is now as complete as possible and is shown in Table 4.20.

Balanced equation $CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_{5(l)} + H_2O_{(l)}$				
No. moles initially	$\frac{180}{60} = 3$	$\frac{115}{46} = 2.5$	0	0
Change in no. moles	$-x$	$-x$	$+x$	$+x$
No. moles at equilibrium	$3 - x$	$2.5 - x$	x	x
Molar concentration at equilibrium	$\frac{3-x}{0.316}$	$\frac{2.5-x}{0.316}$	$\frac{x}{0.316}$	$\frac{x}{0.316}$

Table 4.20

The equilibrium constant expression, K_c, for the reaction is now written and the molar concentrations at equilibrium entered and the value of K_c is used to solve for x.

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

$$K_c = 4 = \frac{\left(\frac{x}{0.316}\right)\left(\frac{x}{0.316}\right)}{\left(\frac{3-x}{0.316}\right)\left(\frac{2.5-x}{0.316}\right)}$$

Note that the volume terms, 0.316's, cancel. This occurs because there are equal numbers of moles of reactants and products.

$$K_c = 4 = \frac{\left(x^2\right)}{(3-x)(2.5-x)}$$

Next note that in this example the square root of the part of the expression on the right is not known. Solving for x will involve a quadratic expression.

$$4 = \frac{\left(x^2\right)}{7.5 - 5.5x + x^2}$$

$$30 - 22x + 4x^2 = x^2$$

$$3x^2 - 22x + 30 = 0$$

Use the formula

$$x = \frac{-b \pm \sqrt{b^2 - 4\,ac}}{2a}$$

to find the roots of this quadratic expression.

$$x = \frac{22 \pm \sqrt{22^2 - 4 \times 3 \times 30}}{2 \times 3}$$

$$= \frac{22 \pm \sqrt{124}}{6}$$

$$= \frac{22 \pm 11.14}{6}$$

$$= \frac{33.14}{6} \text{ or } \frac{10.86}{6}$$

$$x = 5.52 \text{ or } 1.81$$

Since there were only 3 moles of ethanoic acid in the vessel originally, x cannot have a value of 5.52 moles and this solution to the quadratic is rejected. Therefore, x is taken as 1.81 mol. Therefore there are $(3 - x) = 1.19$ mol of ethanoic acid, $(2.5 - x) = 0.69$ mol of ethanol and $x = 1.81$ mol of ethyl ethanoate and 1.81 mol of water at equilibrium.

Exercise 4.8

Q. 1. The equilibrium constant for the dissociation of iodine into atoms at 1000 K according to the equation

$$I_{2(g)} \rightleftharpoons 2I_{(g)}$$

is 3.76×10^{-5} mol l^{-1}.

Find the equilibrium molecular iodine concentration at this temperature if 1 mol of iodine is placed in a 2 litre vessel.

Answer

Q.1. 0.498 mol l^{-1}.

Appendix

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MODULE 8

Atmospheric Chemistry

CONTENTS

Chapter 1 Oxygen and Nitrogen

Chapter 2 The Greenhouse Effect

Chapter 3 Air Pollution

Chapter 4 The Ozone Layer

CHAPTER 1

OXYGEN AND NITROGEN

1.1 The Atmosphere

When introducing the section on Atmospheric Chemistry to students it is worthwhile to review briefly some relevant points about the atmosphere. A useful analogy is that if the world were a blown-up balloon, the rubber would be thick enough to contain nearly all of the atmosphere. The atmosphere extends about 100 km above the earth's surface and consists of four distinct regions, Fig. 1.1.

Since the atmosphere becomes less dense the higher up one goes, about 90% of all the molecules in the atmosphere are found in the troposphere. Thus, in terms of chemistry, this is the most important region of the atmosphere. Effective mixing of the gases in the troposphere occurs owing to convection currents and the rotation of the earth. It is found that the composition by volume of dry tropospheric air from an unpolluted environment is essentially constant, Table 1.1.

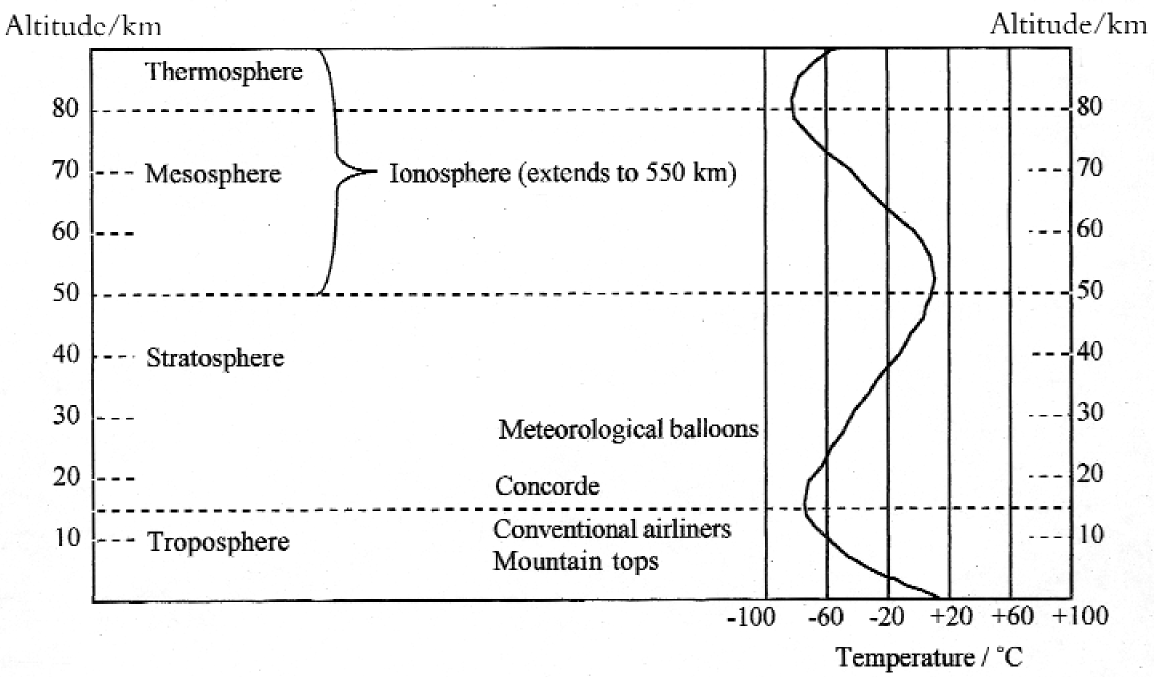

Fig. 1.1 The structure of the atmosphere

Gas	**% (by volume)**
Nitrogen	78
Oxygen	21
Argon	1
	Parts per million
Carbon dioxide	353*
Neon	18.0
Helium	5.0
Methane	1.7*
Krypton	1.1
Hydrogen	0.5
Dinitrogen oxide, N_2O	0.3*
Carbon monoxide, CO	0.1*
Xenon	0.09
Nitrogen monoxide, NO	0.003
Nitrogen dioxide, NO_2	0.003

Table 1.1 *Composition of dry tropospheric air from an unpolluted environment (*variable)*

It is clear that some of the substances in the air are present in such small quantities that they are measured in parts per million (p.p.m.) by volume, e.g. 353 p.p.m. corresponds to a percentage concentration of 0.0353%. While students are required to know only the percentages of oxygen and nitrogen, nevertheless it is interesting to show the range of other gases present in the air.

1.2 The Discovery of Oxygen

The key figure in the discovery of oxygen was **Joseph Priestley** (1733-1804). Priestley studied theology and became a Unitarian Minister. In 1766, he met Benjamin Franklin who was in England trying to settle a dispute with the American colonies over taxation. It appears that this meeting influenced Priestley to take up a scientific career. Shortly after this he moved to Leeds and found himself living next door to a brewery!

He began studying the properties of the gas given off by fermenting grain (now known to be carbon dioxide). He found that this gas was more dense than air, extinguished flames and dissolved in water to produce a refreshing drink. The addition of flavouring and sugar gave rise to the soft drinks industry as we know it today. It was in 1774 that Priestley performed his most famous experiment which ensured his name would live on for ever in the history of chemistry. Using a large converging lens, he focused the sun's rays on a number of substances in order to examine the effect of heat on them. One of the substances he examined was 'calx of mercury', now called mercuric oxide or mercury(II) oxide, HgO. On heating this substance, he discovered that it broke down to give shiny globules of mercury and a colourless gas. Priestley found that a candle burned in this gas 'with a remarkably vigorous flame' and discovered that the gas had a pleasant effect on his lungs when he breathed it.

Priestley had discovered oxygen by decomposing mercuric oxide into its elements by heat.

$$2HgO_{(s)} \rightarrow 2Hg_{(l)} + O_{2(g)}$$

It must be stressed that although Priestley is credited with the discovery of oxygen, he did not realise or understand what was happening. Priestley, a believer in the phlogiston theory, referred to the gas given off as 'dephlogisticated air' and was a convinced believer in this theory until the end of his life.

In 1774 Priestley went to Paris where he met the brilliant French chemist, **Antoine Lavoisier** (1743-1794), and described his experimental work to Lavoisier. Lavoisier was quick to realise the implications of Priestley's work and repeated the experiment to investigate the effect of heat on mercury and on mercuric oxide, Fig. 1.2.

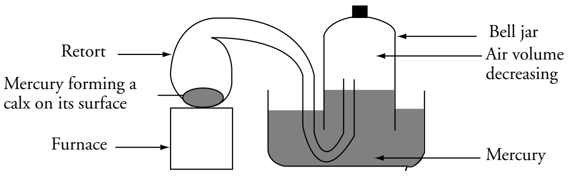

Fig 1.2 *Apparatus used by Lavoisier to study the reversible oxidation of mercury*

Lavoisier placed a known mass of mercury in the retort flask and heated the mercury. The neck of the flask led into a known volume of air trapped in a bell jar over mercury. (In those days it was common practice to collect gases over mercury rather than over water. The mercury in the trough did not play any part in the chemical reaction.) As Lavoisier heated the mercury in the retort flask, a layer of mercuric oxide gradually formed on the surface of the mercury. After heating it for a number of days, he found that the layer no longer increased in size. He allowed the apparatus to cool and measured the volume of air in the bell jar. He found that the volume had decreased by about one fifth of its original volume. He also found that the air remaining in the bell jar did not support combustion. He then collected the layer of mercuric oxide and heated it strongly. He discovered that, just as Priestley had described, it turned back into mercury and gave off a gas. He measured the volume of this gas and found that its volume was equal to the volume of air absorbed during the original heating. Lavoisier named this gas oxygen from the Greek words meaning ‘to give rise to acids’, as he believed that all acids contained this element. (He was wrong in this belief.)

The gas remaining in the bell jar was later given its present name - nitrogen. Lavoisier also discovered that when the oxygen was mixed with nitrogen, the resulting gas had all the properties of air. Thus, he concluded that air was made up of two gases, oxygen and nitrogen.

Note

Since Lavoisier found that mass was neither lost nor gained in his experiment but merely shifted from one point to another, he is often credited with being among the first scientists to verify the law of conservation of mass. He clearly stated this law in a textbook that he published in 1789.

1.3 Industrial Production of Oxygen

Oxygen is produced in large volumes by cryogenic air separation, i.e. separating oxygen from the air at very low temperatures. The oxygen obtained has a purity of 95% - 99.9%. Industrial plants that produce oxygen usually produce nitrogen and argon as well. Most of the output of oxygen from such plants is in liquid form.

In order to produce the above gases, the first step is to remove dust, water and carbon dioxide from the air. The air is drawn in through a filter and compressed to about 6.1 bar (6 atm) by a turbo compressor. The air is then cooled to about $-170\ ^oC$ by continuous heat exchange. Carbon dioxide and water vapour are removed by molecular sieves before heat exchange takes place. Part of the cold compressed air is then taken to an expansion turbine which produces refrigeration. The main flow of air which leaves the heat exchanger is fed into a fractionating column where it is separated into an oxygen-rich fraction at the base of the column and a fraction containing mainly nitrogen at the top of the column. (Boiling point of oxygen = $-183\ ^oC$, boiling point of argon = $-186\ ^oC$, boiling point nitrogen = $-196\ ^oC$). Thus, the air is mainly separated into oxygen and nitrogen. Oxygen collects as a liquid at the bottom of the column where it may be withdrawn as product. Nitrogen is withdrawn as a vapour from the top of the column and is subsequently liquefied using a compressor.

The construction materials used in the plant have to be chosen carefully since air separation plants operate at such low temperatures. Stainless steel and aluminium are usually used since these do not become brittle at low temperatures. Very good insulation is essential in the plant to reduce energy losses. The main parts of an air separation plant are shown in Fig. 1.3.

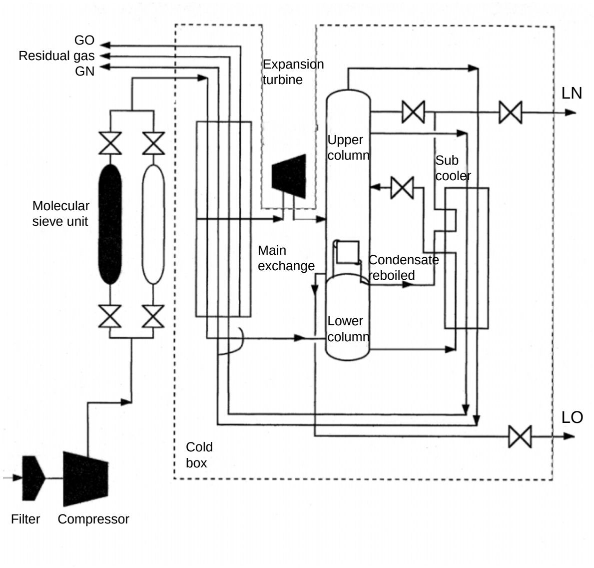

Fig. 1.3 *Simplified flow sheet of an air separation plant*

Oxygen is transported in colour-coded cylinders (black) under a pressure of about 131.7 - 162.1 bar (130 – 160 atm) and by pipeline. It is also transported as a liquid in partial-vacuum insulated tankers.

Note

It is also possible to separate oxygen from the air using a non-cryogenic process. The method is called the Pressure Swing Adsorption Process and involves passing a stream of clean, dry air through a bed of highly efficient synthetic molecular sieves. Nitrogen is retained (adsorbed) on this sieve leaving an oxygen-enriched gaseous stream to pass through. Over a period of time the zeolite sieve becomes saturated with nitrogen and must be regenerated. This is done by reducing the pressure of the gas and the nitrogen is then desorbed back into the gaseous phase and released as waste. To provide a continuous stream of gaseous oxygen, plants operate two or more adsorption beds that are out of phase with one another. Typical industrial plants can produce product with 90 - 93% oxygen content. These plants are usually installed on the site of the user and the oxygen gas is piped directly to the particular industrial process.

1.4 Nitrogen and the Nitrogen Cycle

The only important large-scale process for producing nitrogen is the liquefaction and fractional distillation of air as described in the previous section. Since the mass of the earth's atmosphere is approximately 5 x 10^9 million tonnes, the supply is unlimited! About two thirds of the nitrogen produced industrially is supplied as a gas, mainly in pipes (for industrial use) but also in cylinders under pressure. The remaining one third of the nitrogen is supplied as a liquid, as this is a very convenient source of the dry gas.

One of the main uses of nitrogen is as an inert atmosphere in the iron and steel industry. In many chemical processes, nitrogen is used where the presence of oxygen might give rise to a fire or an explosion. Nitrogen is also very useful in preventing unwanted oxidation of products. Nitrogen is very widely used as a purge in the petrochemical industry, i.e. to prevent a build up of vapours in tanks, pipes, etc. It is also used in the electronics industry to give an inert atmosphere during silicon chip manufacture.

About 10% of nitrogen produced is used as a refrigerant. Liquid nitrogen is particularly suitable for freezing food as the food is frozen much faster than in an ordinary freezer. If food is cooled slowly, the water slowly passes out of the cells. This water then freezes and forms ice crystals in the spaces between the cells. The sharp crystals can damage the cell walls. This spoils the texture of the food. However, if the food is frozen very quickly, the water does not have time to pass out of the cells. It forms small ice crystals inside the cells and this causes less damage to the texture of the food. Nitrogen is also used for the preservation of biological specimens, e.g. semen for artificial insemination. In engineering, liquid nitrogen is particularly suitable for shrink fitting of components. Commercially produced nitrogen is a highly purified product typically containing less than 20 p.p.m. oxygen.

Although we are surrounded by air which is 78% nitrogen, our supply of food is limited more by the availability of fixed nitrogen than by that of any other plant nutrient. Fixed nitrogen is simply nitrogen which is incorporated in a chemical compound and which can be used by plants.

Nitrogen in the air is very unreactive, except to the few organisms that can convert it into a form that can be used by plants. A small amount of atmospheric nitrogen is fixed by occurrences which cause ionisation in the atmosphere, e.g. lightning, cosmic radiation, etc. These phenomena provide the high energy needed for the nitrogen to react with oxygen. Micro-organisms in the soil provide the largest natural source of fixed nitrogen in nature. Nevertheless, the amount of nitrogen fixed in nature is not sufficient to satisfy the world's needs.

The industrial fixation of nitrogen takes place on an enormous scale. Since 1950 there has been a fivefold increase in the amount of nitrogen fixed annually for the production of fertiliser. For example, the amount of nitrogen fixed in industry in 1968 was approximately 30 million tonnes. The amount of industrially fixed nitrogen in 2000 is estimated to exceed 100 million tonnes.

Before the large-scale manufacture of fertilisers by the Haber-Bosch process (synthesis of ammonia from hydrogen and nitrogen) became widespread, it is generally accepted that the amount of nitrogen removed from the atmosphere by natural fixation was balanced by the amount of nitrogen returned to the atmosphere by denitrifying bacteria, i.e. bacteria that convert organic nitrates to gaseous nitrogen. However, there is now concern that the denitrifying processes are not keeping pace with the fixation processes. This imbalance becomes obvious when eutrophication of rivers and lakes takes place. This is caused when an excess of nitrogen compounds are washed into waterways, giving rise to algal blooms. This causes the level of oxygen dissolved in the water to drop, thus destroying many of the organisms living in the water. Eutrophication is the enrichment of water by nutrients which results in deoxygenation.

When teaching the nitrogen cycle to students, it is important to distinguish the terms fixation and nitrification. The term fixation has already been discussed above. Nitrification is not simply the addition of nitrogen to some other substance. The term nitrification refers to a special series of reactions in which certain micro-organisms convert ammonium ions (NH_4^+) to nitrite (NO_2^-) and nitrate (NO_3^-) ions.

The bacteria (called *nitrosomonas* and *nitrobacter*) carry out this process in order to obtain energy for respiration. The nitrification process occurs in two stages.

Stage 1

$$NH_4^+{}_{(aq)} + {}^3/{}_2\, O_{2(g)} \rightarrow NO_2^-{}_{(aq)} + 2H^+{}_{(aq)} + H_2O_{(l)} + \text{energy}$$

$$\begin{array}{ccc} \text{N (-III)} & \xrightarrow{-6e^-} & \text{N (+III)} \\ s^2p^6 & & s^2p^0 \end{array}$$

In stage 1, ammonium ions are oxidised to nitrite ions by *nitrosomonas*. The nitrite ions produced are rapidly oxidised to nitrate ions in the next stage.

Stage 2

$$NO_2^-{}_{(aq)} + {}^1/{}_2 O_{2(g)} \rightarrow NO_3^-{}_{(aq)} + \text{energy}$$

$$\begin{array}{ccc} \text{N (+III)} & \xrightarrow{-2e^-} & \text{N (+V)} \\ s^2p^0 & & s^0p^0 \end{array}$$

The bacteria that carry out the second stage of the process are called *nitrobacter*. Overall, there is an eight electron transfer in the nitrification process.

The term denitrification refers to the reactions in which certain micro-organisms convert nitrites or nitrates to molecular nitrogen, N_2.

When the oxygen content of the soil is low, anaerobic bacteria reduce nitrate ions in the sequence:

$$\begin{array}{ccccccccc} NO_3^-{}_{(aq)} & \rightarrow & NO_2^-{}_{(aq)} & \rightarrow & NO_{(g)} & \rightarrow & N_2O_{(g)} & \rightarrow & N_2 \\ \text{N(V)} & \rightarrow & \text{N(III)} & \rightarrow & \text{N(II)} & \rightarrow & \text{N(I)} & \rightarrow & \text{N(0)} \end{array}$$

In flooded soils (e.g. in rice cultivation), losses by denitrification can be high.

Very little was known about the organisms in the soil that fix nitrogen until the end of the 19th century. Denitrifying bacteria had been discovered about that time and there was considerable concern among scientists that these bacteria would deplete the reserves of fixed nitrogen in the soil and adversely affect farm productivity. In fact, the English physicist, **Sir William Crookes** (1832-1919), gave an address to the Royal Society and painted a very bleak picture of world food production unless an artificial means of fixing nitrogen was soon developed. At that time it was the saltpetre reserves in Chile which were the main source of fixed nitrogen for the manufacture of fertilisers and explosives. It was the demand for explosives that provided the main incentive for the development of the Haber-Bosch process in Germany in 1914. This process is covered in detail in the module on Industrial Chemistry.

It is worth considering what would happen to the nitrogen cycle in the absence of denitrifying bacteria. If such bacteria did not exist, nitrogen could not be returned to the atmosphere. Most of the atmospheric nitrogen would now be in the oceans! This would make seawater slightly more acidic and carbon dioxide would be released from carbonate rocks. Thus, the balance of carbon dioxide would also be upset.

Without doubt, the most intriguing aspect of the nitrogen cycle is the fact that nitrogen-fixing bacteria can accomplish under normal conditions of temperature and pressure a process for which a modern ammonia synthesis plant requires high temperatures and pressures.

There is growing concern expressed in the scientific literature on the increasing levels of nitrogenous wastes carried in runoff waters to our rivers and lakes. Research is taking place to utilise bacterial denitrification to control these increasing levels of fixed nitrogen. The problem of nitrogen disposal is made more difficult by the high levels of nitrogen compounds contained in the organic waste of an increasing world population. In ideal circumstances, this waste nitrogen should be recycled back to the soil. However, efficient methods of carrying this out have not yet been developed. It is still more economical for farmers to continue adding industrial fertilisers to crops. Clearly, it is essential that the nitrogen cycle be kept in balance and this is presenting the scientific research community with an enormous challenge.

CHAPTER 2

THE GREENHOUSE EFFECT

2.1 Introduction

Most of us are aware that there is considerable concern among scientists about how the ‘greenhouse effect’ will affect our climates in the future. The term ‘greenhouse effect’ as commonly used usually refers to the fact that the average air temperature of the earth will be increased as a result of the increasing concentrations of certain gases in the atmosphere. These gases are commonly referred to as greenhouse gases.

An important distinction to be made to students at the outset is that between the ‘greenhouse effect’ and the ‘enhanced greenhouse effect’. The greenhouse effect is a completely natural phenomenon. It maintains the temperature of the layer of air just above the surface of the earth at an average value of about 15 ^{o}C and ensures a climate that will support life. The fact that our atmosphere is involved in keeping the earth at a comfortable temperature may be deduced by comparing the earth and the moon. The moon is almost the same distance from the sun as the earth. However, the moon does not have an atmosphere and the average surface temperature is about –18 ^{o}C. The temperature rises to 100 ^{o}C on the sunlit surface and falls to –150 ^{o}C at night.

The fact that increasing levels of greenhouse gases in the atmosphere may be causing the temperature of the earth to rise is referred to as the ‘enhanced greenhouse effect’ to distinguish it from the effect that has been operating for millions of years. The enhanced greenhouse effect gives rise to what is commonly known as global warming. It should also be emphasised that there is considerable uncertainty in the scientific literature in regard to the timing and the extent of future temperature increases and predictions vary widely.

Many articles in the scientific literature express concern at our changing weather patterns and question if this is due to the enhanced greenhouse effect. Average world temperatures have generally increased over the last century. Seven of the warmest ten years since records began to be kept in the 1850s have been in the last fifteen years. Top of this list was 1988 with 1987 being the second hottest. However, there is considerable debate as to whether this is as a result of the enhanced greenhouse effect - some scientists feel that alternative natural explanations are possible. For example, between 1940 and 1960, world temperatures dropped despite the fact that greenhouse gases continued to be pumped into the atmosphere.

2.2 Greenhouse Gases

The earth is kept warm by energy which comes from the sun. The radiation emitted by the sun includes infrared radiation (wavelength > 700 nm), light (wavelength = 400 to 700 nm), and ultraviolet radiation (wavelength < 400 nm). Much of the ultraviolet radiation is absorbed by the stratosphere and does not reach the surface of the earth. It has been estimated that about 50% of all the energy radiated towards the earth by the sun reaches the surface and is absorbed. (If all the energy emitted by the sun reached the earth’s surface, the temperature of the earth would be too high to support life.) A further 20% is absorbed by gases in the atmosphere. The remainder is reflected back into space and is not absorbed by the earth.

Heat energy is lost from the earth in the form of infrared radiation. If this radiation were to be directly lost from the earth, the temperature of the earth would drop to about −18 °C. However, there are certain gases in the air which absorb infrared radiation. Some of this absorbed infrared radiation is then radiated back towards the earth where it is reabsorbed. This is the greenhouse effect that prevents the earth from being a frozen planet. The problem of global warming arises due to the fact that if we increase the concentrations of certain gases in the atmosphere, less infrared radiation will escape from the earth. This enhanced greenhouse effect will increase the average temperature of the earth above 15 °C.

What gases in the atmosphere are responsible for absorbing infrared radiation? The two main gases are carbon dioxide and water vapour. The concentrations of some greenhouse gases in the atmosphere are given in Table 2.1.

Gas	**Concentration (p.p.m.)**	
	Pre-Industrial	Now
Carbon dioxide	275	350
Methane	0.8	1.7
CFCs	0	0.001
Nitrous oxide	0.28	0.31

Table 2.1 *Concentrations of certain gases in the atmosphere (CFC = chlorofluorocarbon)*

In general, these greenhouse gases come from our need for energy, from agriculture and from industrial processes. Some gases in the atmosphere, e.g. carbon dioxide, water vapour and methane, are capable of absorbing infrared radiation while other gases, e.g. oxygen and nitrogen, do not absorb electromagnetic radiation in the infrared region of the spectrum. A molecule absorbs radiation when the frequency of the radiation is the same as that of the natural frequency of vibration of the atoms of a bond relative to each other. These natural vibrations are caused by the stretching and bending of bonds relative to each other. Note however that molecules of different substances absorb infrared radiation to different extents.

Carbon Dioxide, CO_2

Carbon dioxide levels in the atmosphere have been measured regularly in Hawaii since 1958, the International Geophysical Year. These measurements are important because they are taken well away from any major sources of industrial pollution. The results are shown in Fig. 2.1.

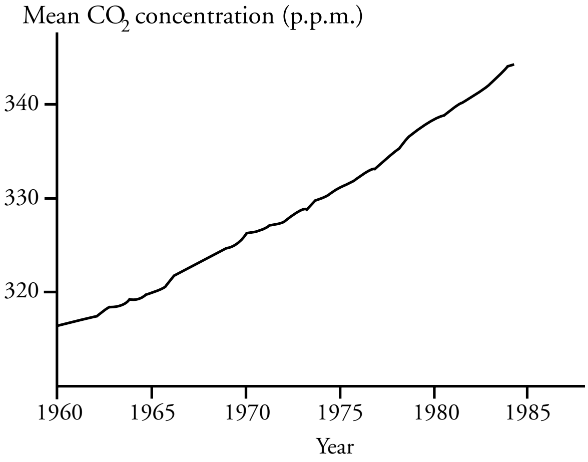

Fig. 2.1 *Increase in carbon dioxide levels in the atmosphere*

Seasonal fluctuations in concentrations are observed and are due to the growth of plants in spring and summer - this removes carbon dioxide from the air in the process of photosynthesis. This causes the levels of carbon dioxide in the atmosphere to fall. The levels rise again in the autumn and winter as plants decay.

Measurements of the concentration of carbon dioxide in air trapped in ice indicate that the level of carbon dioxide in the atmosphere remained steady for about 10 000 years, at a level of about 270 p.p.m. (parts per million by volume). However, the levels began to rise with increasing industrialisation in the 19th century. This was as a result of the burning of increasing amounts of fossil fuels - mainly coal, oil and natural gas. Carbon dioxide is produced when fossil fuels are burned to heat our homes, when our cars are driven, when factories are in operation, etc.

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$$

It has been estimated that industrialised countries produce ten times more carbon dioxide per capita than developing countries. However, there is considerable concern at the increasing amounts of carbon dioxide being produced by developing countries also. The deforestation of vast areas of Brazil, where the rain forests are disappearing at an alarming rate, is an example quoted by many authors. This type of deforestation is also occurring in Asia, Central America and many other countries in South America. The burning of wood which accompanies deforestation also serves to increase the level of carbon dioxide in the atmosphere.

In trying to minimise the amount of carbon dioxide being emitted to the atmosphere, consideration is being given to the fact that different fossil fuels give different amounts of carbon dioxide per unit amount of energy produced. It has been found that natural gas is a better fuel than either oil or coal in this regard.

Research is also being undertaken into methods of removing carbon dioxide from the chimneys of power plants that use fossil fuels as sources of energy. One suggestion being explored is that the carbon dioxide could be pumped into the depths of the ocean, where it would react with the calcium carbonate from seashells to form calcium hydrogencarbonate that would remain dissolved in the ocean.

$$CO_{2(g)} + H_2O_{(l)} + CaCO_{3(s)} \rightarrow Ca(HCO_3)_{2(aq)}$$

Since approximately half of the carbon dioxide produced comes from power stations this suggestion is feasible but considerable costs are involved. It has been estimated that because of the expense of removing the carbon dioxide from the flue gases before they are released to the atmosphere, the cost of electricity could possibly be doubled. Another suggested method of carbon dioxide disposal is to combine it with some cheap mineral like calcium silicate (in slurry form) and convert it into calcium hydrogencarbonate.

$$2CO_{2(g)} + H_2O_{(l)} + CaSiO_{3(l)} \rightarrow SiO_{2(s)} + Ca(HCO_3)_{2\,(aq)}$$

The calcium hydrogencarbonate could then be disposed of in the oceans.

Water Vapour

As far back as 1863, the Irish scientist **John Tyndall** (1820-1893), published a paper about the effect of water vapour as a greenhouse gas. Although water is a less efficient absorber of infrared radiation than carbon dioxide, water vapour is the most important of the greenhouse gases because it is so widely distributed in high concentrations. Since the concentration of water vapour in the air increases dramatically with an increase in temperature, the warming effect of water vapour will increase as a result of any global warming caused by the other greenhouse gases. Most authors do not list water vapour as one of those gases whose increasing concentrations are giving rise to global warming. The increase in temperature due to increased concentrations of water vapour is usually included with the warming caused by the other greenhouse gases.

Methane, CH_4

A molecule of methane causes about 20 times the warming effect of a molecule of carbon dioxide. The reason for this is that a methane molecule absorbs a greater proportion of the infrared radiation that passes through it than does a molecule of CO_2. However, the fact that the levels of carbon dioxide are increasing at such a rapid rate means that methane is less important than carbon dioxide in contributing to global warming. However, the concentration of methane in the atmosphere has almost doubled over the past hundred years, Fig. 2.2.

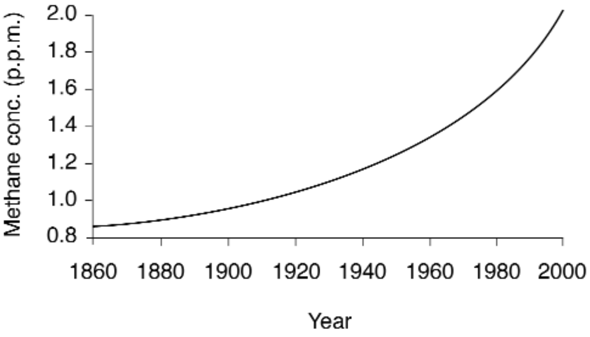

Fig. 2.2 *Increase in methane concentration in the atmosphere*

This increase is thought to be due to various human activities like increased production of food, increasing levels of deforestation and increasing use of fossil fuels. Methane is produced in large quantities where plant material decomposes under anaerobic conditions, e.g. under water, as happens in rice paddies. Methane is also produced in large quantities in swamps - the original name for methane was 'marsh gas'. Animals like cattle and sheep (ruminants) produce large quantities of methane when they digest food. This methane is subsequently lost into the air. The huge increase in the world population of cattle and sheep is thought to make a significant contribution to the increased levels of methane. Another significant source of methane arises from landfill sites where rubbish decomposes under anaerobic conditions. In some countries this methane is collected and burned as a fuel rather than allowing it to escape into the atmosphere.

Dinitrogen Oxide (Nitrous Oxide), N_2O

This gas, commonly called 'laughing gas', is a significant greenhouse gas and is up to 200 times more effective per molecule than carbon dioxide in causing global warming. Like some of the other greenhouse gases already discussed, the levels of dinitrogen oxide in the atmosphere have increased relative to pre-industrial values. It is often referred to as a 'trace greenhouse gas', as its concentration is of the order of 310 p.p.b. (parts per billion).

The gas is formed by processes occurring in soils. Under aerobic conditions it is produced by the process of denitrification and under anaerobic conditions it is produced by the process of nitrification. In denitrification, nitrate ions are reduced mainly to molecular nitrogen. In nitrification, ammonia and ammonium ions are oxidised to nitrite and nitrate ions. N_2O is formed as a by-product in both cases. (Nitrification and denitrification are discussed in detail in section 1.4.) In recent years, it has been established that the nitrification process is the more important source of N_2O.

The burning of fuels in cars also releases dinitrogen oxide into the atmosphere. This is formed when the $NO^\bullet$ free radical is converted to N_2O rather than N_2. However, new catalytic converters are being developed to try to solve this problem. (Catalytic converters are discussed in section 3.3.)

Chlorofluorocarbons, CFCs

Chlorofluorocarbons are considered in detail in Chapter 4. However, it is worth briefly discussing the role of CFCs in global warming at this stage. CFCs are used in refrigerators, air conditioning units, aerosol cans (up to recent times), etc. CFCs are highly efficient in absorbing infrared radiation and each CFC molecule has the ability to cause the same amount of global warming as thousands of CO_2 molecules. (Commonly quoted figures are in the range 21 000 to 25 000. The precise value depends on the actual CFC in question.) The Montreal Protocol banned the production of CFCs from 1995. The replacements for CFCs absorb infrared radiation less efficiently and therefore they cause less global warming. However, a problem will arise as their levels of production increase. The concentrations of the HCFC and HFC replacements are already beginning to increase in the atmosphere and it is predicted that they will make a significant contribution to the enhanced greenhouse effect in the future if steps are not taken to limit their release into the atmosphere. Many countries are already taking steps to remove these substances from equipment before its disposal.

2.3 Implications of Global Warming

There is considerable debate in the scientific literature about the implications of global warming. Unfortunately, because the earth's climate mechanisms are so complex, it is extremely difficult to predict the precise implications of global warming. Research over the past twenty years has used computer modelling in an attempt to predict how the increased concentrations of greenhouse gases will affect the future climates of the earth. A number of problems have been encountered in making such predictions, e.g. not all of the sources of the greenhouse gases are fully understood and considerable research is still taking place on the reactions which many of these greenhouse gases undergo in the atmosphere.

The increases in temperature and sea level that have been predicted in recent years are smaller than were previously predicted but they are still a cause of concern[1-3], Fig. 2.3. There is general agreement that weather disturbances will become more violent and less predictable as a result of global warming.

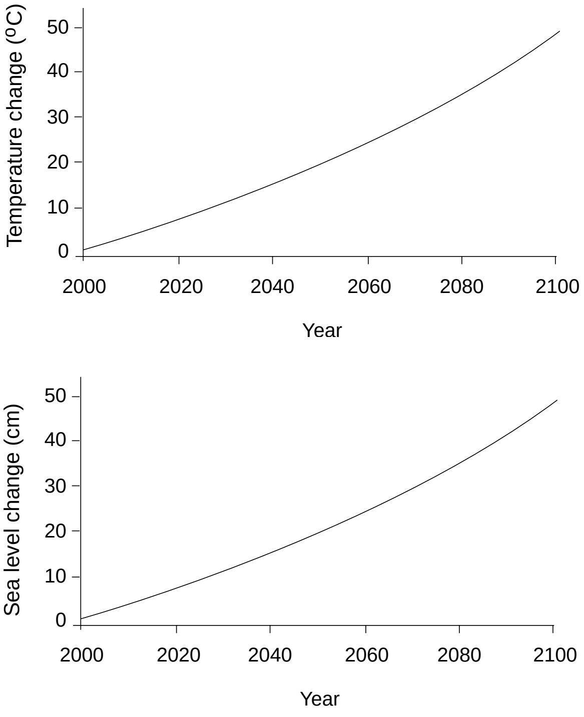

Fig. 2.3 *Predicted increases in (a) global average air temperature, (b) sea level*

One of the most worrying consequences of global warming is the effect on sea level. In the 20th century, sea level has risen by 15 cm. The rise in sea level is consistent with the increase in the average temperature of the atmosphere. The rise in sea level is mainly due to the expansion of water as it becomes warmer; the addition of water to the sea is not a major contributing factor. Most models predict that the extent of the sea level rise will be between 20 cm and 120 cm up to the year 2030.

A rise in sea level is most serious for low-lying countries. For example, Bangladesh is already subjected to serious flooding at regular intervals. It is not possible to apply the strategies adopted in the Netherlands to Bangladesh, as the latter is such a large underdeveloped country. It is predicted that the solution will involve people moving to land in higher areas, making the problem of the present over-crowding even worse.

Increased levels of carbon dioxide in the atmosphere will also have an effect on agriculture. Provided that crops have enough light, water and various other nutrients, it is known that increased levels of carbon dioxide increase the rate at which plants grow. Laboratory experiments have shown that if the concentration of carbon dioxide in the atmosphere is increased to three times the normal level, the rate of photosynthesis increases by up to 50%. However, many scientists feel that this advantage could be counteracted by increased growth in weeds and flooding of crops, as a result of changes in climatic conditions.

It is also predicted that there could be shifts in the food growing areas and supplies of food could be less secure because of droughts and soil erosion in some areas and wetter conditions in others. Also, there could be loss of supplies of fresh water in some areas because of the changing pattern of rainfall.

An increase in the average global temperature could also mean that some species of plants and animals may become extinct, as they fail to adapt to changing conditions. Natural ecosystems depend on the interactions of various organisms and not all of these may be affected equally by climate changes. Ecosystems will be disrupted and some may be destroyed completely. For example, some trees in the tropics flower and bear fruit only in the dry season. If there are increased levels of rainfall, there may not be a dry season. Also, coral reefs grow very close to the surface of the sea. Their rate of growth is very slow and may not be able to keep up with changes in sea level.

It is predicted that the effects of global warming would not be uniform, and some regions would be more affected than others. For example, the American corn belt could move further north and parts of Russia which are frozen wasteland could become fertile agricultural land.

The social disruption caused by the above changes would be considerable. Some authors predict ‘greenhouse refugees’, as low lying land is flooded. Drought could destroy farming communities in places like Oklahoma, forming ghost towns and areas of desert. Major movements of population could cause famine in some regions, giving rise to civil unrest, and possibly war in some countries.

Implications for Ireland

A number of studies have been made on the effect that global warming will have on the climate of Ireland[4]. A number of working assumptions on possible outcomes suggested by ‘state of the art’ climate models have emerged. These working assumptions that have been developed assume that the following changes will take place in Ireland between now and the year 2030.

Average annual temperature: an increase of the order of 2 ^{o}C
Precipitation: 5% - 10% increases in winter,
5% - 10% decreases in summer

Mean sea level: a rise of 18 cm

In addition, as ‘best’ and ‘worst’ cases, the implications of the following alternative scenarios have been studied.

Average annual temperature: an increase of the order of 1 ^{o}C
Precipitation: little change
Mean sea level: a rise of 9 cm

and

Average annual temperature: an increase of the order of 3 ^{o}C
Precipitation: increase of 15% on average annual rainfall
Mean sea level: a rise of 30 cm

The effect of these assumptions may be considered under a number of headings.

(a) Agriculture

The agricultural production potential of Northern Europe would be enhanced if the climate were to change along the lines envisaged. Ireland would share in this advantage - perhaps even to a disproportionate extent if prolonged summer droughts did not become a problem. The production options available would be increased, new crops could be cultivated and the overall costs of agricultural production would be likely to be less than at present.

The climatic change would probably have a beneficial effect on grass growth. An increase in the national yield of about 20% might be expected due to higher average temperatures and changes in rainfall patterns, and a further increase of about 10% due to elevated levels of atmospheric carbon dioxide is not impossible. Clover yields and nitrogen fixation performance should also improve. This enhanced growth would have significant implications in many related areas of agricultural activity, e.g. the length of grazing season, grass conservation, over-wintering and the housing of farm livestock. Livestock farmers would be able to grow other forage crops like maize, fodder, beet and red clover, which would lead to the development of new grassland management systems, as well as to a significant reduction in nitrogen fertiliser use.

Present indications from crop modelling suggest that there would be little or no increase in cereal yields. However, yields of other tillage crops like sugar beet and potatoes could increase by up to 20%, although there are many uncertainties about the possible effects of climate change on these crops. Pests and weeds might pose a greater problem than at present.

Arable crops, currently grown predominantly in the South and Midlands, might find northern regions equally amenable. Similarly, the cultivation of a number of new crops - such as maize, sunflower and flax - might become viable over much of the South and Southeast.

Significant changes would be likely in horticulture. The cultivation of French beans, courgettes, summer cauliflower, celery and early potatoes could become more common. Also, apples, pears and cherries could be grown over wider areas than is currently the case - assisted by a reduction in the frequency of late spring frosts. The successful harvesting of gooseberries and raspberries west of the Shannon would become possible.

It is unlikely that there would be a dramatic increase in the area given over to oil crops - with the exception of oilseed rape which might benefit from better climatic conditions. It is also possible that vine-growing might become viable in the East and Southeast.

The principal agricultural input industries could expect a reduced demand for their products, despite the predicted increases in agricultural output. The feed and fertiliser industries (which at present account for nearly 60% of direct costs in agriculture) would probably be the most adversely affected. Processors of livestock products, however, should be poised to benefit from an increased throughput and stronger demand for their goods.

Overall the changes envisaged are likely to give Ireland a competitive advantage in the international arena since costs will tend to decrease.

(b) Forestry

Any change which occurs in the Irish climate over the next forty years or so will influence not only the tree crops being planted today, but also many of the trees and forests already growing on this island. Higher temperatures and carbon dioxide levels are likely to alter the productivity of forests both directly and indirectly. The influences at work will include changes in the rates of photosynthesis, in water-use efficiency and in damage from various agencies. However, many of the possible responses of trees and forests to these influences are difficult to predict in detail, since current climate models are inexact and the forest-level response is unknown.

Of the variables likely to affect growth, temperature is thought to be the most important and it will have an enhancing effect. Higher levels of carbon dioxide will also act positively, but the impact will be less significant. Forests can react to the new scenario in one of two ways:

(i) increased productivity, where soil water is not a limiting factor and where nitrogen availability is enhanced;

(ii) decreased productivity, where the availability of water and nitrogen become limiting factors.

As the availability of both water and nitrogen depend on the type of soil, the regional effects of climate change on forestry will depend on the distribution of various soils nationally. Many of the forests planted in the West of Ireland have been established on peat. These areas are recognised for their high rainfall and low evaporation and they would benefit from many of the projected changes in climate. As the climate becomes warmer and drier, the peat could be expected to produce more productive forests. If however these soils are not properly drained, reduced aeration may prevent the trees from taking full advantage of the higher temperatures in terms of improved growth - particularly if winter rainfall increases, as has been suggested.

From studies carried out by An Roinn Comhshaoil[4], it is considered to be too soon to predict with any confidence the biological or economic effects of global warming on Irish forests or on the forest products industry.

(c) Flora and fauna

As already stated, increased concentrations of carbon dioxide lead to an increased level of growth in plants. There is also evidence that vegetation produced at elevated carbon dioxide levels decomposes more slowly than that produced at present-day concentrations. Significant increases in the amount of soil organic matter could therefore be expected as carbon dioxide levels rise, and this would affect soil nutrients and water storage capacity. The assumed increases in temperature are unlikely to be sufficient to alter directly the survival ability of any of the species common in Ireland at present. They will, however, respond in their individual ways to the new environment, each having an optimum range of temperature for maximum growth and this may have an effect on their competitive ability. Higher winter temperatures would also influence other developmental processes that depend on low temperatures. The continued growth of many species throughout the winter could be expected and also the earlier seasonal development and flowering of some plants. The effect of climate change on woodlands would probably be beneficial.

Peatlands however, would suffer serious damage if the climate were to change along the lines envisaged. The key process in maintaining peatlands in a satisfactory condition is the inhibition of decomposition. In the new scenario, increased summer soil water deficits will lead to accelerated decay rates of peat. This would lead to a net carbon loss from bogs. It has been suggested that the deterioration of peatlands would be the most damaging outcome of climatic change in Ireland.

Sand dunes, dependent on vegetation for their stability, would benefit from the higher average temperatures, and from the increased nitrogen input to the coastal environment from terrestrial sources. Storm incidence, however, would also be important, since dune growth seawards is a balance between summer accumulation of sand and winter ‘comb-down’ by waves.

A change in climate would result directly in a corresponding change in the distribution patterns of many insect species. Bird life would be indirectly rather than directly affected, through the abundance of their food supply locally, or by changes in other parts of their range, since many of the species are either partial or total migrants. There are some animals that are at present at the northern limit of their distribution in Ireland. One example is the Kerry slug (*Geomaculus maculosus*) and this might be expected to spread northwards if a suitable habitat were available. Estuarine ecosystems are likely to be modified by several consequences of climatic change, although the impact on coastlands and estuaries will result more from changes to mean sea level than from climatic change directly. Any reduction of the inter-tidal area would have a serious effect on estuarine winter bird populations and on passage migrants. The impact would be greatest on the smaller waders of the eastern and southern coasts of Ireland.

(d) Freshwater resources

It is likely that the envisaged climate change would have significant effects on the hydrology of Ireland, and on the quality and quantity of its freshwater resources. The hydrological behaviour of the River Brosna has been analysed in considerable detail[4] and the results have been used as a case study from which the implications of climate change can be deduced on a national scale.

Ireland’s ‘saucer shaped’ topography means that much of the centre of the country is prone to flooding, owing to the relatively poor carrying capacities of rivers of small gradient. In the new scenario of global warming, the average winter water level in rivers, lakes and the soil would be higher than at present. Serious flooding would occur more frequently. In areas that currently experience regular flooding, it would be of greater severity and duration, while some areas, which do not experience flooding at present, may experience flooding on an occasional basis. The increased incidence of serious flooding would also have hygiene and health implications, as sewers may not have the capacity to cope with increased water flow. On the positive side, however, the increased flow due to higher winter rainfall would provide sewerage systems discharging into fresh water with increased dilution capacity. The opposite could be the case with lower rainfall levels in summer.

Climate changes could also alter the response of some areas to heavy rainfall. Warmer, wetter weather could lead to greater vegetative cover that could tend to retard the catchment response to rainfall. Flood peaks would therefore be delayed and reduced somewhat in magnitude. Warmer, drier summers could result in less vegetation towards autumn, so that a catchment would respond more rapidly to rainfall - perhaps by producing flash floods. Flood peaks would tend to follow more quickly after rainfall and be greater in magnitude.

Climate changes would bring new challenges in the managing of our freshwater resources. Lower average summer flow rates in river catchments could result in less recharge for reservoirs during the summer period. Water shortages could occur regularly, and the duration of low water levels would be longer than at present. There would be increased losses due to evaporation from reservoirs, and warmer drier weather would bring increased demands for fresh water. Higher rainfall intensities in winter would result in increased soil and riverbank erosion, ultimately causing increased siltation in lakes and reservoirs and reducing their storage capacities. Some experts suggest that it will be necessary to make greater use of Ireland’s extensive groundwater resources that are under-used at present. Water quality in some areas could be expected to deteriorate periodically in the global warming scenario, owing to a combination of summer drought and higher water temperatures. This would be particularly so in cases where sewerage systems discharge into fresh water - providing a contrast to the winter situation already discussed. Rivers and streams must be capable of diluting the effluent sufficiently to maintain the downstream biochemical oxygen demand (BOD) below a given maximum level (see module on Environmental Chemistry: Water).

By contrast, however, drier warmer summers with higher soil moisture deficits would decrease the risk of surface and groundwater contamination from agricultural waste. Higher soil moisture deficits allow less percolation and this prevents contamination from reaching water sources. Since in rural areas agricultural waste has a much greater potential to pollute than domestic effluent, this aspect of water pollution may be improved by a change in climate.

Those who have made detailed studies of the above effects point out the importance of responding to the challenge of climate change and its effect on our waterways, so that better planning can be carried out as changes in our climate become more evident.

(e) Sea level

Much of the impact on Ireland of any rise in mean sea level will be associated with occasional storms. Little is known about the regional aspects of any future changes in our climate and the lack of confident predictions about future storminess in the vicinity of Ireland is a major hindrance in assessing the risk associated with changes in sea level. Sea level changes are not new to Ireland. Mean sea level has varied significantly over the past 15 000 years for both geological and climatic reasons. In the South of Ireland, for example, global warming since the last ice age has resulted in a considerable rise in the level of the sea. The last 2000 years has seen a steady rise in sea level of about one millimetre per year, very close to the global average over the same time period. Approximately 176 square kilometres or 2.5% of the Republic of Ireland is believed to be at risk from sea level rise. This includes areas that will be eroded, flooded, etc. The largest proportion of this land is in the West but there are also vulnerable areas in the eastern region. The risks are of two types. Firstly, there is the possibility of the gradual inundation of low-lying lands through a combination of rises in the groundwater level and occasional marine incursions. The areas most sensitive to this are in estuaries (e.g. Malahide, Wexford Harbour, Shannon), bays (e.g. Dundalk, Dublin, Dingle, Tralee, Sligo) or behind barriers (e.g. between Wicklow and Bannow in the Southeast and north of Fenit in Co. Kerry). Some of the most vulnerable lands are reclaimed areas which will require considerable protection and de-watering if they are to remain agriculturally viable. The second type of risk involves the problem of the impact of storms. If these coincide with high tides, considerable damage can be caused. They could have a major impact throughout Ireland. The west coast, particularly those areas at the heads of estuaries, may suffer most in terms of flooding, while dune coasts (common in counties Mayo and Donegal) may become unstable and release large amounts of wind-blown sand. The east coast, while experiencing lower wave energy levels, has far more potential for shoreline erosion. Very approximate calculations suggest that increased erosion of 15 - 20% per year may happen in the new scenario, although the complex control systems that govern erosion may reduce this figure. The movement of coastal sediment could lead to in-filling of estuaries and re-stimulate marsh growth. Predicting the response of estuaries is difficult - some could expand and lead to extensive marginal erosion and flooding. Others may contract causing increasing tidal asymmetry and shoreline adjustments.

While much of the Irish coast will be affected by sea level rise, those areas with human activities will be most seriously at risk. Human use of the Irish coast is quite intense and there are often competing demands. Over one third of the Irish population live on or near the coast. Low-lying areas around the cities of Dublin, Cork and Galway have seen spectacular increases in population density in recent times. Several key industries also have predominantly low-lying coastal locations. In several places, especially south of Dublin, transport routes follow the coast and these could be endangered by increased erosion or flooding. It is well to remember that there are many facilities built or located near the coast that rely on the coast for their livelihood. Fishing, aquaculture, etc. rely on coastal locations and are of considerable economic importance to the country. The sea is often used for waste disposal, particularly storm water and sewage. Pipe outlets would easily be impaired if sea level rises.

The possible overall cost of sea level rise is very difficult to quantify without information on replacement values. However, the cost of protecting the coast by building sea-defences is easier to calculate. One estimate is that 100 km of conventional protection would cost from €65 - €570 million (IR£50 - IR£450 million), depending on the type of structure and the degree of risk. To protect all of the vulnerable Irish coast in this manner could cost as much as €340 billion (IR£270 billion) - clearly a figure that could not be contemplated! Other possible strategies include abandonment of land, stronger planning control in coastal areas, financial penalties for coastal developers, etc.

(f) Fisheries

The success or failure of commercial fishing depends on the seasonal production cycle that is directly related to seasonal variations in the climate like temperature, light, nutrient availability and circulation in the ocean. A general warming of the coastal waters, should it occur, would probably result in shifts in the range and distribution of commercial species. It would also cause changes in their migration patterns and in predator/prey relationships. Some northern species such as salmon, cod, haddock, herring and mackerel are likely to show altered distribution and migration patterns in such circumstances. The more southern species like pilchard and hake might become more abundant. Some flatfish species like plaice may also become more plentiful. Lobsters would be expected to thrive since higher temperatures tend to extend their active feeding periods and provide better conditions for the survival of lobster larvae.

The expected changes in rainfall levels could have adverse consequences for the life cycle of species of fish (e.g. salmon, sea trout) which migrate from fresh water and feed in the oceans. Increased rainfall in winter combined with effects such as increased storms and siltation may result in the disruption of the gravel beds used for spawning. It may also bring about excessive leaching of acid from carboniferous forest soils causing increased acidity in rivers and lakes. A reduction in summer rainfall may cause migration difficulties for salmon and the rise in average temperature, with consequent reduction in the dissolved oxygen content of rivers and lakes, may reduce the viability of salmon since they have high oxygen requirements.

It is expected that the consequences for aquaculture will be varied. In the case of salmon, higher sea temperatures might well cause an increase in sea or salmon louse infestation and a potential risk of an increased rate of spread of various fish diseases. Salmon smolt production in freshwater hatcheries may show decreased productivity in a regime of higher average water temperature. Rainbow trout would experience similar problems to those faced by salmon. In the case of shellfish, the consequences of change in climate would be expected to be generally beneficial. Higher temperatures accelerate growth in cold-blooded organisms and therefore a warming of the seawater might be expected to have a slightly favourable or neutral effect on their culture. For example, the native oyster is at its northern limit of distribution in Irish waters and a potential rise in temperature may enhance its growth and its potential for spawning in the wild. The cultivation of mussels should also be enhanced and the production rates of clams and scallops will also improve.

Adverse consequences are also possible. Higher temperatures may increase the risk of the more rapid spread of potentially damaging diseases. Changes in rainfall patterns may increase the sediment load in rivers and this could disrupt riverbeds and reduce yields. Increased siltation rates may also clog the feeding apparatus of fish. Monitoring of red tides will become more important, as will the need for more efficient toxin detection techniques.

The extent to which climatic change may affect the majority of Ireland’s marine flora is difficult to determine. Change may prove detrimental to some species but the rate of climate change is also of importance since some populations may be able to adjust to gradual climatic change by natural selection, but would be unable to cope with rapid and extreme fluctuations.

2.4 Energy Policy and Global Warming

Most of our planet’s energy production relies on the burning fossil fuels. There is considerable debate in the scientific literature about the best way to try to control the rate at which these fuels are being burned. One argument is that switching some of our energy demand to nuclear energy could help not only to reduce the amounts of carbon dioxide released into the atmosphere but also to meet the increasing demand for energy. On the other hand, there is a lack of public confidence in the nuclear energy industry as a result of a number of accidents in nuclear power stations. In addition, the arguments about the cost effectiveness of nuclear power are questionable when additional costs of increased safety, disposal of nuclear waste and decommissioning of old nuclear power stations are taken into account.

One of the problems of continuing to use large quantities of fossil fuels is that the known reserves are beginning to drop at an alarming rate. As already stated, natural gas is the most efficient fuel in terms of energy released and levels of carbon dioxide emitted. However, of all the fossil fuels, natural gas is in the shortest supply. One of the suggested methods of slowing down the rate of increase of global warming is for each country to ‘freeze’ the current levels of fossil fuels being burned. However, there is considerable resistance to this from many of the developed countries due to a possible reduction in living standards.

The two main methods of generating electricity without the emission of carbon dioxide utilise hydroelectric power and nuclear power. These, at present, are used to generate approximately 37% of the world’s electricity. It has been estimated that this saves the emission of about 3.75 billion tonnes of carbon dioxide each year. The scope for expanding hydropower is limited by the lack of suitable sites in industrialised countries and by environmental considerations.

Considerable research is taking place in the use of renewable energy sources to generate electricity, e.g. wind, waves, tides, sun, etc. However, these technologies are at an early stage of development and are unlikely to become dominant methods of electricity production over the next few decades.

Nuclear power has a 16% share of the world's electricity production and there are many who believe that this share should be expanded. Many analysts predict that nuclear power growth will have to accelerate as the levels of fossil fuels drop. It is predicted that coal and oil fired generating stations will gradually be replaced with nuclear power stations. Some countries already have a high percentage of their electricity generated by nuclear power plants, e.g. about 70% of France's electricity is generated from nuclear energy. It took only 30 years for France to reach this position. One of the major problems encountered in trying to expand the nuclear energy industry is the difficulty of building nuclear power plants close to population centres due to resistance from the general public.

It is expected that by the end of the 21st century the world population will have doubled. It is predicted that living standards for many people in the developing countries will be higher than they are today. Therefore, even if energy is used very efficiently, the world demand on energy could be twice what it is at present. At present rates of consumption, natural gas will have run out, oil will be in short supply and coal will be the only significant fossil fuel left. It is predicted that the use of coal will be severely limited in an effort to minimise carbon dioxide emissions. Therefore, there would be heavy dependence on power sources that do not emit carbon dioxide.

It must be emphasised that the greenhouse effect is a global problem and therefore requires a global solution. No single country can solve it. It is not practical to expect the developing countries with their rapidly increasing populations to accept major restrictions on improving their often low standard of living. The developed countries will have to take a lead - and that includes us!

CHAPTER 3

AIR POLLUTION

3.1 Introduction

The term ‘air pollution’ suggests the presence of unwanted substances in the air. These substances are released into the atmosphere from many different sources and cause damage to the environment. The substances are commonly referred to as pollutants. Thus, the air around us is polluted when its natural quality is changed. The sources of these pollutants can be natural or man-made. For example, erupting volcanoes release large quantities of pollutants into the air, e.g. sulphur dioxide and nitrogen oxides. Pollution arises in cities from the burning of large quantities of coal; this results in the production of suspended solids, sulphur dioxide and carbon dioxide.

Different sources give different definitions of air pollution. One definition describes air as being polluted when a constituent in the air is present to the extent that there is a significant hazard to present or future health or to the environment. Thus, according to this definition an emission to the atmosphere is not air pollution per se - air pollution arises when the concentration of the emission in the air reaches a level which is harmful. Other definitions consider any man-made emission to the atmosphere to be a pollutant.

The most commonly quoted definition[5] of air pollution is **that situation which exists when a constituent in the air is present to the extent that there is a significant hazard to present or future health or to the environment.** The pollutants in the air around us can be either particles, droplets or gases. One of the biggest problems caused by air pollution is damage to health - we cannot avoid inhaling air into our lungs! It is estimated that, in 1952, 4000 people died from bronchitis, pneumonia, etc., in London during the infamous smog. (Smog is a mixture of smoke and fog.) This was caused by air pollution that came from burning coal in people’s homes and from power stations. The smoke combined with fog to form a deadly smog and the still weather at the time meant that this smog was not dispersed. This problem led to the introduction of the 1956 Clean Air Act that banned the burning of certain fuels in cities. The creation of smokeless zones resulted in a dramatic fall in the level of air pollution and in associated mortality rates.

Research has shown that, if air pollutants are present in sufficiently high concentrations, adverse effects on our health result. The common consequences of air pollution are an increase in respiratory and cardiovascular disease. With very high concentrations, the effects are particularly damaging to those who already have respiratory illnesses and the very young and older members of the population. It is less easy to determine the long term consequences of exposure to lower concentrations of pollutants. There is a widespread belief that this could play an important role in the development of bronchitis, pneumonia, cancer and other related diseases.

In more recent times, the extent of air pollution in many countries of Eastern Europe has been in the news, following the collapse of the Soviet Communist Bloc where facts on pollution data were not available to the outside world. Also, the massive air pollution caused by the burning of vast quantities of oil during the Gulf War in 1991 was one of the worst environmental disasters in modern times.

Air pollutants may be divided into two categories: primary and secondary. Primary pollutants are those which are emitted into the atmosphere from an ‘emission source’ and are pollutants in their own right. They can have damaging effects in the form in which they are emitted without undergoing conversion to another substance. Secondary pollutants are pollutants that derive from primary pollutants which undergo transformations in the atmosphere.

3.2 Sources of Air Pollution

The main sources of air pollution may be listed as particles, carbon monoxide (CO), sulphur dioxide (SO_2), oxides of nitrogen (NO_X) and lead. A brief summary of each of these is now considered.

Particles

There is a considerable amount of particles in the troposphere. The particles include both solid and liquid dispersed material. Both industrial and natural particles are formed by a number of mechanisms.

(a) The condensation or sublimation of products produced by combustion or volatilisation, e.g. particles of soot or fumes from metals.

(b) Mechanical processes such as weathering or grinding, e.g. salt from the sea and particles of milled flour are emitted into the atmosphere by this method.

(c) Small particles can coagulate to form large particles of mixed composition, e.g. soot and fume particles coagulate in this manner.

(d) Chemical process can produce particles in combustion reactions, e.g. emissions from fossil fuel power plants, incinerators, car engines, etc.

One of the most common sources of particles in the atmosphere is smoke. Smoke is formed when fossil fuels, wood, paper, etc., are incompletely burned. Smoke consists of unburned carbon (soot) with tiny particles of tar and various hydrocarbon chemicals. Smoke particles from household chimneys where ordinary coal (bituminous) is burned in open fires are far smaller than those from industrial chimneys. They may, however, contain over twenty times as much tar and hydrocarbons as smoke from other sources.

One of the obvious effects of particles in the atmosphere is that they reduce visibility by scattering light. They exert a cooling effect on the earth by reflecting radiation from space and preventing it from reaching the earth’s surface. Particles in the air also present a health hazard when inhaled. The smaller the particle, the greater is its health hazard. Larger particles may lodge in the nose and the back of the throat. However, smaller particles may reach the lungs where they can cause serious damage, as they may be transported by the blood to other organs.

Carbon Monoxide, CO

Some of the carbon monoxide in the air is formed naturally when methane (resulting from the decay of plant material in swamps, etc.) is oxidised in the atmosphere. The process of oxidation is quite complicated and involves various free radicals.

$$CH_{4(g)} + {}^\bullet OH_{(aq)} \rightarrow {}^\bullet CH_{3(g)} + H_2O_{(l)}$$

$${}^\bullet CH_{3(g)} + O_{2(g)} \rightarrow {}^\bullet CH_3O_{2(g)}$$

$${}^\bullet CH_3O_{2(g)} + {}^\bullet NO_{(g)} \rightarrow {}^\bullet CH_3O_{(g)} + {}^\bullet NO_{2(g)}$$

$${}^\bullet CH_3O_{(g)} + O_{2(g)} \rightarrow HCHO_{(g)} + HO_2{}^\bullet{}_{(l)}$$

$$HCHO_{(g)} \overset{uv}{\rightarrow} H_{2(g)} + CO_{(g)}$$

The main cause of concern with regard to carbon monoxide is the fact that it is emitted by internal combustion engines and concentrations of this gas can reach dangerous levels where there is a high volume of traffic. The normal atmospheric concentration of carbon monoxide is 0.1 p.p.m. In areas with high traffic levels, this can rise to 100 p.p.m. The burning of petrol is responsible for about 30% of all emissions of carbon monoxide. Most of the carbon monoxide is produced when engines are idling or when they are decelerating since the combustion mixture is rich in fuel under these conditions. The best way of reducing levels of carbon monoxide is to use engines with a high ratio of air to fuel. The use of catalytic converters also reduces the emission of carbon monoxide. Carbon monoxide is particularly dangerous because it forms a complex with iron(II) in haemoglobin in the blood, which is too stable to be broken down by body processes. This prevents haemoglobin combining with oxygen. The fact that the gas is colourless, odourless and tasteless makes it difficult to detect.

Sulphur Dioxide, SO_2

Most fossil fuels contain quantities of sulphur and various nitrogenous compounds. When fossil fuels are burned, the sulphur combines with oxygen in the air to form sulphur dioxide which is emitted to the atmosphere.

$$S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)}$$

Some sulphur dioxide also enters the atmosphere from volcanoes and from the decay of organic matter. Hydrogen sulphide, H_2S (rotten egg gas) which enters the atmosphere is rapidly oxidised to sulphur dioxide.

$$H_2S_{(g)} + {}^{3}/{}_{2}O_{2(g)} \rightarrow H_2O_{(l)} + SO_{2(g)}$$

Sulphur dioxide is a dangerous pollutant causing harm to animals, plants and materials. It is an important component in the formation of acid rain. In non-industrialised areas, the concentration of sulphur dioxide in the atmosphere is low, usually of the order of 0.1 p.p.b. (parts per billion). However, in industrialised areas, levels can increase dramatically due to the burning of fossil fuels. Sulphur dioxide attacks the human respiratory system and aggravates respiratory diseases like asthma, chronic bronchitis and emphysema. On a global scale, the amount of sulphur dioxide released by human activity has increased rapidly over the past 100 years. In 1985 there was a total annual release of sulphur (as sulphur dioxide) of 90 million tonnes[7], Fig. 3.1.

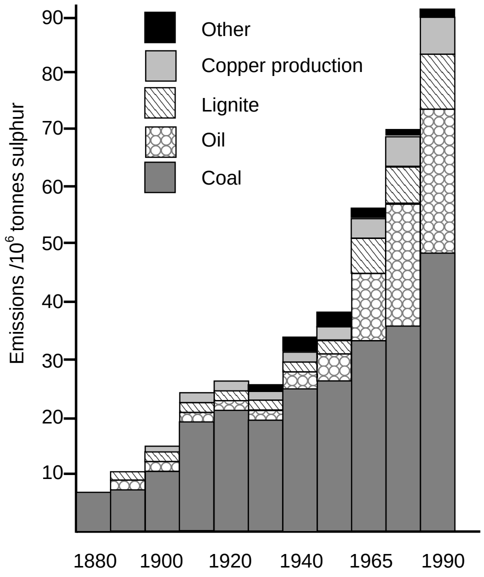

Fig. 3.1 *Global sulphur dioxide emissions, excluding natural sources*

One of the main sources of sulphur dioxide is from power stations and from industries that burn coal and oil. Efforts are being made to reduce sulphur dioxide emissions by taking various measures either before or after combustion takes place. For example, before the fuel is burned, it could be decided to change from a high sulphur content fuel to one which contains a lower sulphur content (the sulphur content of coal can vary from as much as 5% sulphur to 0.5% sulphur). Natural gas generally contains almost no sulphur and many crude oils have a low sulphur content. The petrol used in cars generally contains about 0.05% sulphur. In some cases fuels are blended by making a mixture of high and low sulphur containing fuels. During combustion, it is possible to reduce the emissions of sulphur dioxide by mixing the coal with finely ground limestone and carrying out combustion using a process called fluidised bed combustion. Limestone is injected into a special burner and this helps to neutralise the sulphur in the fuel. After combustion, the flue gases can be ‘scrubbed’, or desulphurised, using a chemical like lime or limestone to remove the sulphur dioxide:

$$CaCO_{3(s)} + SO_{2(g)} \rightarrow CaSO_{3(s)} + CO_{2(g)}$$

This method of removing sulphur dioxide is now becoming widely used in power stations.

Sulphur dioxide in the atmosphere is oxidised to sulphur trioxide which dissolves in rain to form sulphuric acid:

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$$

$$SO_{3(g)} + H_2O_{(l)} \rightarrow H_2SO_{4(aq)}$$

This gives rise to the problem of acid rain. Rainwater is normally slightly acidic, with a pH of about 5.6. However, sulphur dioxide emissions can reduce the pH to as low as 2. (Sulphur dioxide is not the only gas responsible for this problem. As we shall see later, oxides of nitrogen also play a part in reducing the pH.) Acid rain increases the acidity of lakes, destroys aquatic life, leaches various nutrients from soils and enables many toxic metal ions to dissolve more readily. Fish life has been destroyed in many Scandinavian lakes because aluminium ions are leached out of soil into these lakes. The aluminium compounds formed interfere with the operation of fish gills by clogging them. In addition, acid rain causes damage to limestone buildings, increases the rate of corrosion of metals and adversely affects the growth of trees.

We have already referred to problems caused by smog. Three things are needed for smog to form: water, particles in the air and sulphur dioxide. The water vapour condenses on the particles which act as a surface for the oxidation of sulphur dioxide to sulphur trioxide. Sulphuric acid, H_2SO_4, is formed in the small water droplets and, if these droplets are inhaled, severe damage may be caused to the respiratory system.

Oxides of Nitrogen

The two main oxides of nitrogen are nitrogen monoxide, NO, and nitrogen dioxide NO_2. (They are sometimes represented as NO_X gases). The combustion of fossil fuels in air gives rise to most of the oxides of nitrogen from man-made sources. It is estimated that 100 million tonnes a year are produced during fossil fuel combustion. However, natural sources like biological processes in the soil, lightning discharges, etc., produce even more than the above quantity. Nitrogen oxides are formed when fossil fuels are burned at high temperatures, e.g. in power plants and car engines. At these high temperatures, the nitrogen in the air reacts with oxygen to produce nitrogen monoxide:

$$N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)}$$

$$N(0) \xrightarrow{-2e^-} N(II)$$

The nitrogen monoxide then reacts with oxygen in the air to form nitrogen dioxide:

$$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$$

$$N(II) \xrightarrow{-2e^-} N(IV)$$

The nitrogen dioxide dissolves in water to form a mixture of nitrous and nitric acid:

$$\begin{array}{lll} 2NO_{2(g)} + H_2O_{(l)} & \rightarrow HNO_{2(aq)} & + HNO_{3(aq)} \\ N(IV) & \rightarrow N(III) & + N(V) \end{array}$$

Sometimes, if the levels of nitrogen dioxide in the air are high (particularly in industrialised areas), the yellowish haze of the nitrogen dioxide is visible in what is often called a photochemical smog. This was first observed in Los Angeles in the 1940s. The smog is formed by the presence of ultraviolet radiation, hydrocarbons and nitrogen oxides. During rush hour, there is a build up of nitrogen monoxide from cars and this reacts with oxygen to form nitrogen dioxide. The ultraviolet rays from the sun convert the nitrogen dioxide back into nitrogen monoxide.

$$NO_{2(g)} \overset{uv}{\rightarrow} {}^{\bullet}NO_{(g)} + {}^{\bullet}O_{(g)}$$

These oxygen atoms then react with oxygen atoms in the air to produce ozone:

$${}^{\bullet}O_{(g)} + O_{2(g)} \rightarrow O_{3(g)}$$

As we shall see in the next chapter, ozone is very beneficial in the stratosphere. However, it does considerable harm at ground level - irritates eyes, harms lungs, etc. In fact, by measuring the concentration of ozone at ground level, scientists obtain a measure of the severity of the photochemical smog. Hydrocarbons, which are emitted into the atmosphere from spilled petrol or exhaust fumes from vehicles, react with the ozone and nitrogen oxides to form pollutants called peroxyalkanoyl nitrates, RCO_3NO_2. Even small traces of these types of compound cause irritation to the respiratory system and to the eyes. Photochemical smog is prevalent in sunny areas where there is considerable traffic.

Lead

Lead exists naturally in the earth’s crust and is also found in small quantities in water, air, soil and dust - mainly because of our exploitation of it as a metal. It is used in roofing to seal joints, in the manufacture of paints to improve the drying and protective qualities of the paint and in the manufacture of car batteries. However, it is also added to petrol in the form of tetraethyllead, $Pb(C_2H_5)_4$, to prevent the engine ‘knocking’ (see module on Hydrocarbons). The ethyl radicals generated by the decomposition of the tetraethyllead in the hot combustion chamber of the engine are radical chain terminators, which reduce the likelihood of explosive combustion. To prevent the build-up of lead deposits in the engine, 1,2-dichloroethane, $Cl(CH_2)_2Cl$, and 1,2-dibromoethane, $Br(CH_2)_2Br$, are added. These compounds work by reacting with the lead to form volatile lead halides which are removed from the engine in the exhaust gases. Exhaust gases contain the compounds $PbCl_2$, $PbBr_2$ and PbBrCl.

Levels of atmospheric lead concentration have been increasing throughout the world. Greenland ice, which has layers preserved from as long ago as 800 BC, indicate how lead has been accumulating in the environment, Fig. 3.2.

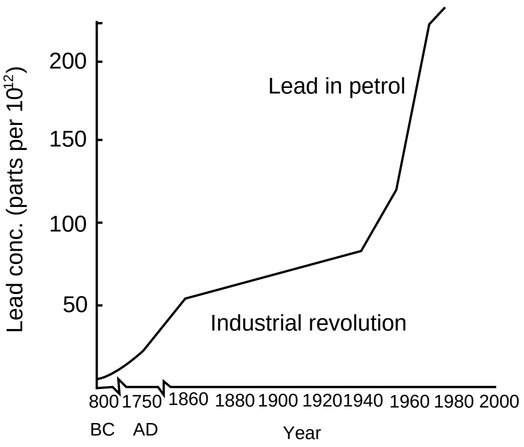

Fig. 3.2 *Increase in lead content of Greenland ice*

For example, ice deposited from snow which fell around 1700 contained less than 0.001 p.p.b. of lead. However, during the Industrial Revolution the content of lead increased steadily. Tetraethyllead was introduced into petrol in the 1930s. Snow that fell in the 1950s contained around 0.2 p.p.b. of lead - a huge increase. The source of this pollution is now on the decline with the increasingly widespread use of unleaded petrol.

Exhaust fumes from cars, which burn leaded petrol, contain lead compounds in the form of very fine particles. These particles can be spread over a wide area and lead levels in soil measured as a function of distance from roadways clearly show that these particles can travel great distances. Lead tends to remain in topsoil rather than be removed by leaching, as it forms stable complexes with various organic materials in the soil. Levels of lead in street dust have been found to be very high - between 500 and 10 000 p.p.b.

The effects of low lead levels are not fully known. Research has shown that people who live in cities have more lead in their blood than people who live in rural areas. When lead is inhaled into the lungs, it is estimated that about 40% of the lead is absorbed into the bloodstream. Lead forms complexes with DNA, RNA and many enzymes and therefore many of the normal processes in the body can be disrupted. High concentrations of lead in the bloodstream cause damage to nerves, brain and kidneys. People who are at particular risk from lead poisoning are workers in lead smelters and in plants that manufacture car batteries, and those who spend a lot of time soldering. Research has shown that young children are particularly susceptible to lead poisoning. The most serious aspect of lead poisoning for children is that it damages their brains while they are still in the stage of development and this damage is permanent.

3.3 Air Pollution Caused by Vehicles

Controlling the pollution from cars is one of the biggest problems facing scientists. One possible solution would be to burn fuel more completely by using a leaner mixture of fuel, i.e. less fuel and more air. This would cause less carbon monoxide and hydrocarbons to be emitted into the air but it would cause a loss in power. It would also increase the emissions of oxides of nitrogen. Burning a rich mixture (with less air) causes high carbon monoxide and hydrocarbon emissions, but low nitrogen oxide levels.

The development of catalytic converters is helping to reduce levels of pollution caused by cars. Catalytic converters were first introduced in the early 1970s in the USA. A catalytic converter is simply a cylindrical container made of stainless steel, open at both ends to enable the exhaust gases to pass through it. The container has a honeycombed ceramic block inside it - the idea of the honeycombed structure is to give a large surface area. The honeycombed surface is then coated with transition metals like platinum, palladium or rhodium. The earlier types of catalytic converter got rid of hydrocarbons and carbon monoxide by oxidising them to carbon dioxide and water. These catalytic converters were known as oxidation catalytic converters. The catalysts usually used were either platinum or a mixture of platinum and palladium. Air was put into the catalytic converter using an air pump system to enable the oxidation reactions to occur.

$$2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}$$

$$C_xH_{y(g)} + O_{2(g)} \rightarrow H_2O_{(l)} + CO_{2(g)}$$

The newer types of catalytic converter are often referred to as three-way converters or redox converters, since oxidation and reduction reactions take place in them - the nitrogen oxide gases are reduced to nitrogen and oxygen and the hydrocarbons and carbon monoxide are oxidised to carbon dioxide and water.

$$2NO_{(g)} \rightarrow N_{2(g)} + O_{2(g)}$$

$$2NO_{2(g)} \rightarrow N_{2(g)} + 2O_{2(g)}$$

$$2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}$$

$$C_xH_{y(g)} + O_{2(g)} \rightarrow H_2O_{(l)} + CO_{2(g)}$$

The original three-way catalytic converters were similar to the oxidation converters except that they had two beds containing the catalysts. The first bed contained platinum and rhodium and reduced the nitrogen oxide gases. The second bed contained platinum and palladium and oxidised the hydrocarbons and carbon monoxide.

In 1975, a modified system was introduced for catalytic converters. This three-way converter contains all three transition metal catalysts - platinum, palladium and rhodium. When the ratio of air/fuel mixture is 14.7:1, the catalysts selectively catalyse the redox reactions involving the hydrocarbons, carbon monoxide and oxides of nitrogen. The net result is that up to 90% of the pollutants are eliminated.

The following are the main reactions that occur in the catalytic converter:

$$2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}$$

$$C_xH_{y(g)} + O_{2(g)} \rightarrow H_2O_{(l)} + CO_{2(g)}$$

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$$

$$2NO_{(g)} + 2CO_{(g)} \rightarrow N_{2(g)} + 2CO_{2(g)}$$

$$2NO_{(g)} + 2H_{2(g)} \rightarrow N_{2(g)} + 2H_2O_{(g)}$$

$$C_xH_{y(g)} + NO_{(g)} \rightarrow N_{2(g)} + H_2O_{(g)} + CO_{2(g)}$$

$$2NO_{(g)} + 5H_{2(g)} \rightarrow 2NH_{3(g)} + 2H_2O_{(g)}$$

$$CO_{(g)} + H_2O_{(l)} \rightarrow CO_{2(g)} + H_{2(g)}$$

$$C_xH_{y(g)} + H_2O_{(l)} \rightarrow CO_{(g)} + CO_{2(g)} + H_{2(g)}$$

One of the requirements for this new type of catalytic converter is that the air/fuel mixture must be 14.7:1 in order that the various oxidation and reduction reactions occur. If the ratio is greater than this (i.e. more air and less fuel) the extra oxygen reacts with H_2 rather than NO and the hydrogen is oxidised instead of the NO being reduced. If the ratio is less than 14.7:1 (i.e. too much fuel) there will be a shortage of oxygen and the oxidation of pollutants will not be complete.

A system has been developed which keeps the air/fuel mixture at the correct ratio. The system works by having an oxygen sensor in the stream of exhaust gases before the exhaust gases enter the catalytic converter.

This probe sends a signal to a computer that controls the engine’s carburettor or fuel injection system.

A lot of research is currently taking place in the whole area of catalytic converters. Great progress has been made in recent times. The original converters were not very long-lasting and were quite expensive. They also tended to reduce the performance of engines, because there was not an entirely free flow of the exhaust gases through the converter. This problem does not exist in the newer converters. It is important to stress, however, that lead compounds can destroy the catalytic activity of all catalytic converters. The lead binds itself to the catalysts and reduces the surface area of the catalyst. One fill of leaded petrol can destroy the entire catalytic reactivity of a catalytic converter.

CHAPTER 4

THE OZONE LAYER

4.1 Introduction

Ozone, O_3, is present in the stratosphere as a thin ozone layer. The radiation from the sun falling on the stratosphere contains a great deal more ultraviolet radiation than that which reaches the surface of the earth. Ozone has the ability to absorb ultraviolet radiation strongly at wavelengths of 220 - 330 nm. As we shall see later, there is a strong connection between ultraviolet radiation and the occurrence of skin cancer in humans. Therefore, it is important to be aware of any damage that is being done to the ozone in the atmosphere, as any substantial reduction in the 'earth's natural sunscreen' could have devastating consequences. In this chapter, we shall look at the chemistry of the ozone layer and at some of the substances responsible for its damage. We shall also look at the steps being taken to minimise further damage.

4.2 Ozone Layer Destruction

Dr Joe Farman and his colleagues in the British Antarctic Survey discovered the so-called 'hole' in the ozone layer. Their work involved measuring ozone concentrations over the Antarctic. They used ultraviolet spectroscopy to measure the levels of ozone. Ozone absorbs ultraviolet radiation of a particular frequency. By measuring how strongly the atmosphere absorbs ultraviolet radiation of this frequency it is possible to work out the concentration of ozone in that part of the atmosphere. They took measurements over a three-year period and it became obvious to them that a problem existed. The concentrations of ozone were much lower than expected, particularly in October, which is the Antarctic spring. In 1984, new instrumentation was used to check the previous readings and this gave confirmation that there really was a 'hole' in the ozone layer.

NASA satellites were also making similar measurements but did not spot the 'hole'. The problem was that they were collecting enormous quantities of data on all sorts of variables, not just ozone concentrations. The computers analysing the data were programmed to ignore any data that seemed very inaccurate. In the case of the measurements of ozone concentrations, most of the measurements were ignored since they were much lower than expected. None of the NASA scientists believed that ozone concentrations could be so low. When measurements from the British Antarctic Survey showed that the concentration of ozone was so low, NASA scientists re-examined their results and confirmed the measurements of Dr Farman and his colleagues. Their results were published in 1985 in the scientific journal *Nature*.

It was not clear at the time whether the effect was due to a natural occurrence or was as a result of some chemical reaction involving pollutants in the air. It was clear that the 'hole' in the ozone layer appeared each spring over the Antarctic and lasted for several months. To investigate why the hole formed each spring, a research team from the National Oceanic and Atmospheric Administration, USA, travelled to the Antarctic in 1986. The team was able to identify from the specific wavelengths of radiation absorbed by atmospheric gases that certain chemicals were present in the atmosphere above them. Subsequent studies demonstrated clearly that the depletion of ozone occurred as a result of pollution from chlorine compounds.

In recent years, it has been confirmed that the ozone is being depleted not just in Antarctica but throughout the world. This loss of ozone is now a cause of serious concern and governments throughout the world have moved to phase out the production of chemicals responsible for ozone destruction.

Substances differ widely in their ability to absorb radiation of a given wavelength. For example, oxygen and the other constituents in the atmosphere absorb ultraviolet radiation having wavelengths shorter than 220 nm. Thus, no ultraviolet radiation with shorter wavelengths than 220 nm reaches the earth's surface and this protects our skin and eyes from harmful ultraviolet radiation, Fig. 4.1.

Ultraviolet radiation between 220 and 320 nm is filtered from the sun's radiation by ozone molecules in the middle and lower regions of the stratosphere.

Ozone screens out much of the sun's ultraviolet radiation in the region 220 - 290 nm. This region overlaps the region commonly referred to as ultraviolet-C radiation, Fig. 4.1. Ozone does not fully absorb all of the ultraviolet-B radiation as this extends from 280 - 320 nm. Neither ozone nor any of the other gases in the atmosphere absorbs to any great extent in the ultraviolet-A range (320 - 400 nm), so most of this type of ultraviolet radiation does penetrate to the earth's surface. Ultraviolet-A radiation is the least harmful form of the three types of UV radiation. It is ultraviolet-B radiation that is a cause for concern.

Ultraviolet-B radiation is responsible for our skin's tanning and getting sunburned. Overexposure to this type of radiation can cause skin cancer and may also cause damage to our immune system. The main damage is caused because DNA molecules can absorb ultraviolet-B. These molecules are damaged and various reactions leading to cancer can occur. Research has shown that the most damage is caused by absorption at 300 nm approximately and it has been shown that, in fair skinned people, maximum absorption from the sun's radiation occurs at this wavelength.

It is predicted that there will be an increase in skin cancer due to overexposure to ultraviolet-B in the sun's radiation. This is as a direct result of the decrease in concentration of ozone in the stratosphere. Fortunately, most skin cancers in Ireland are not of the fatal malignant melanoma type but there is cause for concern. It is important to realise that the use of sunscreens does not solve the problem completely. Recent research has shown that using sunscreens which block ultraviolet-B but not ultraviolet-A could lead to an increase in skin cancer since they allow people to expose their skins for longer periods without burning.

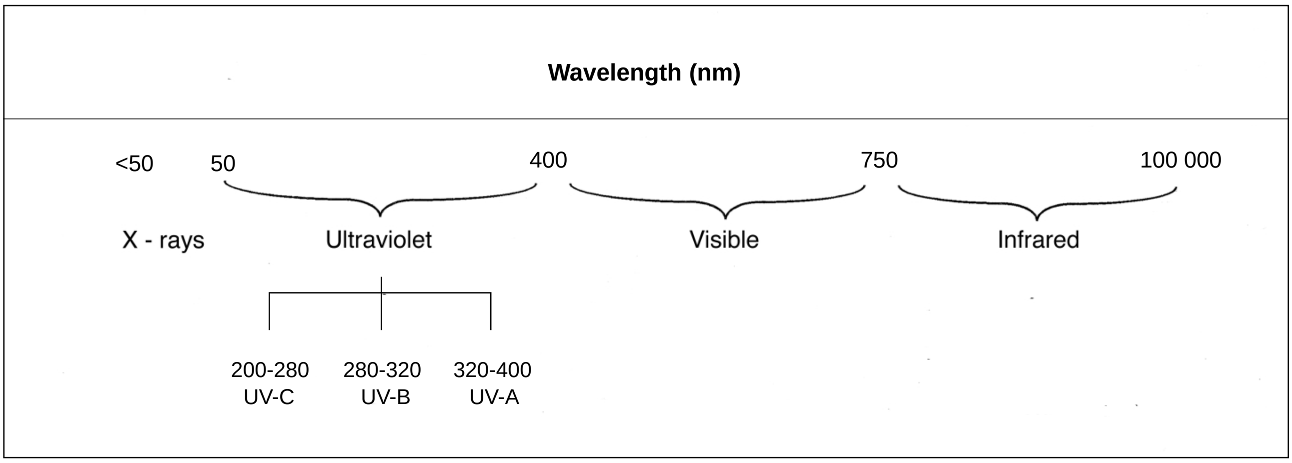

Fig 4.1 *Some of the main regions of the electromagnetic spectrum*

It is worth pointing out to students that there is a considerable time lag, possibly decades, between exposure to ultraviolet radiation and the occurrence of skin cancer. The rise in skin cancers may not only be due to ozone destruction but may also be due to a change in lifestyle, e.g. more holidays in sunny climates, more time spent outdoors, etc.

4.3 The Chemistry of the Ozone Layer

Ultraviolet radiation has a relatively short wavelength and therefore photons of ultraviolet radiation are relatively energetic. Ultraviolet-C has a shorter wavelength than ultraviolet-B which, in turn, has a shorter wavelength than ultraviolet-A.

Wavelength	UV-A > UV-B > UV-C
Photon energy	UV-A < UV-B < UV-C

If a molecule of oxygen absorbs a photon of radiation of wavelength 241 nm or shorter, there is sufficient energy available to dissociate the molecule.

$$O_{2(g)} \xrightarrow{uv} {}^{\bullet}O_{(g)} + {}^{\bullet}O_{(g)}$$

Above the stratosphere, the concentration of molecules is very low (the density of the air is very low) and most oxygen exists in the form of oxygen atoms, since oxygen molecules have absorbed photons of ultraviolet-C radiation. In the stratosphere itself, the concentration of O_2 is much higher as the intensity of ultraviolet-C is much less due to its absorption by the oxygen that lies above the stratosphere. The oxygen atoms created in the above reaction collide with oxygen molecules to produce ozone:

$${}^{\bullet}O_{(g)} + O_{2(g)} \rightarrow O_{3(g)}$$

This reaction is responsible for producing all of the ozone in the stratosphere. The rate of ozone formation depends on the intensity of ultraviolet radiation and the concentration of oxygen molecules at a particular altitude. The ozone layer does not extend any great distance below the stratosphere. The reason for this is that most of the high-energy ultraviolet radiation has been filtered from the sun's radiation before it reaches the troposphere. Thus, at the bottom of the stratosphere little of the oxygen is dissociated and therefore little ozone is formed. At the top of the stratosphere, the intensity of ultraviolet-C is greatest but the density of the air is so low that little ozone is produced since the oxygen atoms simply react with each other rather than with the small number of O_2 molecules. There is general agreement that most of the ozone is located in the range 25 - 50 km above the earth and this is simply referred to as the ozone layer. The above equation shows how ozone is formed. However, ozone undergoes a dissociation reaction if it absorbs radiation of wavelength shorter than 320 nm:

$$O_{3(g)} \xrightarrow{uv} {}^{\bullet}O_{(g)} + O_{2(g)}$$

Most of the oxygen atoms produced in the stratosphere by this reaction react with O_2 molecules to re-form ozone. Some oxygen atoms will react with ozone molecules and convert them to O_2:

$${}^{\bullet}O_{(g)} + O_{3(g)} \rightarrow 2O_{2(g)}$$

It is important to realise that the concentration of ozone in the ozone layer is quite small (around 10 p.p.m.). However, this small amount is enough to remove all the remaining ultraviolet-C and most of the remaining ultraviolet-B from the sun's radiation.

As can be seen from the above equations, ozone is continually being formed and re-formed and hence its concentration should be kept at a reasonably fixed level. However, as already discussed, the 'hole' in the ozone layer over the Antarctic caused scientists to investigate how pollutants from human activities are affecting the ozone layer.

4.4 CFCs

For many years ammonia was used as a refrigerant. However, it had many disadvantages, e.g. it is toxic, corrosive, difficult to handle, etc. In the 1930s a new range of man-made substances came on the market. These were compounds called chlorofluorocarbons or CFCs and were ideal refrigerants. They were non-toxic, non-flammable, non-corrosive, stable and relatively cheap. The first CFC to be used as a refrigerant, CCl_2F_2, was commonly known as CFC-12, Table 4.1. This compound was used in domestic and industrial refrigerators, freezers and air conditioning units.

All CFCs have a code number as shown in Table 4.1. The chemical formula of any CFC may be derived from the code number by adding 90. The number obtained gives the number of carbon, hydrogen and fluorine atoms present in the molecule. For example, to work out the formula of CFC-12, adding 90 to 12 gives 102 and this implies 1 carbon atom, zero hydrogen atoms and two fluorine atoms. Since the valency of carbon is 4, the number of chlorine atoms necessary to satisfy this valency can be deduced. In the case of CFC-12, two chlorine atoms are required, i.e. CCl_2F_2.

The low boiling points of CFC-12 (–29 ^{o}C) and CFC-11 (+24 ^{o}C) meant that they were suitable for blowing into substances like polyurethane. The polyurethane trapped the gas in bubbles and this created a foam material. These foams were excellent insulators and became widely used in refrigerators, freezers and as building materials. Polyurethane foam of 3 cm thickness, blown with CFC-11, provides the same insulation as about 24 cm of concrete.

One of the unique advantages of CFCs was that the size of the bubbles could be controlled. Thus, foam with a rigid outer surface and softer interior could easily be made. This is important in improving the safety of cars, e.g. dashboards that were firm to the touch but gave way on impact.

CFCs were also ideal for use as propellants for aerosol cans – properties like low boiling points, being non-flammable and non-toxic, made them ideal propellants. They were also used for applications like asthma sprays where it was important that the droplet be the right size to penetrate the lungs. The electronics industry welcomed CFCs with open arms. Their non-corrosive nature made them ideal to clean oil and grease from plastics into which designs had been etched.

Common Name	**b.p. (^{o}C)**	**Formula**	**Systematic Name**
CFC-11	+24	CCl_3F	Trichlorofluoromethane
CFC-12	–29	CCl_2F_2	Dichlorodifluoromethane
CFC-113	+47	$CClF_2CCl_2F$	1,1,2-trichloro-1,2,2,-trifluoroethane
CFC-114	+3	$CClF_2CClF_2$	1,2-dichloro-1,1,2,2-tetrafluoroethane
CFC-115	–38	CF_3CClF_2	Chloropentafluoroethane
HCFC - 22	–42	$CClF_2H$	Chlorodifluoromethane
HCFC-123	+28	CF_3CHCl_2	2,2-dichloro-1,1,1-trifluoroethane
HFC-134a	–26	CF_3CH_2F	1,1,1,2-tetrafluoroethane
HCFC-141b	+32	CCl_2FCH_3	1,1-dichloro-1-fluoroethane

Table 4.1 *Some CFCs in common use and some CFC substitutes (HFC = hydrofluorocarbon, HCFC = hydrochlorofluorocarbon)*

But how safe were CFCs? In 1974, two chemists at the University of California, Professor Sherry Rowland and Dr Mario Molina, started investigating CFC compounds as an interesting chemical problem from an environmental point of view. They were interested in the fate of the CFCs in the earth's atmosphere. They looked at all of the processes that could possibly affect CFCs in the troposphere and calculated how rapidly the various reactions would occur. They concluded that these reactions would be very slow and that CFCs could remain unreacted for many decades - even centuries in the troposphere. However, the problem arises when these CFCs eventually reach the stratosphere. Here, they are broken down by the high energy ultraviolet radiation and this breakdown releases free chlorine atoms, e.g. CFC-11 would be broken down as follows:

$$CCl_3F_{(g)} \overset{uv}{\rightarrow} {}^{\bullet}CCl_2F_{(g)} + Cl^{\bullet}_{(g)}$$

Rowland and Molina worked out the number of chlorine atoms that would be formed now and in the future and the reactions that were likely to occur in the stratosphere. They concluded that the chlorine atoms were about a thousand times more likely to react with ozone than with anything else to form chlorine oxide.

$$Cl^{\bullet}_{(g)} + O_{3(g)} \rightarrow ClO^{\bullet}_{(g)} + O_{2(g)}$$

The chlorine oxide radical is very reactive and reacts with oxygen atoms to release more chlorine atoms:

$$ClO^{\bullet}_{(g)} + {}^{\bullet}O_{(g)} \rightarrow Cl^{\bullet}_{(g)} + O_{2(g)}$$

The calculations of Rowland and Molina showed that each chlorine atom on average could destroy up to 100 000 molecules of ozone.

By the late 1970s, the use of CFC-11 and CFC-12 as propellants in aerosol spray cans was stopped in the United States, Canada, Norway and Sweden. However, CFCs in spray cans continued to be used in other parts of the world and in the late 1980s this usage accounted for about one fifth of worldwide CFC consumption and was responsible for the largest single source of CFCs released to the atmosphere.

The banning of such substances began to gain momentum and in 1985 forty-nine countries signed the Vienna Convention for the Protection of the Ozone Layer. In 1987 the Montreal Protocol agreed to a faster reduction in the use of CFCs. The consumption of CFCs was cut by 20% by 1993 and by 50% by 1996.

In 1985, the world production of CFCs was 1 million tonnes a year and by 1995 the production was 360 000 tonnes. The production level is still high because the London 1990 agreement allows developing countries to continue producing and importing CFCs until 2010. The poorer nations received this concession because they argued that it was the richer nations which created the problem in the first place.

It is worth noting that CFCs are not the only source of chlorine compounds in the atmosphere. There has always been chlorine in the stratosphere as a result of monochloromethane gas, CH_3Cl, which is produced when chloride ions in the sea react with decaying vegetation. When these molecules reach the stratosphere, they are decomposed by ultraviolet radiation to produce chlorine atoms:

$$CH_3Cl_{(g)} \overset{uv}{\rightarrow} CH_3{}^{\bullet}_{(g)} + Cl^{\bullet}_{(g)}$$

These chlorine atoms then attack the ozone layer as discussed above.

There is also concern expressed in some of the scientific literature about the possibility that supersonic aircraft could be contributing to the destruction of ozone. These aircraft, to increase speed and improve fuel economy, fly in the intermediate region of the stratosphere. One of the oxides of nitrogen emitted in the exhaust gases is nitrogen monoxide, NO. This compound attacks ozone as follows.

$$O_{3(g)} + NO_{(g)} \rightarrow O_{2(g)} + NO_{2(g)}$$

Other substances giving rise to ozone destruction are the 'halon' chemicals used in fire extinguishers, e.g. bromine compounds like CF_3Br and CF_2BrCl. These compounds are used because they are non-toxic and non-flammable. They are particularly suitable for fires where electronic equipment is involved as the halon compounds evaporate without leaving a residue.

Because these compounds are so stable, they eventually reach the stratosphere and are decomposed by ultraviolet radiation to release bromine atoms. Bromine atoms behave in a similar fashion to chlorine in destroying ozone molecules. Monobromomethane, CH_3Br, is a chemical used in agriculture to sterilise soil before planting, to control termites and to fumigate some crops after harvest. The substance is also formed when wood and vegetation are burned. The molecules of CH_3Br are very stable and eventually rise to the stratosphere where they are photo-dissociated to form bromine atoms which attack ozone. Efforts to find alternatives to CH_3Br in agriculture have not been successful to date as alternative substances are not as effective and are very costly.

It is estimated that about 5% of ozone destruction is caused by bromine. However, it is CFCs that are the main cause for concern in the problem of ozone depletion. For this reason, considerable effort has been made to develop alternatives to CFCs.

4.5 Replacements for CFCs

The applications in which CFCs are used have contributed significantly to our modern lifestyle and, in the process, have generated substantial employment. It would not, therefore, be possible simply to abandon all the applications in which CFCs are used. So, once the problem with CFCs was realised, the search for substitutes began.

The compounds that are proposed as the replacements for CFCs all contain C-H bonds. This ensures that the molecules will be removed from the troposphere by naturally-occurring free radicals in the atmosphere. These replacement compounds are commonly called hydrochlorofluorocarbons (HCFCs).

One of the most commonly used HCFCs is the gas $CHClF_2$, commonly called HCFC-22. It is used in air conditioners, refrigerators, freezers, etc. It has also replaced CFC-11 in blowing foams used in insulation. The effect on the ozone layer of this HCFC in the longer term has been estimated to be only 5% of that of CFC-11. However, the problem of HCFC-22 is that it decomposes to release chlorine more quickly than CFC-11 and therefore there is more significant short-term destruction of ozone.

The compound which is replacing CFC-11 in polyurethane foam production is called HCFC-123, $CHCl_2CF_3$. Its potential for ozone destruction is small as it is easily destroyed in the atmosphere.

Properties of CFCs are linked to the proportions of chlorine, fluorine and hydrogen in them. Fully halogenated compounds have a long atmospheric life. Flammability of the molecules depends on the level of hydrogen. CFCs with the least fluorine are the most toxic.

Attempts to increase the hydrogen content of HCFCs to ensure efficient attack by free radicals have caused problems with flammability. Difficulties have been encountered in maintaining a fine balance between the various elements.

One of the problems about relying on HCFCs as replacements for CFCs is that if the consumption of HCFCs rises with increasing world population there will again be a build up of chlorine in the stratosphere. Considerable research is taking place on compounds that are entirely free of chlorine. Fully fluorinated compounds are not suitable as their lifetimes have been estimated to be tens of thousands of years and they are greenhouse gases. Current research is concentrated on hydrofluorocarbons, HFCs. The compound CH_2FCF_3 is predicted to replace CFC-12 in refrigerators and air conditioners.

Individual HFCs do not possess all the properties possessed by CFCs. Research workers do not expect that there will be a fall in the number of CFC substitutes. Products are being developed that most closely match the needs of the particular application. For example, the air conditioning system of a car requires that the temperature drop to a comfortable level in a very short space of time. However, for a building there is a less dramatic fall in temperature required and this temperature needs to be held constant for a longer period.

The ability of a substance to destroy ozone is usually expressed in terms of its ozone depletion potential. Some values relative to CCl_3F = 1 are given in Table 4.2

Compound	**Ozone depletion potential**
CCl_3F	1.0
$CHClF_2$	0.030
$CHCl_2CF_3$	0.013
$CHClFCF_3$	0.035
CH_3CClF_2	0.038

Table 4.2 *Ozone depletion levels of some CFC and HCFC compounds*

In the early part of the twenty-first century, it is expected that the concentration of chlorine in the stratosphere will be the largest ever recorded. Scientists will be monitoring very closely the levels of ozone depletion to see how much the levels will drop. It is hoped that with the phasing out of ozone depleting compounds, the hole in the ozone layer above the Antarctic will begin to disappear.

4.6 The Ozone 'Hole'

We have already discussed the fact that the levels of ozone over the Antarctic are reduced for several months each year. This 'hole' in the ozone layer occurs during the spring at the South Pole, i.e. September to November. Why is the 'hole' in the ozone layer only found over the Antarctic? A considerable amount of research was carried out in the 1980s and an international expedition by aircraft from the southern tip of Chile made a detailed investigation of the Antarctic stratosphere. There is now a good understanding among scientists of the processes involved in the formation of the ozone 'hole'.

The 'hole' in the ozone layer results from the special weather conditions in the lower stratosphere. Formation of liquid droplets does not normally occur in the stratosphere due to the very low concentration of water. However, the temperature is so low (around -80 to $-90\ ^oC$) over the Antarctic that some condensation does occur and clouds made of icy particles are formed. The stratosphere becomes so cold during the total darkness of winter that the air pressure drops. This drop in pressure, combined with the rotation of the earth, produces a vortex, i.e. a whirling mass of air with enormous wind speeds. Matter cannot penetrate this vortex and the isolated air inside remains very cold for a number of months. The vortex remains well into October.

A number of chlorine compounds, formed from human activities, are normally present in the atmosphere as inactive compounds. The two main inactive chlorine compounds in the atmosphere are HCl and $ClONO_2$, chlorine nitrate. In contrast to the rest of the atmosphere, as the temperature drops, gaseous HCl molecules become attached to the surface of the ice particles. When gaseous molecules of chlorine nitrate, $ClONO_2$, collide with the HCl molecules, chlorine gas is formed:

$$HCl_{(g)} + ClONO_{2(g)} \rightarrow Cl_{2(g)} + HNO_{3(g)}$$

During the winter months when there is no sunlight, molecular chlorine accumulates. Once sunlight appears in the Antarctic spring, the chlorine molecules are decomposed by ultraviolet radiation into chlorine atoms.

$$Cl_{2(g)} \xrightarrow{uv} 2Cl^{\bullet}_{(g)}$$

In addition, the water in the crystals reacts with $ClONO_2$ molecules to give hypochlorous acid, HOCl, which is broken down into chlorine atoms and hydroxyl free radicals.

$$H_2O_{(l)} + ClONO_{2(g)} \rightarrow HOCl_{(aq)} + HNO_{3(aq)}$$
$$HOCl_{(aq)} \rightarrow {}^{\bullet}OH_{(aq)} + Cl^{\bullet}_{(g)}$$

Thus, the hole in the ozone layer is formed as a result of the high level of chlorine atoms in the stratosphere. Since the winds isolate these reactions in an area above the Antarctic, they are confined there.

There is little plant and animal life in the Antarctic region itself to be damaged by the ‘hole’ in the ozone layer. However, there is considerable marine life in the surrounding seas. A slight decline in the amounts of algae and plankton in the top few metres of the ocean has been observed. Since these organisms are at the bottom of the food chain in the ocean, marine life could be severely affected.

Some scientists in this area of research feel that there is a possibility that an ozone ‘hole’ may form over the Arctic at some time in the future. There has been significant ozone depletion in the Arctic of about 10 - 20% but this is less than the 40 - 60% observed in the Antarctic. The main difference between the stratosphere in the Arctic and the Antarctic is that the Arctic stratosphere is warmer than the Antarctic stratosphere. At present, the temperature in the Arctic does not fall low enough to cause ozone depletion. However, with variations in climatic conditions, it is possible that in an unusually cold period in the Arctic, an ozone ‘hole’ could be formed. An ozone hole over the Arctic would be more serious than the hole over the Antarctic. This is because some of the most populated parts of the world would have less protection from ultraviolet radiation.

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MODULE 9

Materials

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Chapter 1 **Polymers**

Chapter 2 **Electrochemistry**

Chapter 3 **Metals**

CHAPTER 1 POLYMERS

1.1 Introduction

Polymers are giant molecules consisting of thousands of smaller molecules (called monomers) combined together to form a large repeating structure. In everyday life the most common polymers we come across are the various plastic materials we see around us. There is no single material called ‘plastic’. Plastics are a large family of materials which have a number of features in common, e.g. they soften, they can be moulded by heat and pressure, etc. Some of the main advances in the history of polymers are summarised in Table 1.1.

Date	Polymer	Pioneers
1823	rubber (for waterproofing)	Macintosh
1830	rubber additives	Hancock
1844	vulcanised rubber	Goodyear
1870	cellulose nitrate	Hyatt
1909	bakelite (first synthetic plastic)	Baekeland
1919	cellulose acetate	Dreyfus
1927	acrylics	Rohm
1930	polystyrene	Staudinger
1931	polyvinyl chloride (PVC)	Klatte, Simon
1933	polyethylene	Fawcett, Gibson
1933	polychloropropene	Carothers
1934	nylon	Carothers, Hill
1938	teflon	Plunkett
1943	butyl rubber	Sparks,Thomas
1944	polyethylene terephthalate (PET)	Winfield, Dickson
1947	epoxides	Castar, Greenlee
1950	polyurethanes	Bayer
1953	linear polyethylene	Ziegler
1954	polypropylene	Natta

Table 1.1 *Some important dates in the history of polymers*

1.2 Plastics

Plastics can have a number of very different properties, e.g. some are hard and brittle while others are soft and waxy. Plastics can be transparent or opaque, many have elastic properties and nearly all are resistant to corrosion. Virtually all of the common plastics are good insulators of heat and electricity.

Plastics are generally classified into two main groups. **Thermosetting plastics** are ones which are unaffected by heat (except at very high temperatures when they are decomposed). The name thermosetting is derived from the fact that they are heated to form the finished article and, while under the influence of heat, they set into their final form and are then no longer capable of being softened by heat. Thermosetting plastics are used for the manufacture of objects like ashtrays or kitchen table tops because they are unaffected by hot objects.

The second group of plastics is the **thermoplastics**. These materials always soften when heated, and then harden again on cooling. The majority of the plastics in common use are of this type, e.g. polythene, polypropene, polyvinyl chloride, etc.

There are other polymeric materials that do not require the action of heat to form them into shape or to harden them, but are ‘set’ by the addition of certain chemicals. Examples of these are polyester resins and epoxy resins. These are often considered as thermosetting plastics.

It is the combination of several properties that has made plastics so highly popular and successful as modern materials. These properties include the following.

1. Low density. The plastic PVC has only about half the mass of an equal volume of aluminium and is six times less dense than copper. In general, plastics are very useful in cars and other vehicles and this results in less fuel being consumed in driving lighter vehicles. Thus, all modern cars have plastic bumpers, fuel tanks, upholstery, etc. Plastic packaging has the advantage that there is little extra cost involved in transporting the packaged article.

2. Shape. Plastic articles can be consistently moulded into any shape and in large numbers at favourable cost. A number of techniques are used to produce different shapes.

(a) Extrusion forces the molten plastic through a specially shaped die. Once outside the die, the plastic is cooled and it sets into a tube the same shape as the nozzle. It is rather like squeezing toothpaste out of a tube. Curtain rails, window frames, hose pipes and other articles sold in long strips are made in this way.

(b) Injection Moulding is used to make buckets, work helmets, milk crates, chairs, etc. Molten plastic is injected into a mould with a hollow cavity with the same shape as the object required. When full, the mould is allowed cool and the plastic inside sets and the mould is opened to release the article. These objects usually have a pinhead mark or spot which shows the point of injection of the plastic into the mould.

(c) Blow Moulding is the process of extruding a molten plastic tube into an open mould. The process is used for making bottles. The mould closes and one end, the neck, is open while the bottom is sealed. Compressed air is introduced down the open neck and this forces the plastic outwards against the mould.

(d) Rotational Moulding involves adding powdered polymer, usually polythene, to a mould. The mould is then heated to allow the powder to soften and flow in the mould. The mould is then cooled by spraying water over it while still rotating until the plastic sets, still coated on the inside of the mould. The mould is then opened to release the object. Litter bins, oil storage tanks and surfboards are made in this way.

(e) Calendering is the process of rolling a sheet of semi-molten plastic over a number of rollers. It is allowed to set gradually as it passes over the rollers and it may be printed upon or have a pattern stamped into it as it proceeds. Sheets of wallpaper and vinyl for flooring, covering briefcases and bags, etc., are made in this manner.

(f) Foaming is the introduction of bubbles of gas into the plastic as it sets. As a result the size of the sample of plastic increases dramatically as does its heat insulating properties. In addition, its density is greatly reduced. Polymers made by this process are used in upholstery foam, sponges, low-weight packaging for eggs, padded steering wheels, cups for hot liquids in fast food outlets, etc.

3. Transparency. The nature of the plastic and the method of manufacture will determine this property. Clear, translucent or opaque plastics can be formed as required.

4. Colour. Colour is generally absent from the original plastic but colours can be added during manufacture, giving the colourful array of plastic objects we know. The fact that plastics can be coloured, as required, has made it easy for them to replace traditional materials, e.g. terracotta flower pots were replaced by plastic pots of the same colour, real sponges have been replaced by artificial versions, etc. Many warning articles make use of bright colours of plastics, e.g. work helmets, traffic cones, plastic barrier strips on roadworks, etc.

5. Solubility. Most plastics are insoluble in water and this makes them very useful in protective clothing, building materials, etc.

6. Durability. Most plastics are not easily broken down in the environment (non-biodegradable) and so are extremely durable. They may however discolour in strong light and bend, become brittle, or split if subjected to strong heat from the sun over long periods. Durability, while usually a desirable property, presents a problem when plastic articles are to be discarded. This problem and the growing awareness of the necessity to recycle plastics is discussed in section 1.7.

7. Insulation. In general, plastics are good insulators of heat and electricity. Foamed plastics in particular are good heat insulators and are used to prevent heat loss from hot water pipes, hot food, etc. The fact that plastics are good heat insulators leads to rather long cooling times during their manufacture. PVC is used in electrical flex because of its excellent insulation properties. Very thin coatings of PVC in a single flex can insulate hundreds of conductors from one another.

8. Stability upon heating. All thermoplastics soften on being heated. The range of softening temperatures varies from 70 °C for polyethene to over 300 °C for PTFE (Teflon). Hot ashes from a fire will 'soften' a plastic dustbin. Household tubs and containers may become distorted at the high temperatures in a dishwasher. Other plastics decompose when heated strongly and turn brown or black as the plastic decomposes.

Note

The burning of plastics presents a particularly difficult problem. Plastics contain the elements carbon, hydrogen and possibly oxygen, nitrogen, chlorine, etc., depending on the specific compound in question. Thus, when they burn, a number of products may be formed. Invariably carbon monoxide (CO) and carbon dioxide (CO_2) as well as soot result from the carbon content, water vapour from hydrogen, hydrogen chloride gas if chlorine is present, noxious nitrogen compounds, including hydrogen cyanide, if nitrogen is present. Dense smoky fumes are characteristic of burning plastics. Not all plastics can be ignited, e.g. Teflon is non-flammable, PVC is difficult to ignite and is usually self-extinguishing; polyurethanes used in upholstery burn easily unless specially formulated. Legislation now controls the foams used for upholstery. An important hazard associated with burning plastic, in addition to the poisonous products, is the melting caused by the heat of the fire. Drips from plastic materials overhead can cause severe burns as well as carrying flames from one location to another.

A brief overview of some of the more common plastics is given below.

(a) Polyethene (polyethylene or polythene)

Polythene is one of the simplest of the polymers and consists simply of a long chain of carbon atoms (varying from 2000 to 40 000 in length) where each carbon atom is also bonded to two hydrogen atoms, Fig. 1.1. However, this structure is a simplified picture as the long polymer chains develop some side branches in the later stages of polymerisation. This affects the density of the polythene and is discussed in more detail in section 1.2.

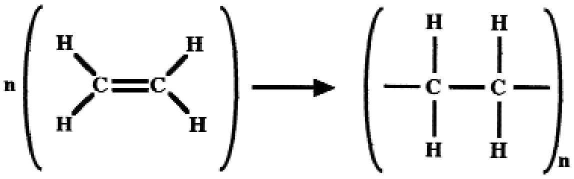


Fig. 1.1 *Structure of polythene*

High density polythene is used in substances like bleach bottles and milk bottle crates. Low density polythene is used to manufacture substances like rubbish bags, fertiliser bags, flexible bottles for washing up liquid, milk bottles, film for wrapping food, etc.

(b) Polypropene (polypropylene)

Polypropene has a similar structure to that of polyethene except that methyl groups are attached to every second carbon atom (head to head and head to tail polymerisation is possible), Fig. 1.2

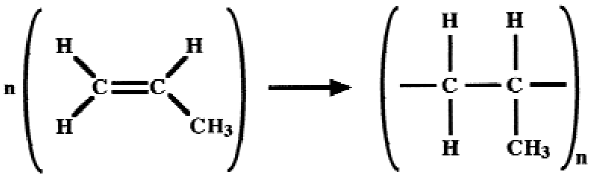


Fig. 1.2 *Structure of polypropene*

The presence of the methyl groups means that the groups of atoms arrange themselves in a kind of helical screw pattern along the length of the chain to cause the minimum interference with each other. This regular pattern means that polypropene is less flexible than polyethene and this also causes the polypropene to be harder and slightly stronger than polyethene. Polypropene is used in the manufacture of buckets, bowls, toys, laboratory sinks, etc.

(c) Polyphenylethene (polystyrene)

Polyphenylethene is similar in structure to polyethene and polypropene except that phenyl groups are attached to every second carbon atom in the carbon chain, Fig. 1.3.

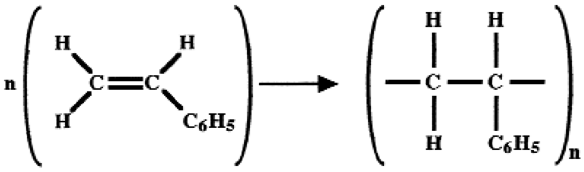


Fig. 1.3 *Structure of polystyrene*

Rigid polystyrene is used to manufacture items like yoghurt pots, food containers, disposable drinking cups, flower pots, etc. Expanded polystyrene is used in insulating houses, ceiling tiles, egg boxes, packing for computers, etc.

The presence of the bulky benzene rings makes the chain even stiffer than that of polypropene and thus it is much more brittle and liable to crack when used in unsuitable applications. To overcome this, a certain proportion of buta-1,3-diene is mixed with the monomer before it is polymerised. This process of combining two different monomers in the same polymerisation stage is called **copolymerisation**. The final long chain molecule then contains buta-1,3-diene groups interspersed throughout its length. These provide more space between the phenyl groups and permit the long carbon chain of the molecule to be more flexible. This copolymer is called **toughened polystyrene** or **high impact polystyrene** (HIPS) and the more buta-1,3-diene it contains the higher is its impact strength.

(d) Polychloroethene (polyvinyl chloride or PVC)

Polychloroethene is obtained by polymerising chloroethene (vinyl chloride), Fig. 1.4. The large size of the chlorine atom, coupled with the fact that the chlorine atoms are not arranged in a regular pattern around the backbone of the chain, means that the molecules of this polymer are not able to move about freely.

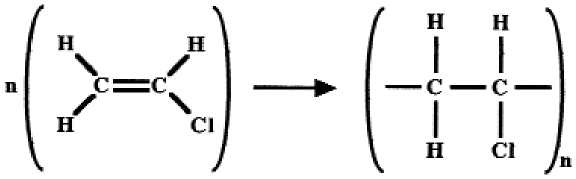


Fig. 1.4 *Structure of PVC*

The plastic is a hard, rigid and tough material that is used to make rods and pipes such as those used for guttering. It is also used to manufacture curtain rails, bottles, clear corrugated roofing, etc.

PVC can also be used for applications that require a much softer and flexible plastic and this is achieved by mixing the polymer with a material called a plasticiser. The molecules of this substance are generally long and flexible and these permit a greater degree of movement between the rigid polymer chains. This process has a similar effect to the incorporation of buta-1,3-diene into polystyrene polymers. The principal difference is that buta-1,3-diene forms part of the polystyrene chains whereas plasticisers remain separate from the polychloroethene chains and fill the spaces between them. Plasticised PVC is used for the insulation of electric cables, manufacture of soft toys, rainwear, shower curtains, car upholstery, etc.

(e) ‘Perspex’ and related polymers

Perspex is commonly referred to as an ‘acrylic’ polymer. Acrylic acid or propenoic acid is formed when one of the hydrogen atoms of ethene is replaced by a carboxyl group. This compound is the parent of the acrylic family of monomers, Fig. 1.5.

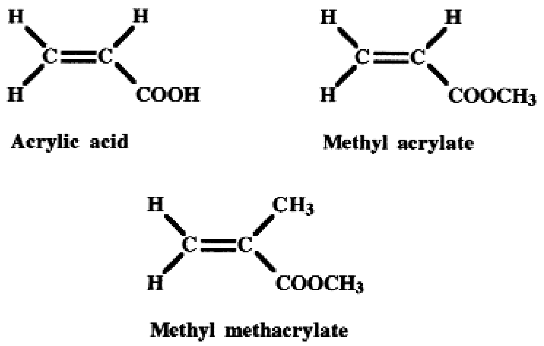


Fig. 1.5 *Acrylic monomers*

Perspex is one of the most widely used acrylic polymers. Its systematic name is poly(methyl 2-methylpropenoate) and its traditional name is polymethyl methacrylate. It is a tough material with outstanding optical properties. This polymer is used for contact lenses, spectacles, lighting displays, signs, etc. It is best known by its trade name of 'Perspex'.

Another important member of the acrylic family is poly(propenonitrile) or polyacrylonitrile. This is obtained by replacing the carboxylic acid group with the nitrile group. This is an extremely tough material that can withstand very high temperatures. It decomposes before it melts and for some time was thought to be completely useless because of the problem of moulding it. The reason for this behaviour is that the nitrile group possesses a small electric charge that attracts the neighbouring polymer chains and holds them together. Eventually, a solvent was discovered which permitted the polymer to be spun into acrylic fibres. These fibres, sold under names such as 'Orlon' and 'Acrilan', are strong and possess a silky lustre. Acrylonitrile is usually copolymerised with various co-monomers to achieve the best balance of properties for the required use. Polyacrylonitrile is also used to manufacture cases for food mixers, light covers, etc. A further application of propenonitrile (acrlyonitrile) is its use in superglue.

(f) Nylon

Nylon is an example of a condensation polymer. Condensation polymers are formed by the combining together of two or more different substances - usually with the elimination of water or another simple compound such as hydrogen chloride. The monomers for this type of polymer must have two reactive groups per molecule.

Nylon was the first synthetic fibre to be prepared by polymerisation. The most common variety, nylon 6,6 is formed by the condensation of hexane-1,6-dioic acid (adipic acid) and hexane-1,6-diamine, Fig. 1.6.

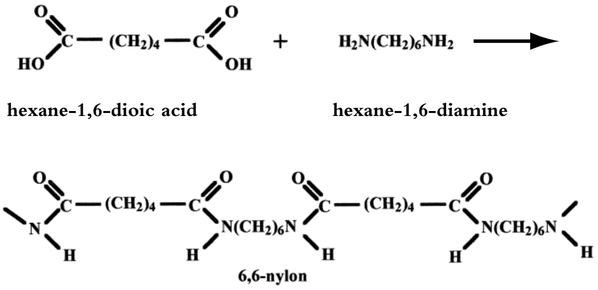


Fig. 1.6 *Formation of nylon 6,6*

The value of '*n*' is about 50, making the relative molecular mass of the compound about 12 000. Nylon is described as a polyamide because the repeating structure contains an amide group. The name nylon 6,6 is due to the fact that each of the monomers has six carbon atoms per molecule. Nylon 6,10 is also widely used. In this variety, the adipic acid is replaced by sebacic acid, which has 10 carbon atoms per molecule. In modern terminology, nylons are referred to as PA66, PA610, etc.

The nylon polymers have an excellent blend of toughness, flexibility, abrasion resistance and strength and lend themselves to a wide range of applications. In the form of fibres, nylon is widely used to make shirts, tights, ropes, parachutes, brush hairs, carpets, etc.

(g) Terylene

Terylene is an example of a polyester, i.e. a polymer containing the ester linkage. It is formed by the condensation of benzene-1,4-dicarboxylic acid (commonly called terephthalic acid) and the dihydric alcohol ethane-1,2-diol (ethylene glycol), Fig. 1.7.

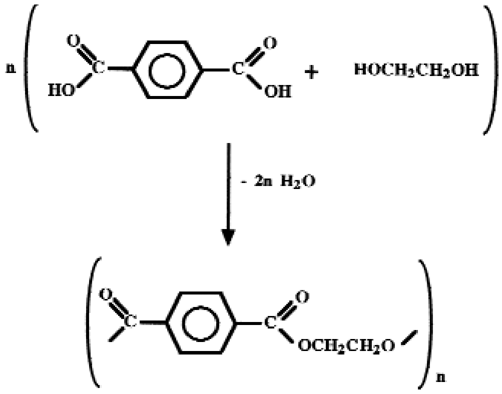


Fig. 1.7 *Formation of terylene*

'Terylene' is a trade name derived from the common names for the two monomers. Terylene produced as a fibre is very strong and is resistant to shrinkage, creasing, abrasion and sunlight but does not have the degree of chemical resistance shown by other condensation polymers. Terylene is used in clothes, photographic film, recording tape, carbonated soft drink bottles, etc.

(h) Epoxy resin

The epoxy or epoxide group is a ring structure in which an oxygen atom is linked to two bonded carbon atoms. The simplest compound containing this is epoxyethane (ethylene oxide). One of the most widely used epoxides is produced by a condensation reaction between 1,2-epoxy-3-chloropropane and 2,2-bis-(4-hydroxyphenyl)propane, Fig. 1.8.

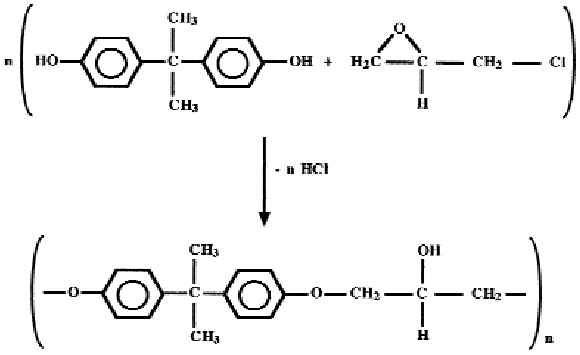


Fig. 1.8 *Formation of a typical epoxy resin*

The polymer can be cross-linked via the epoxy group using a variety of agents including amines, acid anhydrides or organic acids, to produce thermosetting networks. Epoxies are particularly suitable for corrosion prevention. Epoxies are extremely stable to heat, and resistant to the action of chemicals. They are strong and possess excellent adhesive properties. They are particularly suitable for corrosion-resistant paints, adhesives, and electrical insulation for applications such as printed circuit boards.

(i) Bakelite (Phenol-methanal or phenol-formaldehyde)

This was the first synthetic plastic. It dates from 1910 and was produced by a chemist called Baekeland, from whom its name is derived. It results from the condensation of phenol and methanal, water being eliminated in the process, Fig. 1.9.

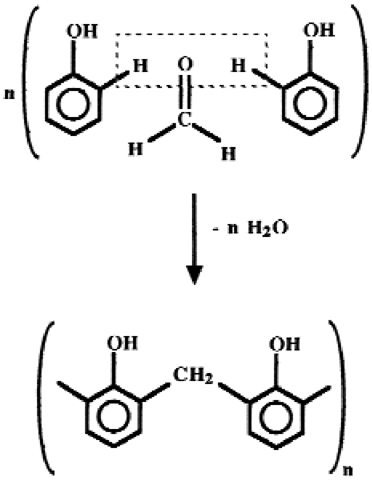


Fig. 1.9 *Formation of bakelite*

The long chains that are produced can then be linked to each other to produce a three-dimensional network by further condensation reactions. In practice this last stage is carried out in a heated mould under pressure so that the final reaction actually forms the finished product - which further heating cannot soften. Phenol-formaldehyde resins are used for the manufacture of handles for pots, plug tops, buttons, etc.

1.3 The Discovery of Polythene

Polythene was discovered in the 1930s and was of great use to the Allies in World War II. The reason for this is because it was used for insulation of cables and hence made electronic instruments more effective. Polythene was discovered in 1933 at the ICI plant in Northwich, Cheshire. Research was taking place on the effect of very high pressure on chemical reactions. Some fifty reactions were tried but the results were disappointing - no interesting or valuable products were formed. One of these experiments was the reaction between benzaldehyde and ethene at high pressure that was being studied by **Eric Fawcett** and **Reginald Gibson.** They were hoping these two chemicals would react together to form a ketone, Fig. 1.10.

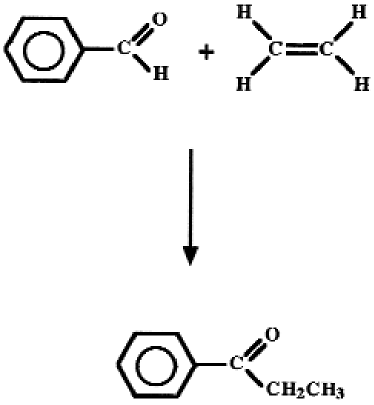


Fig. 1.10 *Reaction between benzaldehyde and ethene*

The mixture was left to react over the weekend but fortunately, as it turned out, the apparatus leaked and at one point they had to add extra ethene. When the vessel was opened on the following Monday, they observed that a 'white waxy solid' (as Gibson described it in his notebook) had been formed. When analysed, this white solid had the empirical formula of CH_2. What really puzzled them was that they were not always able to get the same results from this experiment. Sometimes they got the white solid and other times the mixture exploded, forming just soot. For this reason, the work was halted in July 1933 because of the very dangerous nature of the reaction.

Work was restarted in December 1935 when Fawcett and Gibson found that they could control the heat given out in the reaction if they added cold ethene at the correct rate. The mixture was kept cooler in this way and no explosion occurred. They found that both the rate of the reaction and varying the pressure could control the relative molecular mass of the solid. The new material had all the typical properties of polymers - it could be melted, moulded, used as an insulator, etc. They then set about investigating why the reaction initially gave such unpredictable results. **Michael Perrin** took charge of the project in 1935 and discovered that the presence of oxygen played a crucial role in the process. The polymerisation process will not occur if no oxygen is present. If too much oxygen is present, the reaction runs out of control. The addition of the correct amount of oxygen is crucial to the process. Fortunately, the leak in the apparatus had let in just the right amount of oxygen to catalyse the formation of the polymer. If there had not been a leak in Fawcett and Gibson's apparatus, polythene might never have been discovered! Perrin showed that the benzaldehyde is not necessary for the polymerisation reaction to occur.

The British Telegraph Construction and Maintenance Company which was involved in the production of underwater telegraph and telephone cables, heard about the discovery of polythene and decided to test its insulating properties on underwater cables. In 1939 ICI made enough polythene for one mile of underwater cable and it was found to be ideal for this purpose and a small plant was built by ICI for the specific manufacture of polythene. Towards the end of World War II underwater cables insulated with polythene were laid between England and France. During the war, polythene was also used for insulating the cables used for radar equipment. This polythene was produced by ICI in England and by Du Pont and Union Carbide in the United States.

Polythene became well known to the general public after the war and the first polythene bowls appeared in the shops in 1948. Polythene was also used for food packaging, carrier bags, etc. This kind of polythene is commonly called low-density polythene. The low density is caused by the fact that the chains are extensively branched and coil around each other in a random fashion, taking up a lot of space and thus lowering the density. It was found that this branching also lowered the strength of the polythene. A method of increasing the density of the polythene resulted from discoveries made by **Karl Ziegler**.

In 1953 Karl Ziegler was the director of the Max Planck Institute for Coal Research in Muelheim in Germany. He was particularly interested in the catalytic effects of organometallic compounds, i.e. compounds containing a metal atom bonded to an organic group. These compounds contain a covalent metal-carbon bond. He was attempting to bring about the polymerisation of ethene at lower pressures than those used by ICI. Initially, the experiments produced ethene polymers that were not large enough to be of use. However, on one occasion they found that an experiment did not give them a polymer at all but only a dimer of ethene, i.e. only two molecules of ethene had joined together. Ziegler and his co-workers looked for the cause and after several weeks found that the vessel in which the reaction had been performed contained a small amount of a nickel compound that remained after a previous experiment.

Ziegler and his co-workers then began a systematic investigation of the effects of nickel and various other metal compounds on the reactions of ethene. They found that some metal chlorides in combinations with organometallic aluminium compounds served as very effective catalysts for the production of polythene of a very high molecular mass and without the branching of the low-density polythene. Not only was the density of the polythene increased but so also was its melting point and this was a great advantage in subsequent applications where high temperatures are experienced, e.g. sterilising equipment for hospitals, dishwashers, etc. This high-density polythene is used for manufacturing water tanks, piping, washing-up bowls, etc.

If there are few side branches, the chains fit together more snugly. Thus, many of the polymer chains form themselves into neatly packed crystalline regions. This can be controlled to some degree by the manufacturing process used. Low-density polythene has a crystallinity of about 55-70% while in high-density polythene the amount of crystallinity is in the region of 75-95%. An increasing degree of crystallinity leads to greater strength and stiffness.

The low-density form is a very flexible material and softens at about 85 °C. It is easily moulded into a wide variety of household objects, film and sheeting. When the film is stretched it increases the proportion of crystals and makes it almost completely transparent. This, together with its flexibility and low permeability to water vapour, makes it an excellent packaging material.

High-density polythene has greater rigidity and a higher softening point, of around 120-130 °C, enabling items made from it to be steam sterilised. It has similar uses to those of the low-density variety, particularly for items such as large containers and crates.

One of the great advantages for manufacturers of high-density polythene was the fact that the polymerisation could be carried out without the need for high pressure and temperature. The catalyst which worked best was a mixture of titanium tetrachloride, $TiCl_4$, and triethylaluminium, $(C_2H_5)_3Al$. Although titanium compounds are expensive, this is not a problem as the catalyst is not used up in the polymerisation process and may be used over and over again.

Professor Giulio Natta, an Italian chemist working with the Montecatini Chemical Company in Italy learned about Ziegler’s catalysts as the Montecatini Company and Ziegler’s institute had a number of commercial contacts in common. In 1954 Natta used Ziegler’s catalysts to try to polymerise propene and succeeded in producing polypropene of high density and high melting point.

Using these new catalysts, commonly called **Ziegler-Natta catalysts**, it now became possible to make synthetic rubber identical to natural rubber (using isoprene). These catalysts also gave chemists control of the way in which the units of isoprene in rubber were joined together to give a spiral shape to the polymer molecule in rubber. It is this structure that gives rubber its elasticity. This was a great breakthrough as it allowed the manufacture of synthetic rubber with the same properties as natural rubber. In fact, the composition of rubber in car tyres depends upon the price of natural and synthetic rubber as mixtures are often used.

In recognition of their outstanding contribution to polymer chemistry, Ziegler and Natta shared the Nobel prize for chemistry in 1963.

1.4 The Story of Teflon

Teflon is the trade name of the chemical polytetrafluoroethene discovered by **Roy Plunkett** of the Du Pont company in the USA. It is used in non-stick frying pans, space suits, artificial heart valves, etc. It was discovered in 1938 and the story of its discovery is an excellent example of the importance of the 'prepared mind' when faced with an unusual observation.

Roy Plunkett was born in New Carlisle, Ohio in 1910. He graduated in chemistry from Manchester College, Ohio in 1932 and, as he could not find employment during the depression era, he went on to further studies at Ohio State University. He received his PhD in 1936 from Ohio State University and was employed as a research chemist by Du Pont. He was assigned to research on fluorocarbons as refrigerants and was using gaseous tetrafluoroethene to try to prepare a non-toxic refrigerant from it. When he turned the valve of the tank on the cylinder of this gas, nothing came out! He could not understand this as the mass of the cylinder indicated that it was full of the gas! Instead of just discarding the cylinder for a fresh one, he called his assistant, **Jack Rebok**, and checked that the valve on the cylinder was not faulty. To satisfy their curiosity, they sawed off the top of the tank and found a greasy white powder inside the tank. They immediately realised that what must have happened was that the molecules of the gaseous tetrafluorethene had polymerised to form a solid material, Fig. 1.11.

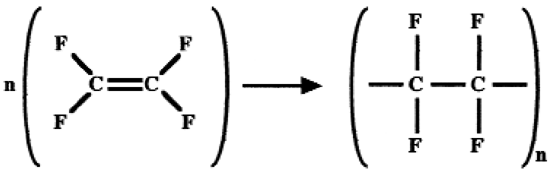


Fig. 1.11 *Formation of Teflon*

The polymerisation of tetrafluoroethene had never been observed before but clearly it had occurred inside the tank. Being a curious type of individual, Plunkett carried out some preliminary tests on it - rubbed it between his fingers, sniffed it, tested it for flammability, added some acid to it. He found that this greasy white solid had remarkable properties: it was extremely inert and was not affected by strong acids, bases or heat. He tried to dissolve it in various solvents and failed. A really unusual property of it was that it was very slippery. (It is listed in the Guinness Book of World Records as having the 'lowest coefficient of static and dynamic friction of any solid'.) The new polymer was named *Teflon* by Du Pont - the prefix 'tef' was derived from the name tetrafluoroethene and the suffix '-lon' was chosen by Du Pont for many of its products, e.g. nylon, Orlon, etc.

Although the properties of this new material were unusual, it was expensive to make and therefore further research into the polymer would probably not have been carried out on it had it not been for World War II. Scientists in the USA were involved in building the first atomic bomb and needed an inert material for gaskets that would not be affected by the very corrosive gas uranium hexafluoride, one of the materials used to produce uranium-235 for the atomic bomb. When the US army heard that Du Pont had discovered this very inert new plastic material, the polymer was tested to see if it was resistant to the corrosive uranium hexafluoride. It worked perfectly and was made into gaskets and valves. The Du Pont company produced Teflon specifically for this use during the war and its existence was kept secret until after the war. In fact, Teflon did not become commercially available until 1948 and did not become widely used until the late 1950s. The reason for this is that it took a number of years for the Du Pont chemists to understand the chemical properties of Teflon and to work out methods of producing it commercially for the manufacture of coatings, wire insulation and component parts. It was not until 1960 that the first Teflon-coated muffin tins and frying pans were manufactured commercially. Teflon was so slippery that in the early days it was found difficult to bond it to metals and it was removed by repeated scouring of pots and pans. It was not until 1986 that Du Pont solved this problem. Research at Du Pont showed that the bonding of the Teflon to the metal was improved by imbedding the polymer in the metal. This product was called Silver Stone.

However, the more important uses of Teflon are in other areas. Since Teflon is so inert, it is one of the few substances that the human body does not reject. Many people are alive today because a Teflon aorta or pacemaker has been fitted for them. Teflon is also used for artificial corneas, knee joints, substitute bones for chin, nose, skull, ear parts, bile ducts, tracheas, etc.

Teflon is the insulating material used for electrical wires and cables that must resist the radiation of the sun during space exploration. The heat shields, fuel tanks and nose cones of space vehicles as well as the outer skin of space suits are all fabricated from Teflon.

The expansion and contraction of bridges may be taken into account by placing the ends of the bridges on rollers. These rollers are often made of Teflon. Teflon coatings are used in the Statue of Liberty to insulate the copper skin from the inner stainless steel coating, thus preventing corrosion.

The discovery of Teflon is a perfect illustration of Pasteur's famous maxim: In the field of observation, chance favours only the prepared mind.

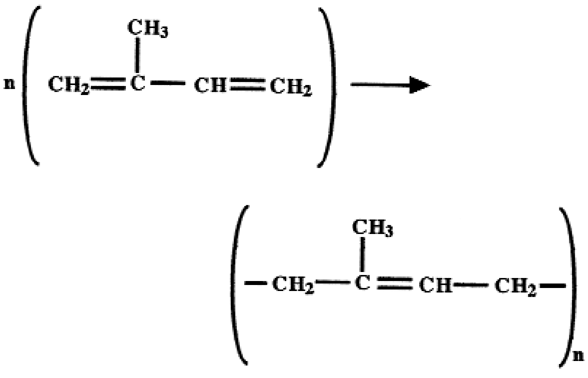
1.5 Natural and Synthetic Rubber

In the sixteenth century, Columbus noticed South American Indians playing games with a ball made from an emulsion called latex which exuded from certain types of tree. Some of this 'Indian gum' was brought back to Europe where it was observed that it could 'rub' out pencil marks - hence it was given the name rubber. For almost two hundred years no great use was made of this rubber as it became soft and sticky at high temperatures and hard and brittle at low temperatures. Although some efforts were made to manufacture shoes from rubber, people became annoyed with shoes that became stiff in winter and too soft in summer. It was an American called **Charles Goodyear** (1800-1860) who solved the problem in 1839.

Goodyear was born in Hew Haven, Connecticut, USA in 1800 and became interested in trying to change the properties of rubber to make it more useful. The work with rubber became such a compulsion with him that, at one stage, he ended up in a debtor's prison having spent all his money on research. He recognised that rubber was a good waterproofing material - in fact the Scot, **Charles Macintosh**, had used it in making coats. To try to overcome the problems of rubber becoming stiff in the winter and very soft in the summer, Goodyear tried various experiments. He was not a great chemist and it appears that a lot of his work involved trial and error - his first experiments were carried out in the debtor's prison! During one of his experiments, Goodyear accidentally allowed a mixture of sulphur and rubber to touch a hot stove. To his surprise, the rubber did not melt but only charred slightly. The physical properties of the rubber were improved in a spectacular manner - the rubber became less sensitive to changes in temperature. He nailed a piece of the rubber outside the kitchen door in the intense cold and in the morning he found it as flexible as when he put it out. In 1839 Goodyear took out the original patent for curing the rubber with sulphur but he made little commercial progress on his discovery. In 1843 **Thomas Hancock**, who was working on adding chemicals to rubber using his rubber mixing machine, took out a similar but improved patent to that of Goodyear. Hancock's co-worker, **William Brockenden**, gave it the name vulcanisation after Vulcan, the god of fire.

After the discovery of vulcanisation, Hancock developed compounds using zinc oxide, sulphur, chalk and soot (carbon black). He realised the potential for rubber and eventually persuaded a renowned botanist **Sir Henry Wickham,** to collect the Hevea seeds from the Amazon jungles, bring them back to Kew gardens in London, cultivate them and then ship them out to the colonies to establish the plantations. This is how the rubber plantations were developed in Ceylon, Borneo and Malaya.

By the year 1900, only 1000 tonnes of rubber were produced annually. However, with the development of the motor car and the need for tyres, the plantation production expanded to 300 000 tonnes by 1920. Rubber is a linear polymer of isoprene (2-methylbuta-1,3-diene), $CH_2{=}C(CH_3)CH{=}CH_2$. Natural rubber may be thought of as the product of the polymerisation of isoprene, Fig. 1.12



$$n\left(CH_2{=}C(CH_3){-}CH{=}CH_2\right) \longrightarrow \left({-}CH_2{-}C(CH_3){=}CH{-}CH_2{-}\right)_n$$

Fig. 1.12 *Rubber is a linear polymer of isoprene*

Polyisoprene in the form of latex is found in almost 2000 shrubs and trees world-wide but only one tree, *Hevea brasiliensis*, produces significant quantities of the latex. In the plantations, this tree produces about 1 tonne of solid rubber per acre per year.

Currently about five million tonnes of plantation rubber are produced annually. Very little comes from the Amazon. The trees lose their output after about forty years and they are felled and used for wood flooring. The trees are replaced by young saplings and start to produce latex in useful quantities after about 10 years. Rubber trees are a renewable resource!

Vulcanisation forms cross-links between the linear polymer chains of rubber. This stabilises the matrix of chains and caused the rubber to be less sensitive to temperature changes. Soft rubber contains about 1% to 2% sulphur and hard rubber contains up to 35% sulphur. Goodyear spent a lot of his time in court cases defending his patent and died in debt in 1860. The Goodyear Company was founded in Ohio in 1870 and his name lives on in this brand name of car tyres. It was these tyres which came to represent the major use of the improved rubber he had invented.

Once the repeating unit in natural rubber was identified, a number of attempts were made to manufacture a synthetic rubber. A number of different catalysts were tried but all without success. It was only after the discovery of Ziegler catalysts that it became possible to make synthetic rubber that is almost indistinguishable from the natural substance. As already discussed, the decision to use natural or synthetic rubber in tyres is made on the basis of the price of the raw materials.

As well as Charles Goodyear, another well-known name in the rubber industry was that of **John Boyd Dunlop** (1840-1921). Dunlop was born in Ayrshire, Scotland. He began studying as a veterinary surgeon at Irvine’s Academy in Edinburgh and at the early age of 19 was awarded the diploma that enabled him to start work as a veterinary surgeon. He began a successful career and in 1867 after eight years working in Edinburgh he moved to Belfast where he set up his practice. Over the next twenty years he became well established and became a valued member of the profession.

Dunlop’s life would probably have been uneventful were it not for the fact that bicycles were becoming extremely popular at the time. However, the bicycles at the time were not very comfortable due to the solid rubber tyres. Dunlop himself suffered from ill health and the constant shaking of the bicycle as he cycled around the cobbled streets of Belfast was not very helpful for his delicate bones! He set about solving this problem and his first idea was to take a length of rubber tube, fill it with water and fasten it around the wheel. It didn’t work! He then thought about filling the tube with air under pressure. He nailed a tube of linen cloth around a solid wooden disc that was the same size as a bicycle wheel. He then inserted a rubber tube filled with air inside the linen tube. To test the air cushioned disc he rolled both the disc and a conventional bicycle wheel down along a cobbled courtyard. The disc he made went faster and further than did the bicycle wheel. In addition, the disc did not vibrate or wobble as much as the wheel did. Dunlop was convinced of the worth of his idea. After devising a simple one-way valve to take the air into the tube, he commissioned a local bicycle manufacturer to build a complete tricycle fitted with the pneumatic tyres that he had designed. He demonstrated the model to a number of businessmen and was encouraged by the response. He was granted a patent for his invention in 1888 and the ‘safety bicycle’ (so called because if you fell off it you had less distance to fall than with a penny-farthing) with pneumatic tyres had been born. Dunlop’s invention was timely, as cycle racing had become an extremely popular sport in the 1880s. The new pneumatic tyres were a tremendous success in the field of racing and this sport helped to put Dunlop’s invention before a very wide audience. The old solid rubber tyres were abandoned by cyclists in favour of the pneumatic ones. By this time Dunlop was thinking of retirement and sold his patent rights for a relatively small amount of cash and shares in a new company called the Pneumatic Tyre and Booth’s Cycle Agency set up in Dublin. The tyres did sell very well but there were some initial problems. One of these problems was repairing a puncture. As the tyres were glued to the wheel and not easily detached, repairing a puncture required a major effort.

In 1890 Dunlop was officially informed that his patent was invalid because a patent by **Robert William Thomson** for a pneumatic tyre (called an ‘aerial wheel’ at the time) in 1846 had pre-dated Dunlop’s patent. This meant that other companies were free to make and sell pneumatic tyres. Dunlop was disillusioned and in 1895 he resigned from the company having made a profit of £100 000. However, his name was incorporated into the new name of the company, the Dunlop Rubber Company, in 1900. Dunlop spent a happy retirement in Dublin until his death in 1921, The company which he founded went from strength to strength with the dawn of the age of the motor car.

1.6 Polyvinyl Chloride

Polyvinyl chloride (PVC) is one of the most common plastics we see around us. (The systematic name for PVC is polychloroethene but this is rarely used outside the academic world.) When we hear the term ‘plastic money’ used to refer to the use of credit cards, the plastic in question is PVC, as rigid PVC is used to manufacture these cards. PVC is one of the most commonly used plastics in our lives and many of its uses are not apparent, e.g. in a house it insulates the wiring behind the wall (flexible PVC) and the pipes under the floor of the house are often made from rigid PVC. Although PVC occurs widely in our lives, it is not readily recognisable. The plastic window frames, the multi-coloured floor covering and the shiny kitchen apron are all made from PVC.

PVC is second only to polythene in terms of quantity used. PVC has an increasing number of uses and European consumption has more than quadrupled over the past twenty-five years. The many uses of rigid PVC and flexible PVC have already been discussed.

The origins of PVC lie in the search for alternatives to the highly flammable plastic celluloid. Originally it was made in 1912 by reacting ethyne and hydrogen chloride and polymerising it to PVC. However, the product formed was unsatisfactory and alternative methods of production were explored. Hydrochlorination of ethyne remained the main route to the vinyl chloride monomer until the 1950s when the present process based on ethene and chlorine was developed.

Although PVC is a thermoplastic and may be softened at only 100 °C, it is not suitable to be moulded in this form as it loses its colour and decomposes readily, giving off hydrogen chloride. It is also unstable in the presence of sunlight. In the 1930s, materials were developed which could be added to the PVC during manufacture and which would help to improve its properties. These include heat stabilisers, lubricants and processing aids which affect the behaviour of the polymer during processing and are essential ingredients in most PVC formulations. Other additives affect the appearance or properties of the finished article and are optional, depending on the application concerned. If transparent PVC is required, e.g. for packaging, the additives must be chosen with particular care.

The unpromising properties of raw PVC can thus be transformed into desirable attributes by a range of additives. Stabilisers inhibit decomposition, allowing higher temperatures to be used for softening, while lubricants help the softened mass to flow more easily. Modified in this way, PVC can be extruded in continuous lengths (e.g. pipes, window frames and guttering), rolled into flat sheets (e.g. credit cards) or moulded by various techniques. Adding pigments and fillers to the mix provides colour and opacity; impact modifiers can be incorporated to improve toughness and uv stabilisers, which prevent degradation by sunlight, can also be added. In addition, it is now possible to produce various grades of PVC suitable for a wide range of applications.

Regardless of shape or colour, however, the products would all be hard and rigid at room temperature. Only thin sheets and bottles would show a small degree of flexibility, but even they would be stiff for their thickness. The product, rigid PVC, is a thermoplastic and is capable of being moulded into various shapes. Intermolecular attractions hold the polymer molecules in fixed positions, preventing flexibility.

Another additive - one whose molecules can get between the polymer chains, reducing the intermolecular forces of attraction which hold the polymer chains together - allows the plastic to become flexible. This is the role of a plasticiser, conferring softness to the otherwise rigid solid. If enough is added, the softening point is lowered to well below room temperature and the product becomes completely flexible as in garden hoses, wiring insulation or leather-cloth.

Plasticisers also allow more flexibility in the usage of PVC, opening up a wide range of applications quite separate and distinct from those of the rigid unplasticised form, commonly referred to as uPVC, i.e. unplasticised PVC.

PVC is unique in being compatible with such a wide range of additives, each application requiring a particular blend to provide the desired combination of properties. The range of additives used includes the following.

Heat stabilisers inhibit the thermal degradation of PVC, e.g. by reacting with the released hydrogen chloride, which would otherwise act as an autocatalyst for the decomposition.

Lubricants function by reducing viscosity, thereby improving flow, or by preventing the melt sticking to the mould, again helping flow but also improving the product’s surface finish.

Processing aids increase the elasticity of the melt, so that it does not shear apart as it flows along the mould or between the rollers of a calendering machine.

Impact modifiers provide extra toughness by increasing impact resistance, especially at low temperatures.

Plasticisers transform the rigid polymer into one that is more rubbery and flexible by interfering with the intermolecular attractions that hold the polymer chains in rigid positions.

Light stabilisers inhibit degradation of the PVC by the ultraviolet radiation in sunlight.

Pigments or dyes provide colour for the otherwise colourless polymer. White is also considered a colour, requiring a pigment such as titanium dioxide.

Fillers can improve impact strength, stiffness, or electrical properties and also extend the bulk and thus reduce costs.

Why is PVC so widely used? The choice of material for any job depends on many factors, but above all it must be suitable for the purpose. Additives are the key to the versatility of PVC and a major reason for its success. The properties, inherent or brought about by the addition of additives, that make PVC an ideal choice for so many diverse applications include the following.

- *Strength* and *toughness* for building materials, pipes, conveyor belts, footwear, bottles and packaging.

- *Water resistance* for reservoir/pool liners, vehicle underseal, protective clothing and to provide wipe-clean surfaces for furniture, floor and wall coverings.

- *Chemical resistance* for vessels and pipework in chemical or food processing plants and laboratories.
- *Abrasion resistance* for flooring.
- *Durability* resulting from the above characteristics, colourfastness and freedom from corrosion or rotting.
- *Low maintenance* since periodic repainting is not required.
- *Excellent insulation* properties for cables and wiring and moulded-on plugs for appliances.
- *Stiffness* or *flexibilit*y as required from rigid window frames to flexible packaging film.
- *Good fire resistance* for building materials and electrical applications. It is self-extinguishing, i.e. it does not continue to burn when the source of flame is removed.
- *Optical transparency* similar to glass without the weight, thickness or brittleness - perfect for packaging.
- *Inertness* prevents contamination of package contents - approved for contact with food, pharmaceuticals and medical products.
- *Low permeability* to gases for food packaging.
- The heat shrinkage property of PVC is ideal for shrink-wrap packaging.

Another advantage of PVC is the relatively low dependency on oil. Only 43% of the mass of the PVC molecule is derived from oil - the remaining 57% (chlorine) comes from salt. It is consequently less affected by fluctuating oil prices than other plastics.

In addition there is considerable energy saving during production as the production of PVC consumes less energy than that of say, aluminium, copper, steel, nylon, polystyrene, etc. It does, however, consume more energy than polythene or polypropylene. Low consumption of energy benefits prices and energy conservation. The lower melting point of thermoplastics also means that much less energy is required to mould them than to fabricate metals.

When PVC is being used in various products, it is also responsible for saving energy. Most of the PVC produced is used in long-term products. Durability reduces the energy required for maintenance, e.g. eliminating the need for painting, repairing and replacement. Lightness in packaging, particularly bottles, reduces the energy required for transport. A litre of cooking oil in a glass bottle is 38% heavier than in a PVC bottle. This cuts down considerably on transportation costs.

PVC as a Packaging Material

Rigid PVC is an ideal packaging material, being light, tough, shatterproof and, when required, crystal clear. Food containers are the most obvious example, but we also find it in bottles and tubs for toiletries and cosmetics, and blister packs for pharmaceuticals and DIY goods. However, because of the international trend away from PVC as a packaging material, other plastics are replacing many of these applications.

In the supermarket fruit and vegetable section, the cleanliness and shine of PVC containers projects an image of freshness, hygiene and quality. The combination of transparency and resilience allows customers to inspect the contents without causing contamination or damage. For some foods, air in the sealed pack is replaced with nitrogen to prevent oxidation during storage. Rigid PVC is 20-40 times less permeable to oxygen than other plastic films, so is also ideal for this purpose. Meat packaging on the other hand requires a limited permeability to oxygen to maintain a fresh red appearance. Plasticising the PVC increases its permeability and by careful formulation a suitable degree of permeability is obtained.

The safety of plastic bottles compared with glass is obvious but their lightness is more significant. It makes them easier for the shopper to carry, allowing larger volumes per bottle, with consequent price savings. PVC bottles are used in preference to polythene when high clarity is desired or when low oxygen permeability is important to prevent oxidation, e.g. for vegetable oils. Their carbon dioxide permeability is also low, although not quite as low as PET, which is more suitable for packaging highly carbonated drinks.

Plastic bottles also save energy costs as they are lighter than glass. Improved formulations and new processing methods, e.g. stretch blow moulding, can make further savings. A modern PVC bottle is nearly 30% lighter than its 1975 glass counterpart.

The use of plastics, especially in packaging, has been portrayed by some environmentalists as squandering our diminishing oil reserves on materials which are soon thrown away but are not biodegradable, thereby causing long-lasting litter problems.

To put this into perspective, we must remember that over 80% of crude oil is converted into fuels and burned away. Only 4% is used to make plastics, less than half of which becomes packaging. One cannot realistically blame any pending shortage of oil on packaging, nor on the plastics industry as a whole. Only 12% of PVC is used for consumables, while 64% is incorporated into articles with a long life expectancy. Disposal is therefore less of an immediate problem.

In a landfill, PVC is as inert as it is in the open. The polymer itself does not decompose and the additives are not leached out in significant amounts. It is very wasteful to simply bury plastics in landfill sites. The problem is that once buried, a potentially useful material and its energy content are lost. It is far better to re-use plastics instead. The recycling of plastics is covered in the next section.

1.7 Recycling of Plastics

The world's production and use of plastic material has increased from less than 5 million tonnes in the 1950s to about 80 million tonnes today. Annual consumption of plastics in Western Europe is 28 million tonnes. In total, Western Europe produces some 11.5 million tonnes of plastics waste each year. An average European family of 4 throws away around 40 kg of plastics each year.

There are a number of reasons why it is necessary to recycle plastics.

(i) Plastic recycling saves natural resources. Most plastics are produced from oil and therefore contribute to the depletion of that limited resource. Coal and natural gas are also used in the production of some plastics. Using these resources for short-life products that end up as waste, is cause for concern.

(ii) Plastic recycling makes economic sense. It is predicted that oil prices will continue to increase as global resources are depleted. Recycling plastics will significantly decrease the cost of plastic production when oil becomes too costly a raw material.

(iii) Recycling of plastics cuts waste disposal costs. Plastics make up 8% by mass of municipal solid waste and as much as 20% by volume. Although plastic has a high calorific value and could be incinerated to produce heat, most waste plastics end up in landfill sites. One of the great advantages of plastics - their durability - now becomes a vice. It can be argued that they provide a stable base for landfill, as they are chemically inert. However, the fact that plastics are contributing to the growing quantities of non-degradable solid waste in our landfill sites is cause for concern.

(iv) Plastic recycling reduces litter. Plastic bottles, bags and plastic ring holders for six-packs are all too familiar types of litter. These materials do not degrade and represent some of the worst forms of litter.

(v) Plastics recycling creates employment. Research and development in plastics recycling and the resulting initiatives have provided employment for a whole range of workers in a wide variety of areas.

The commonly used plastics have been given a code number that is found on many products. This coding system may be used to help identify plastics when separated by hand, Fig. 1.13. The triangular symbol indicates that the product may be recycled.

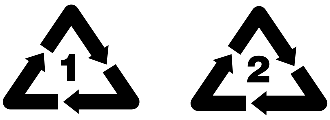


Fig. 1.13 *Coding symbols for recycling plastics*

Thus, the advantageous properties that have been used to create an industry are now seen by some to cause problems once their useful life has finished. As mentioned above, they are inert, so cause no problems in landfill sites - in fact plastic materials are used to line landfill sites to prevent leaking into watercourses. However, they do take up space and could be reclaimed into secondary uses. Most plastics are made from petroleum and could be used as a fuel alternative, having recoverable energy values greater than paper or wood and, depending on the actual type of plastic, recoverable energy values greater than coal. Over 90% of West European petroleum feedstock is burned for generation of power, heating or transport. The 4% of petroleum used for the manufacture of plastics could be reclaimed in this way.

Municipal solid waste contains plastics mainly in the form of sheet films, trays, bottles and tubs. This form of plastic waste amounts to around 8 – 8.5 million tonnes a year in Western Europe. Municipal solid waste also contains used plastics from large domestic articles like old refrigerators, freezers, washers and TV sets. If segregated before entering the waste stream then a good proportion of this plastic can be reclaimed. Other areas where plastics can be recovered are the agricultural, transport, construction and the distribution business sectors. Adding used plastics from these sources it is estimated that approximately 10-13 million tonnes are available for reclamation in Western Europe.

Where it is easy to segregate and collect used plastics, e.g. recycling of polyethylene agricultural films and shrink wrap packaging from supermarket distribution chains, profitable recycling activities have been established for many years. Recycling rates of over 40% have been achieved in the latter sector.

Recycling of plastics, which are disposed of at home, has not yet been very successful because of the difficulties associated with collection and segregation. This can be very costly in time, wages and particularly fuel for transport and these costs could outweigh the savings in materials that can be achieved. However, renewed efforts are being made to recover and recycle from this source. Many schemes to evaluate the most effective procedures are now in operation all over Europe.

How much used plastic is it feasible to recycle or reclaim? This is not an easy question to answer but some studies have been carried out to estimate potential recovery rates and how much of the recovered material it is possible to reclaim. Some studies in the UK have indicated that it could be feasible to expect no more than 50% of materials from municipal solid waste to be separated, cleaned and made available for reprocessing. This figure is supported by estimates made in Switzerland, which suggest a figure of 45%.

Some countries that incinerate municipal solid waste and recover the energy by using it to heat industrial parks, municipal offices or housing estates can claim to recover almost all the plastics in their domestic waste streams. Denmark burns 70% of its municipal solid waste, 60% with energy recovery, and it is estimated that this boosts its recovery of all used plastics to approximately 50%. On the same basis, the figure from Switzerland is around 70%. However, the UK, which incinerates only 2% of its municipal solid waste with energy recovery, could only claim to recover about 6%.

The European Commission is taking positive steps to encourage material recycling and a recent directive targeted at packaging is suggesting that 60% of recovered material should be recycled. Recycling of used plastics is now being practised widely throughout Europe. There are now over 500 recycling companies in Europe. One of the most successful businesses is the recycling of used polyethylene films. One UK company recycles approximately 10 000 tonnes in the manufacture of plastic refuse sacks and agriculture mulch films. Another company mixes industrial waste plastic with that recovered from the distribution sector and manufactures extruded sections similar to wooden planks or metal rods. These sections can then be used to construct a wide variety of products like outdoor furniture and agricultural fencing. Similar sections are used for protection of river banks and seashores from water and coastal erosion.

If extruded in the form of reinforced sheet (approximately 2 - 4 cm thick) the products are used for construction of pigsties and other farm structures to contain animals. This is an ideal end use where the rot-proof properties and resistance to wet, humid and harsh conditions are highly beneficial.

Old telephone handsets have been recycled for many years back into new ones or alternative products. Plastic casings from old car batteries become new cases or horticultural plant containers. Scrap from industrial processes like manufacture of piping, thermoforming of cups, trays, buckets and tubs, are all recycled consistently with considerable success. Reprocessing the material back into the original product is the usual practice here. Where this is not possible the surplus is cleaned and re-granulated by secondary processors and either used or sold back into the market.

Surplus industrial polyethylene terephthalate (PET) has been recovered as fibre for manufacture of anoraks, duvets, carpets and filter cloths. (PET is the material in large clear plastic bottles used for soft drinks.) This business is now extending to recycling of soft drinks bottles into similar products.

There are three plants in Northern Ireland currently recycling scrap plastics. They accept sorted plastics from industry and merchants. The plastics are cleaned and melted down to produce granules that are subsequently sold to the manufacturing industry for use in the production of a range of non-food contact packaging such as flower pots and kitchenware. To meet the requirements of these plants, a number of merchants now collect plastics from industrial and commercial outlets. Materials include packing plastic, clothes hangers and pre-domestic consumer packaging.

In the Republic of Ireland, only a limited quantity of the wide variety of plastics is recycled at present. One company, Wellman International, uses PET. Wellman was set up in Ireland in the late 1970s (before PET bottles came on the market) to recycle polyester fibre and the PET used in X-ray film, etc. Now they have a central collection depot in Holland that collects PET bottles in Europe. They grind it into flake which is then shipped to Ireland to be converted to fibre. Another company recycles contaminated industrial and mixed household waste for conversion to many useful products, such as slatted flooring for animals.

Waste PET bottles are a source of quality material for the manufacture of fibres for the textile industry. Students will be aware of the typical ‘fleece’ jackets they buy in the shops. These jackets are made from the PET polyester under the brand name of POLARTEC. A typical 1.5 m length of this fabric is made from fifteen recycled 2.2 litre bottles! A typical fleece jacket may therefore contain 10 to 20 recycled bottles depending on the size of bottle!

Off-cuts and extruded PVC sections used in the manufacture of doors, windows and secondary glazing have also been recycled effectively and, as is the case for PET recycling, the PVC users are looking to use PVC bottles as a raw material. In recent times companies have been set up to separate PVC, PET and polyethylene bottles collected from public sources. Other companies have been formed to collect plastic bottles for recycling and are working with local authorities and supermarkets to recover these containers. Polythene is separated by water flotation as PVC and PET are both more dense than water and will sink. The PVC and PET are then separated by use of an X-ray detection device that recognises the chlorine in PVC and activates a separation procedure.

Technology is being developed in France which recycles used PVC mineral water bottles back into new pipes, cable coverings, shoe soles, etc. Polypropylene bumper bars from cars are now being collected and recycled back into new ones by Dutch companies.

In the UK there is now a polystyrene recycling organisation that is targeting fast food outlets, vending machines and other sources for used materials. Polystyrene can be used very effectively in building, where its thermal insulation properties are exceptional.

As public interest and participation in recovering materials increases, so will industry develop better processes and products. Wherever clean, so-called generic materials can be segregated, the value is high and end-uses are available.

Even the mixed plastic materials recovered from domestic household waste can be recycled. Technology is available which will take the whole of this mixture without separation, shred it, melt it and extrude it into either long ‘timber-like’ sections or sheet structures suitable for partitions or even moulded articles. As used plastics are collected on a consistent and regular basis industry is slowly investing to make use of this valuable raw material.

It is very important when considering recycling operations that the end-use really has a value. It is not very helpful to the environment or conservation of resources if the very process of recycling uses up more oil, energy and resources than it saves. The overall environmental equation has to balance for this to be worthwhile. A very useful technique to apply to the area of industrial operations and product manufacturing is ‘eco-balance’ analysis. This type of analysis monitors the whole life cycle of a product from the very beginning: the amount of raw material and energy used and the amount of solid, liquid and gaseous emissions produced until final disposal. This technique is now being developed to conduct environmental accounting, in a similar way to financial accounting, to ensure that materials are used with maximum effectiveness and minimum environmental impact.

Note

Sorting of plastics is simpler if restricted to bottles, which comprise half the plastics in domestic waste, and are predominantly either PVC, polythene or PET - hence plastic bottle banks and kerbside collection schemes are now found in some countries like Germany. The three types are sorted manually by sight, though at present the enhanced value does not compensate for the labour costs involved.

Mechanised separation is a complex task, but PVC helps by having a unique marker - the chlorine atom. The use of X-rays allows PVC bottles to be distinguished from polythene and PET, which are then separated by density difference. A process, patented by the USA company National Recovery Technologies, is being developed in the UK by Reprise Ltd, jointly owned by European Vinyls Corporation and PVC Reclamation Ltd. In Italy, Tecoplast, in which European Vinyls Corporation has an interest, has developed an automated sorting process and a reverse vending machine which will only accept plastic bottles, and issues a refund token.

Reprise was set up in 1990 primarily to reclaim PVC from industrial scrap as well as bottles. Sources include European Vinyls Corporation’s own in-house waste, scrap cables (after recovery of the copper) and vinyl wall coverings (after recovery of the paper). Applications of recycled PVC include drainage and sewerage pipes, shoe soles, flooring and non-food packaging. Once the separation technology has proven itself, Reprise will encourage local authorities and waste-management companies to take it up, with a guarantee that the industry will buy back the reclaimed polymers.

CHAPTER 2 ELECTROCHEMISTRY

2.1 Introduction

Electrochemistry is the branch of chemistry where the use of electrical energy to bring about chemical reactions and the generation of electrical energy from chemical reactions are investigated.

A voltaic (galvanic) cell is one where electrical energy is generated from chemical reactions. In a voltaic cell or galvanic cell electricity is generated in an apparatus containing electrodes joined by a conductor and immersed in an electrolyte. Everyday ‘penlight’ type cells and car batteries are examples of chemicals producing electrical energy as required.

Electrolysis is the breaking up of a chemical due to the passage of an electrical current through it or a solution of it. The chemical or solution of the chemical through which the electricity passes is called the electrolyte. Electrolysis is carried out in an apparatus called a voltameter or electrolytic cell that consists of electrodes and a container holding the electrolyte.

Electrodes are conductors which carry the current from the external circuit to the chemical or solution of the chemical. Electrodes are commonly made of graphite or platinum. If the electrodes participate in the electrolysis reactions, e.g. copper in the electrolysis of aqueous copper sulphate, they are termed active electrodes. If the electrodes do not participate in the electrolysis reactions, e.g. platinum in the electrolysis of acidulated water, they are termed inert electrodes. In electrolysis the negative terminal of the battery is connected to the electrode called the cathode and the positive terminal of the battery is connected to the electrode called the anode (The mnemonic CNAP is helpful is remembering this in electrolysis.) Reduction takes place at the cathode and oxidation at the anode (CROA). The latter is more useful as it also applies to galvanic cells. In a galvanic cell, reduction takes place at the cathode and oxidation at the anode (CROA) but in this case the anode is the negative electrode and the cathode is positive.

Electrons flow from the negative terminal of a cell to the positive terminal. Electrons are charged species and therefore charge flows as the electrons move through the conductor *en route* from negative to positive terminal. The symbol for charge is Q and it is measured in coulombs (C). One mole of electrons carries a total charge of 96 500 C and this quantity of charge is given a special name - the faraday.

Charge on one electron $= 1.6 \times 10^{-19}$ C

Number of electrons in a mole $= 6.022 \times 10^{23}$

Charge on one mole of electrons $= 1.602 \times 10^{-19} \times 6.022 \times 10^{23}$

$= 96\ 472$ C

$\approx 96\ 500$ C

$= 1$ faraday

The electric current, i.e. the rate of flow of electric charge, I, is the charge which passes a particular point in one second. If a charge of one coulomb passes in one second the current flowing is one ampere or one amp. Originally it was thought that electric current was a flow of positive charge from a positive terminal to a negative terminal. When it was established that electric current in a metal is actually a flow of electrons from negative to positive, it was decided, to avoid confusion, not to correct the notion that electric current flows from positive to negative - provided it is understood that electrons are actually travelling in the opposite direction.

Quantity of electric charge (coulombs) =
current (amps) × time (seconds)

$$Q = I\,t$$

Electrons will only flow from one point to another if there is an electrical potential difference, V, measured in volts, between the two points. A potential difference exists between two points if energy is released or required to move a charge between them. Energy is released if a positive charge is moved towards a point of lower potential, i.e. towards an environment of greater electron density, and is required if the positive charge is moved towards a point of higher potential.

In a voltaic cell a potential difference is generated between the electrodes by spontaneous chemical reactions which occur at the electrodes. In electrolysis a battery or other electrical power supply maintains a potential difference between the electrodes and causes non-spontaneous chemical reactions to take place.

The definitions given here are required in the description of generating electrical energy from chemical reactions, section 2.2, and in the electrolysis of molten and aqueous electrolytes, section 2.3.

2.2 Generating Electricity from Chemical Reactions

Galvani, Volta, Davy and Faraday

In 1786 the Italian physician **Luigi Galvani** (1737-1798) discovered 'animal electricity'. He observed contractions in the muscles of frogs' legs which were hooked to an iron bar by brass hooks. Galvani thought that this was a property peculiar to an electrical fluid in animal tissue. He was later shown to be incorrect in his account of the twitching of the frogs' legs. However, Galvani is given the credit for finding the method for the production of an electric current which requires two dissimilar metals in a moist conducting solution and thus inspiring Volta to invent the battery.

Galvani is remembered when measuring small quantities of current using a device called a galvanometer and in the term 'galvanising' which involves coating iron and steel with zinc. The zinc coat provides electrochemical protection of the iron from corrosion as the outer zinc layer is more easily oxidised than iron. Galvani's name is used for the sensation of pain in the mouth when a piece of metal, e.g. foil from chocolate wrapper, makes contact with saliva in the mouth and the metal of a dental filling. This is termed 'Galvanic pain' and is caused by an electrical current being generated in the circuit consisting of the two dissimilar metals and the saliva electrolyte. This current stimulates a nerve and causes a pain to be registered. Galvani's name is used also for the change in the electrical resistance of the skin due to changes in the behaviour of the sweat glands when stimulated by the sympathetic nervous system under conditions of attention, stress or emotion. This is called the 'Galvanic skin response' and is monitored by the polygraph or lie detector to give an indication that a person is lying. Lying requires more attention than telling the truth and therefore is stressful and stimulates sweating and changes in the skin's response to the passage of weak currents through it.

Count Alessandro Giuseppe Volta (1745-1827) was an Italian physicist who, having read about the 'animal electricity' experiments of Galvani, invented the first battery, known as the 'Voltaic pile' in 1800. This device was the first source of continuous electric current in modern times. (There is some archaeological evidence, in the form of porous pots containing traces of metals that have been found in digs in the Middle East, that earlier civilisations might have had a similar device.) Volta showed that the ‘animal electricity’ reported by Galvani was not unique to animal tissue and could be produced with solutions not associated with living tissue. He used alternating plates of zinc and silver separated by discs of paper or leather soaked in salt solution. By increasing the size of the plates and/or the number of plates the size of the electrical effects observed increased. Of course, in the early 1800s there were no electrical appliances for the battery to operate and Volta had to content himself with passing the current produced through people to demonstrate its abilities. The unit of electrical potential, the volt, is named in his honour.

Sir Humphry Davy (1778-1829) was an English chemist who pioneered the use of electricity in chemical experiments. In 1801 Davy was appointed as a professor in chemistry to the recently established Royal Institution. He was a talented lecturer and demonstrator and his lectures were fashionable social events. Between 1807 and 1808 he used electrolysis to isolate for the first time the elements sodium, potassium, magnesium, calcium, strontium and barium. The salts of these metals could not be reduced by roasting or by reducing agents. The miner’s safety lamp was another achievement of Davy’s. Davy also promoted the career of Michael Faraday, whom he chose as his assistant at the Royal Institution.

In 1813 **Michael Faraday** (1791-1867) was appointed an assistant to Sir Humphry Davy and later became Davy’s successor at the Royal Institution. Like Davy, he was a talented experimentalist and has several important discoveries in physics and chemistry to his credit. In 1825 he discovered benzene. He investigated the amounts of substances discharged at the electrodes during electrolysis and in 1834 published two laws now known as Faraday’s laws of electrolysis. Faraday investigated electromagnetic effects, and in 1831 demonstrated electromagnetic induction which led to the invention of the electrical generator. He also proposed the idea of electrical lines of force.

He instigated the Royal Institution science lectures for children, which are still delivered every Christmas in the original Royal Institution lecture theatre used by Davy and Faraday. The BBC normally televises these lectures. Michael Faraday has the singular honour of having two SI units named after him, the **faraday**, which is the quantity of charge in a mole of electrons, and the **farad**, which is the unit of electrical capacitance.

Cells

A voltaic cell is a device in which electrical energy is generated from chemical energy. Galvani, unknowingly, described the first electrical cell. A battery is a number of cells joined together, usually in series, i.e. alternate positive and negative terminals joined by a conductor. Volta described the first battery, his Voltaic pile. In a cell there are always two different substances, often elements, the electrodes, in contact with a moist electrolyte. One substance undergoes oxidation, the other reduction. The electrodes are separated by the electrolyte and therefore the electrons lost in the oxidation of one element must flow via an external circuit to the other element. In the absence of this conducting path no reaction can proceed at either electrode because oxidation and reduction must occur simultaneously. Oxidation is the loss of electrons from a species. Another species must accept the electrons lost by the metal. These two processes which occur during a redox reaction are called half-reactions and when added together give the overall reaction. The same number of electrons must be transferred in each half-reaction. Cells often use metal electrodes but can also be designed to have liquid or even gaseous electrodes.

The Simple Cell

A device called the simple cell may be used to demonstrate that reactions occur at the electrodes and that electrical energy is produced in a voltaic cell. One type of simple cell consists of a zinc plate and a copper plate dipped in dilute sulphuric acid, Fig. 2.1. The metals are connected to a small bulb. (The bulb must be of very low voltage, e.g. about 1.0 V.)

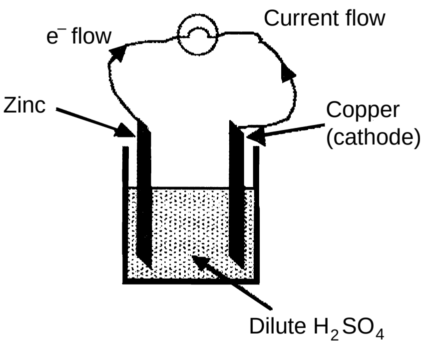


Fig. 2.1 *A simple cell*

Zinc loses electrons and dissolves in the solution as zinc ions. At the other electrode reduction of hydronium ions in solution takes place and bubbles of hydrogen gas appear at the copper rod. The electrons lost by the zinc flow through the bulb, causing it to light, and are consumed in the reduction of the hydronium ions. Zinc ions drift away from the zinc plate (which is called the anode) and hydronium ions drift towards the copper rod (which is called the cathode). The half reactions and cell reaction for the simple cell are as follows.

Anode reaction (oxidation)

$$Zn \rightarrow Zn^{2+} + 2e^-$$

Cathode reaction (reduction)

$$2H^+ + 2e^- \rightarrow H_2$$

Cell reaction

$$2H^+ + Zn \rightarrow H_2 + Zn^{2+}$$

The simple cell has two serious defects that make it impractical as a useful source of electric current. Electrochemical reactions occur between impurities in the zinc and the acid electrolyte. This is called **local action**. As a result the zinc wears away even when the cell is not in use. In addition, when the cell has been in use for some time bubbles of hydrogen gas accumulate at the cathode. This is called **polarisation** and its effect is that an electrochemical reaction also takes place between the hydrogen gas generated at the cathode and the zinc electrode. This reaction tends to drive a current in the opposite direction to that produced by the copper/zinc cell and so reduces the net emf and hence the overall current available from the cell.

If one wishes to light the bulb for a longer period of time, one could use more chemicals in a larger container which will provide and consume electrons at the same rate but for a longer period. If one wishes to make the bulb glow brighter one can try to find a different combination of electrode materials which will provide and consume electrons at a greater rate and therefore generate a larger current or one could join two or more cells together in series. Then the flow of electrons from one cell adds to the flow from the other cell(s) giving a larger current.

Which combination of electrode materials used in a simple cell gives the greatest potential difference between the electrodes? To investigate this, the electrode materials must be systematically tested to establish which elements lose electrons most readily. This will be discussed further in the section dealing with the Electrochemical Series (p. 23).

The Dry Cell

The dry cell takes its name from the fact that the electrolyte, while moist, is made into a paste and therefore cannot spill. The dry cell, unlike some earlier cells, is quite portable. The user does not have to keep the cell upright to avoid spilling the electrolyte. It is therefore a good source of energy for small electrical appliances, e.g. torches, bicycle lamps, Walkmans, TV remote controls, etc. The construction of one type of dry cell is shown in Fig. 2.2. The case, which acts as the anode, is made of zinc. The cathode is a graphite rod and is placed at the centre of the cell. A spacer at the base of the carbon rod prevents it from making electrical contact with the base of the zinc case. There is a brass cap at the top of the carbon rod to make good electrical contact with the appliance to which it is required to supply current. The electrolyte is ammonium chloride made into a paste by the addition of water and flour or sawdust. A porous paper lining inside the zinc case separates the zinc from making direct contact with the electrolyte. A muslin bag containing a mixture of manganese dioxide and powdered graphite is arranged around the cathode. The purpose of the powdered graphite is to reduce the internal resistance of the cell and hence increase the maximum current obtainable from the cell. The contents of the cell are sealed in with pitch to avoid leakage.

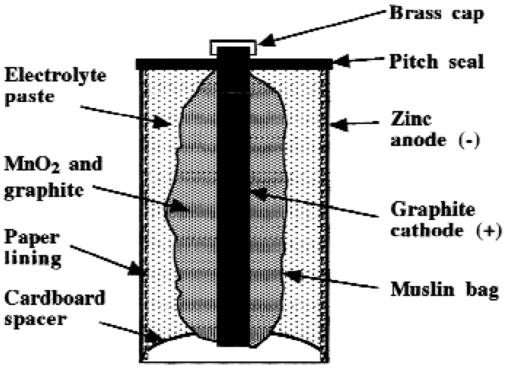


Fig. 2.2 *Dry cell*

During operation, the zinc becomes oxidised and zinc ions enter the electrolyte. The electrons lost in this process flow via the external circuit through an appliance and reach the cathode.

Anode reaction (oxidation)

$$Zn \rightarrow Zn^{2+} + 2e^-$$

At the cathode, a complex reaction takes place that may be represented as follows.

Cathode reaction (reduction)

$$2MnO_2 + 4NH_4^+ + 2e^- \rightarrow 2Mn^{3+} + 4NH_3 + 4OH^-$$

The cell reaction is obtained by the addition of the anode and cathode reactions.

Cell reaction

$$Zn + 2MnO_2 + 4NH_4^+ \rightarrow Zn^{2+} + 2Mn^{3+} + 4NH_3 + 4OH^-$$

A dry cell like this is capable of generating an emf of about 1.5 V. If the cell is used for a prolonged period of time, ammonia gas accumulates around the cathode and insulates it from electrochemical action. The cathode is said to have become polarised. If the cell is allowed rest, the zinc ions formed in the anode reaction combine with the ammonia gas from the cathode reaction to form the complex $Zn(NH_3)_4^{2+}$. This removes the ammonia gas and the zinc ions keeping the potential difference between the terminals fairly constant during the lifetime of the cell and allows the electrochemical action at the cathode to resume. Cells of this type are often observed to recover if left for a time after having been ‘run flat’.

Electrochemical Series

The electrochemical series is a list of metals and other species (ions) in order of their decreasing tendency to undergo oxidation. For the purposes of an initial discussion only metals will be considered, with the element hydrogen as a reference. The metals are placed in the electrochemical series:

(i) in order of decreasing tendency to undergo oxidation (i.e. to lose electrons);
(ii) in the order in which one metal replaces another from a solution of a salt of the latter;
(iii) in order of the their increasing electrode potentials.

This order of metals in the electrochemical series is similar but not identical to the order of metals in the activity series. In the activity series the order is based on decreasing reactivity and is based on the vigorousness of the following reactions of the metals:

(i) reaction with water;
(ii) reaction with acids;
(iii) stability of compounds of the metals upon heating;
(iv) difficulty of reduction of metal oxides.

The electrode potential of an element is the potential difference between the element and a 1 M solution of its ions at 25 °C.

There is no satisfactory way of measuring this potential difference directly.

The standard electrode potentials of all metals are measured with reference to the standard hydrogen electrode. This consists of a platinum wire dipped in a one molar solution of hydronium ions. There is a constant stream of hydrogen gas bubbling over the platinum wire at a pressure of 1 atmosphere and a temperature of 25 °C, Fig. 2.3. A standard electrode for a metal consists of a piece of the metal immersed in a one molar solution of its ions at 25 °C. The standard hydrogen electrode is assigned a potential of zero volts. This arbitrary assignment of a value is equivalent to assigning a temperature of 0 °C to melting ice or assigning zero metres to sea level elevation. Higher temperatures and elevations are given positive values and lower temperatures and elevations are assigned negative values. When comparisons are being made between the temperature of an object compared to the melting temperature of ice, it is unnecessary to know the absolute values of temperature of either object. Similarly, when comparing the height of an object above sea level, it is unnecessary to know the distance from the centre of the earth of either object. Likewise, it is difficult to measure satisfactorily the absolute potential difference between a metal and its salt in a half-cell. However, the potential difference between a metal electrode and the hydrogen electrode is very useful in comparing the ease of loss of electrons by each metal from a set of metals. If the metal tends to lose electrons to hydrogen it is assigned a negative standard electrode potential. If the hydrogen loses electrons more easily than the metal, the metal has a positive standard electrode potential.

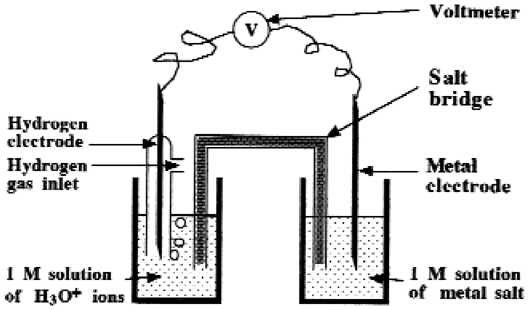


***Fig. 2.3** Determining standard electrode potentials*

To measure the standard electrode potential of a metal relative to the standard hydrogen electrode, the following apparatus is required: the standard hydrogen electrode, the standard electrode for the metal under investigation and a salt bridge. The salt bridge of sodium chloride (or another salt) connects the two electrolytes and a conducting circuit is set up. The salt bridge maintains the ionic balance between the two solutions. One of the two elements, hydrogen or the metal, will lose electrons more easily than the other. Most metals tend to lose electrons more easily than hydrogen so this case will be considered first.

The metal loses electrons and more metal ions enter the salt solution. To keep the ionic balance, negative ions enter the metal salt solution from the salt bridge. The electrons lost by the metal travel to the hydrogen electrode via the conducting circuit, and there reduce hydronium ions, forming hydrogen gas and water. The loss of hydronium ions is compensated for by the migration of positive ions from the salt bridge. If a potentiometer is placed across the conducting circuit, between the two electrodes, the potential difference between the electrodes (i.e. the standard electrode potential of the metal with reference to the standard hydrogen electrode) may be determined. The potentiometer supplies a potential difference equal to that between the electrodes but in the opposite direction. This prevents a current flowing and thus avoids energy losses, due to heating, as the current passes through the electrodes and electrolyte. Thus, the potentiometer reading gives the maximum potential difference between the electrodes. A voltmeter of high resistance could also be used but a slightly smaller value for the potential difference between the electrodes is measured, as there is now a small current flowing.

Electrical potential is the work done when unit charge is moved from one point to another. If the second point is at a higher electrical potential (a greater density of positive charge) than the first, energy must be supplied to move a positive charge from the first point to the second, and if the second point is at a lower potential (more negative), energy is released when a positive charge moves. Conversely, if a negative charge moves in an electric field towards a point of higher potential, energy is released. The concept of electric potential is analogous to gravitational potential. Potential energy is released when an object falls from a point of higher potential to a point of lower potential, and work must be done to move an object from a low potential to a higher potential. An object in a gravitational field will spontaneously move from high to low potential, releasing energy. A positively charged object in an electric field will also spontaneously move from high to low potential and also release energy. The difference in potential energies between objects at different heights is often given instead of the actual potential energies with reference to the surface of the earth. Similarly, the electrical potential difference between two points, neither of which is at zero potential, is usually used rather than absolute potentials with reference to a point at zero potential.

If electrons move spontaneously in an electric field, e.g. in a cell, then energy is released by the cell and can be harnessed to light a bulb, drive a small motor, etc. In the cell described above, where the metal loses electrons more readily than hydrogen, there is a spontaneous flow of electrons from the metal to the hydrogen electrode, releasing electrical energy, and the metal is assigned a positive standard electrode potential for oxidation. Conversely, the metal ion has the same standard electrode potential, but with a negative sign, for its reduction.

On the other hand, if the metal used in the cell were less inclined to lose electrons than is hydrogen, then the reactions described would be reversed. The hydrogen gas would become oxidised to hydrogen ions, which would immediately react with water molecules to become hydronium ions. This would cause an increase in the concentration of the hydronium ion solution in contact with the platinum. To compensate for the additional positively charged ions entering this solution, chloride ions would migrate from the salt bridge. The electrons released would travel *via* the wire to the metal electrode where they would reduce metal ions in solution to neutral metal atoms, which would then deposit on the electrode. The concentration of positive metal ions in solution would tend to be reduced but positive sodium ions from the salt bridge would migrate to keep the ionic balance. The flow of electrons in this cell is away from the hydrogen electrode and the *spontaneous* reduction of the metal ion occurs. The metal ions are given a *positive* standard electrode potential for their reduction.

A simple experiment to compare electrode potentials can be carried out by cutting out a cross-shaped piece of filter paper and placing samples of four different metals in contact with a solution of their salts as shown in Fig. 2.4. A salt bridge of potassium nitrate serves each arm of the cross. The potential difference between any pair of metals can be used to determine the relative positions of each metal on the electrochemical series.

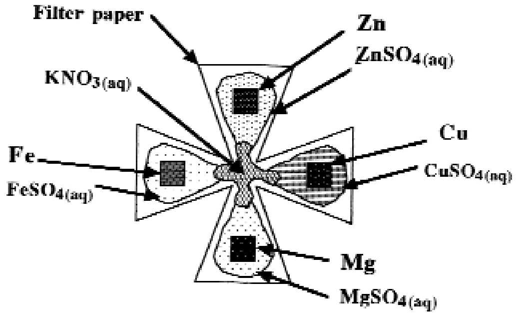


Fig. 2.4 *Comparing electrode potentials*

The order of metals in the electrochemical series is shown in Fig. 2.5. Note again that the list differs from the activity series in listing the metals strictly in order of increasing standard electrode reduction potential and not in order of decreasing reactivity. Here lithium is at the top of the list (above the other alkali metals) because it has the most negative standard electrode reduction potential. In the activity series, however, lithium is listed after potassium and sodium because it reacts with water and acid more slowly, and its oxide is more easily reduced than those of potassium and sodium.

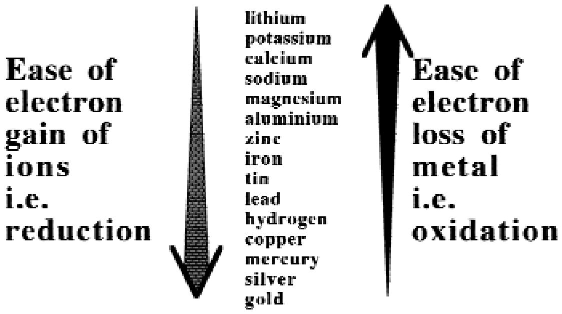


Fig. 2.5 *Electrochemical series*

A list of standard electrode reduction potentials is shown in Table 2.1. Note that if the electrode is not at standard conditions, e.g. at a temperature other than 25 °C or in a solution at a molarity other than 1 M, these values are invalid.

Standard electrode reduction potentials/V	
$Li^+ + e^- \rightarrow Li$	–3.05
$K^+ + e^- \rightarrow K$	–2.93
$Ca^{2+} + 2e^- \rightarrow Ca$	–2.87
$Na^+ + e^- \rightarrow Na$	–2.71
$Mg^{2+} + 2e^- \rightarrow Mg$	–2.37
$Al^{3+} + 3e^- \rightarrow Al$	–1.66
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	–0.83
$Zn^{2+} + 2e^- \rightarrow Zn$	–0.76
$Fe^{2+} + 2e^- \rightarrow Fe$	–0.44
$Pb^{2+} + 2e^- \rightarrow Pb$	–0.13
$2H_3O^+ + 2e^- \rightarrow 2H_2O + H_2$	0.00
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$	+0.41
$I_2 + 2e^- \rightarrow 2I^-$	+0.54
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.77
$Ag^+ + e^- \rightarrow Ag^-$	+0.80
$Br_2 + 2e^- \rightarrow 2Br^-$	+1.07
$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.36
$F_2 + 2e^- \rightarrow 2F^-$	+2.87

Table 2.1 *Standard electrode reduction potentials*

By selecting combinations of electrode materials from the list above, it is possible to predict the emf generated in a voltaic cell and thus design a cell capable of providing a large current through an appliance. The emf of a cell constructed from zinc and copper electrodes, at standard conditions, is predicted to be the difference between their standard electrode reduction potentials, 0.34 – (–0.76) = 1.1 V. However, practical considerations should not be overlooked. For example, the alkali metals cannot be used as electrodes for cells as described above because of their vigorous reaction with water.

Displacement Reactions

When zinc powder is added to a solution of copper sulphate the blue colour clears and a brown precipitate is produced. The zinc reacts with the copper ions of the copper sulphate, and copper metal (the brown precipitate) and colourless zinc sulphate solution are formed.

$$Cu^{2+} + Zn \rightarrow Cu\downarrow + Zn^{2+}$$

$$CuSO_4 + Zn \rightarrow Cu\downarrow + ZnSO_4$$

This happens because zinc oxidises more readily than copper. Copper is below zinc in the electrochemical series, therefore zinc is more stable as an ion than copper, i.e. it is easier to oxidise zinc than copper. Reactions such as this are often termed displacement reactions, as the metal which is higher in the electrochemical series displaces a metal which is lower down the series from its salt.

If, on the other hand, copper powder is added to a solution of zinc sulphate, no reaction occurs.

$$Cu + Zn^{2+} \rightarrow \text{no reaction}$$

$$Cu + ZnSO_4 \rightarrow \text{no reaction}$$

Another displacement reaction very easily demonstrated in the laboratory involves displacing copper with magnesium. In this case a strip of magnesium ribbon is placed in a solution of copper sulphate. The blue colour of the solution fades and the magnesium is eroded. A brown precipitate of copper appears.

$$Cu^{2+} + Mg \rightarrow Cu\downarrow + Mg^{2+}$$

$$CuSO_4 + Mg \rightarrow Cu\downarrow + MgSO_4$$

However, if copper metal is placed in a solution of magnesium sulphate, no reaction occurs.

$$Cu + MgSO_4 \rightarrow \text{no reaction}$$

A third displacement reaction could be carried out to confirm that magnesium displaces zinc from a zinc solution. A strip of magnesium ribbon is placed in zinc sulphate solution. The magnesium reacts and a silvery white precipitate appears. This reaction does not display the same very convincing colour changes as in the previous two experiments involving blue copper sulphate and brown copper metal, but chemical reactions clearly take place. Zinc powder or zinc turnings placed in a magnesium sulphate solution do not react.

$$Zn^{2+} + Mg \rightarrow Zn + Mg^{2+}$$

$$ZnSO_4 + Mg \rightarrow Zn + MgSO_4$$

$$Zn + Mg^{2+} \rightarrow \text{no reaction}$$

This type of reaction finds practical application in the extraction of some metals from their ores. Copper can be extracted from its ore by scrap iron (cf. p. 39) since copper ions in solution can be displaced by iron (because of their relative positions in the electrochemical series). Similarly, silver and gold are extracted by the use of this type of displacement reaction. Silver metal and silver metal compounds are often found together in silver ore. Gold is found chemically uncombined but physically mixed with unwanted material. The bulk material in each case is brought into solution with suitable reagents giving $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$. Any metal higher up the electrochemical series, e.g. zinc or aluminium, can then be used as a reducing agent to displace the silver or gold. This process where a metal is extracted from its ore by a displacement reaction, is termed a **hydrometallurgical process**.

If the lower part of the electrochemical series is examined, it is seen that the strongly electronegative elements found there are easily reduced, Fig. 2.6.

Fig. 2.6 *The strongly electronegative elements*

As with the metals, displacement reactions are also possible here, e.g.

$$Cl_2 + 2Br^- \rightarrow Br_2 + 2Cl^-$$

In general, a halogen will displace another halogen above it (on the electrochemical series) from a solution of its ions. This reaction is used to extract bromine from seawater, where it occurs in small concentrations as bromide ions.

Halogen-halogen reactions can be easily demonstrated in the laboratory.

1. Small volumes of approximately 1 M solutions of potassium chloride, potassium bromide and potassium iodide in water are prepared by dissolving 0.75 g potassium chloride, 1.2 g potassium bromide and 1.7 g of potassium iodide each in 100 cm^3 of distilled water.

2. An orange solution of bromine in water is prepared by breaking a 1 cm^3 phial of bromine under the surface of 100 cm^3 of deionised water. A colourless solution of chlorine in water is prepared in a fume cupboard by generating chlorine gas by the addition of concentrated hydrochloric acid to potassium permanganate [manganate(VII)] crystals and allowing the gas to bubble into deionised water. An iodine solution of 2 g of potassium iodide and 1.25 g iodine in 100 cm^3 of deionised water is also prepared.

3. Samples of chlorine, bromine and iodine solutions of a volume of 5 cm^3 are measured into test-tubes. A 5 cm^3 sample of potassium iodide solution is added to each test-tube and any observations recorded. A colour change is observed in the test-tube containing potassium iodide and chlorine. A brown colour of iodine appears, as the chlorine reduces to chloride and

the iodide ions oxidise to iodine.

$$Cl_2 + 2I^- \rightarrow I_2 + 2Cl^-$$

A more subtle colour change is observed in the test-tube containing potassium iodide and bromine. A brown colour of iodine appears as the bromine reduces the iodide ions to iodine.

$$Br_2 + 2I^- \rightarrow I_2 + 2I^-$$

No colour change occurs in the third test-tube.

4. Samples of chlorine, bromine and iodine solutions of a volume of 5 cm^3 are measured into test-tubes. A 5 cm^3 sample of potassium bromide solution is added to each test-tube and any observations recorded. A colour change is recorded only in the test-tube containing chlorine, as the following reaction takes place.

$$Cl_2 + 2Br^- \rightarrow Br_2 + 2Cl^-$$

The colour changes from almost colourless to orange as the bromide ions are reduced to bromine.

Corrosion

Corrosion is the conversion of a metal to one of its compounds. It is always an oxidation process.

Elements towards the top of the electrochemical series react to lose electrons more readily than those further down the series, hence they show a greater tendency towards corrosion.

Interestingly, if we examine the atmospheric corrosion of metals, the rate at which they corrode is not always in accordance with their position in the electrochemical series. One would expect the rate of corrosion to decrease as one moves down the series. However, the rates at which magnesium, aluminium and zinc corrode are much slower than that of iron. The reason for this is the fact that these metals do oxidise, but a protective layer of a hard oxide is produced which protects the metal from further corrosion by adhering to the metal's surface. Iron, on the other hand, oxidises to produce a brittle oxide that is porous and flakes off, thus giving no protection to the metal underneath.

- Corrosion effectively returns the metal to its ore state and all the energy used to extract it has therefore been wasted.

- Corrosion weakens the structure of metal objects and impairs their surface finish.

It is desirable therefore to prevent corrosion. Several methods are available, including painting, lacquering, enamelling, providing plastic and rubber coatings, oiling/greasing, using chemical inhibitors, alloying, using surface treatments, galvanising, anodising, electroplating, cathodic protection and sacrificial protection.

Painting, lacquering, enamelling, provision of plastic and rubber **coatings, oiling** and **greasing** techniques all prevent access of oxygen and moisture or other aggressive chemicals to the metal.

The use of **chemical inhibitors or negative catalysts** is a more recent development in corrosion prevention. The use of phosphates and silicates to slow down corrosion in car engines and central heating systems is an example.

Alloying is an important method for changing the properties of a metal and making it more resistant to corrosion. Steel containing nickel and chromium is very resistant to corrosion because these metals form a very thin impermeable oxide coating which prevents attack of the metal by air. If this layer is damaged it is self-replacing because the chromium and nickel are distributed throughout the metal and not just at the surface.

Surface heat treatments of iron are used to improve surface hardness and corrosion resistance. Nitrocarburising of alloy steels is carried out over a period of about two hours at a temperature of 570 °C. During the treatment the metal component is exposed to a plasma of nitrogen- and carbon-containing gases, predominantly the former. The result is a thin layer of iron nitride on the surface of the metal and this improves resistance to wear and corrosion.

In the process of **galvanising** of iron, the iron is coated with zinc. Galvanising is done by dipping the iron object into molten zinc. The zinc protects the iron in two ways. Firstly, it forms a hard oxide which prevents further oxidation. Secondly, since zinc is further up the electrochemical series than iron, the zinc acts as a sacrificial metal (see below).

Anodising is an electrolytic process whereby the oxide layer on the surface of a metal, (usually aluminium), is artificially thickened to improve its protective ability.

Electroplating is the transfer of one metal to the surface of another to provide a better finish and protect against corrosion. The metal to be protected is made the cathode in an electrolytic cell. The second electrode is made of the metal used as the coating and the electrolyte is a solution of a salt of the plating metal.

Cathodic protection of metals is carried out by attaching the metal to be protected to the negative terminal of a low voltage power supply (the positive terminal of the supply is earthed). The metal does not become oxidised since it cannot lose electrons. The metal is usually given a coating of some kind as a first defence against corrosion and the cathodic protection is a second line of defence.

Magnesium or zinc is used in the **sacrificial protection** of iron. The more electropositive metal will be preferentially oxidised and be sacrificed to save the other metal. Blocks of magnesium and zinc are often attached to the hulls of ships to protect the iron hulls from rusting. Underground pipelines carrying gas at high pressure are often protected by magnesium blocks.

2.3 Electrolysis

Electrolysis is the breaking up of a compound due to the passage of electrical current through an electrolyte. Ions in the electrolyte are attracted to the electrodes, positive ions to the negative cathode and negative ions to the positive anode. An external battery or power supply creates the potential difference between the electrodes. At the electrodes oxidation and reduction processes take place. These reactions are overall non-spontaneous, i.e. they require energy from an external source. Electrical energy from the power supply permits the oxidation and reduction reactions to take place. The essential processes involved are migration of ions through the electrolyte, separate reduction and oxidation processes at the electrodes, energy supplied by an external battery and redistribution of the electrons lost in oxidation through the external circuit to the cathode where they are required in reduction. The electrolysis of molten and aqueous electrolytes is considered below.

Movement of Ions in an Electrolyte

There are several ways of demonstrating the movement of ions through an electrolyte under the influence of an applied potential difference. One method is described here.

The movement of copper(II) and chromate ions can be demonstrated by making up an agar solution containing 2 g agar, 2 g copper(II) chromate and 5 cm^3 of bench (approximately 3 M) aqueous ammonia solution in 100 cm^3 boiling water. Aqueous ammonia is added because copper chromate is only slightly soluble in water. The green mixture is poured into a U-tube about two-thirds up each arm. The agar is allowed gel overnight. A few cm depth of aqueous ammonia solution is added to each arm of the U-tube. Graphite electrodes are inserted into the arms of the U-tube so that they are partially immersed in the aqueous ammonia solution. A potential difference of about 20 V is applied across the electrodes. The agar gel reduces the rate of diffusion of species in the electrolyte and one observes a blue colour in the aqueous ammonia solution at the cathode side of the apparatus due to the migration of positive copper(II) to the negative cathode and a yellow colour near the anode due to the migration of negative chromate ions to the positive anode.

Electrolysis of Molten Lead Bromide (inert electrodes)

Electrolysis of molten ionic compounds is the oldest industrial electrolytic process and dates back to 1807, when **Humphry Davy** prepared sodium metal by electrolysing molten sodium hydroxide.

Lead bromide is a low-melting-point compound which may be used to demonstrate that ionic compounds conduct electricity in the molten state and that the passage of electricity through the electrolyte produces chemical changes. The lead bromide crystal lattice collapses on heating so that the ions are free to move.

$$PbBr_2 \rightarrow Pb^{2+} + 2Br^-$$

The lead ions drift towards the cathode where they are reduced and the bromide ions drift towards the anode where they are oxidised.

$$Pb^{2+} + 2e^- \rightarrow Pb$$

$$2Br^- \rightarrow 2Br + 2e^- \rightarrow Br_2 + 2e^-$$

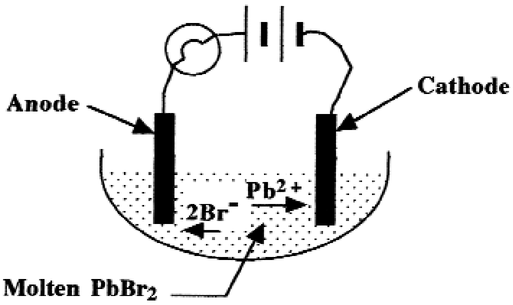


Fig. 2.7 *Conduction of electricity in lead bromide*

The experimental set up is shown in Fig. 2.7. **The experiment must be carried out in a fume cupboard**. The electrons for the reduction are supplied by the negative terminal of the battery and the electrons released from bromide ions during the oxidation return to the positive terminal of the battery. Thus, the electron (e^-) flow in the external circuit is from the anode to the cathode. (Traditionally, the current, *I*, is then said to be flowing in the opposite direction.) The cell reaction is obtained by adding the electrode reactions.

$$PbBr_2 \rightarrow Pb + Br_2$$

The products are lead metal and red/brown bromine gas. Bromine is a liquid at room temperature but at the temperature in the voltameter it appears as a red/brown vapour. The experiment can be demonstrated if an efficient fume cupboard is available. Bromine is very toxic and corrosive and the experiment should be terminated as soon as the first traces of the products are observed.

Electrolysis of Molten Sodium Chloride (inert electrodes)

Theory

The sodium chloride crystal lattice collapses at high temperature, m.p. 801 °C, and hence the ions are free to move.

$$NaCl \rightarrow Na^+ + Cl^-$$

The sodium ions drift towards the cathode where they are reduced. The chloride ions drift towards the anode where they are oxidised, Fig. 2.8.

Cathode reaction

$$Na^+ + e^- \rightarrow Na$$

Anode reaction

$$Cl^- \rightarrow Cl + e^- \rightarrow \tfrac{1}{2}Cl_2 + e^-$$

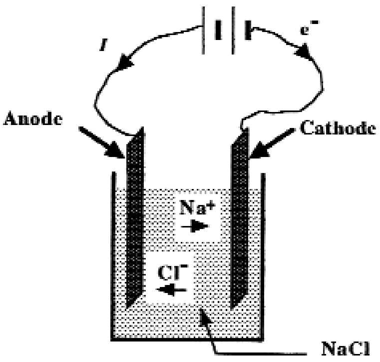


Fig. 2.8 *Electrolysis of molten sodium chloride*

The electrons for the reduction are supplied by the negative terminal of the battery and the electrons released from chloride ions during the oxidation return to the positive terminal of the battery. Thus, the electron (e^-) flow in the external circuit is from the anode to the cathode. The products are sodium metal and chlorine gas. The cell reaction is obtained by adding the electrode reactions.

$$NaCl \rightarrow Na + {}^1/_2Cl_2$$

Industrial practice

In industry, a special voltameter apparatus, known as the Downs cell, is used in the bulk electrolysis of molten sodium chloride. This is the major industrial method of sodium production and also a minor source of chlorine (which is available from several other industrial chemical processes). Nevertheless, chlorine obtained from the Downs cell is a valuable by-product and can be sold for use in the polymer industry, the pharmaceutical industry and to disinfect public water supplies.

The design of the Downs cell prevents the recombination of the elements after they are separated by the electrolysis. A funnel removes the chlorine gas formed at a graphite anode, and the sodium metal is removed from above a set of steel cathodes set in a circle. A cylindrical steel grille is positioned between the electrodes to reduce the tendency for the elements to recombine, Fig. 2.9. Because of the low density of sodium metal, it floats to the surface of the electrolyte. The boiling point of sodium is 883 °C and it is therefore desirable to reduce the operating temperature of the cell to avoid loss of sodium as a vapour. The temperature at which the electrolysis proceeds is reduced from 801 °C, the melting point of sodium chloride, to about 600 °C by using a mixture of sodium chloride and calcium chloride as the electrolyte, in a molar ratio of approximately 3:1. The cell is covered during operation to avoid heat loss. Calcium ions are not reduced at the cathode, provided the concentration of the sodium chloride in the electrolyte is not allowed to fall significantly. The standard electrode potential for this reaction is –2.87 V compared with a standard electrode potential of –2.71 V for the reduction of sodium ions. Modern Downs cells operate with currents of 25 – 40 kA.

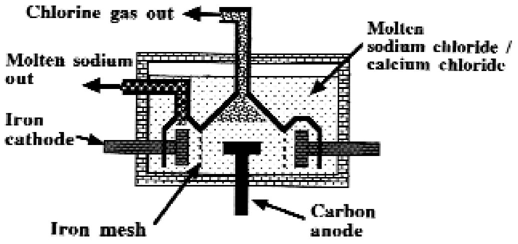


Fig. 2.9 *Downs cell*

The sodium chloride electrolysed in the Downs cell is obtained mainly from salt mines, by the evaporation of seawater or inland salt lakes, or from brines obtained by using water to bring underground salt deposits to the surface. The latter method provides purer salt than seawater or inland lakes. In the salt mines at Salzburg in Austria, Cheshire in England, and elsewhere, the sodium chloride is blasted out leaving large underground cavernous spaces. The sodium chloride rocks extracted are crushed to various sized chunks, coarse and fine powders. In areas where there is an abundance of solar energy, e.g. along Portugal's south coast or at Salt Lake City in the USA, water is evaporated from large concentrating ponds in which salt crystals settle out as the degree of saturation of the solution rises. Seawater contains approximately 25 g sodium chloride per litre.

Sodium metal's reactivity ensures that it has no common applications around the home. Sodium metal is used in street lighting, as the atomic emission spectrum of sodium provides intense yellow light. Sodium metal is also used in the extraction of other less reactive metals. It is a very efficient conductor of heat and molten sodium is used as the coolant in fast-breeder nuclear reactors. However, the compounds of sodium are much more widely used than the metal itself. NaOH, NaCl, $NaHCO_3$ and Na_2CO_3 are all commonly-used chemicals in industry and in the home. In the home, NaOH is used to free drains blocked with grease and other organic matter, NaCl is used for preserving and flavouring foods, $NaHCO_3$ is used as the principal component of 'bicarbonate of soda' for cooking and baking and for the relief of indigestion. Na_2CO_3 is used as washing soda and in bath salts for softening water.

Electrolysis of Molten Aluminium Oxide (inert electrodes)

The aluminium oxide crystal lattice collapses at very high temperature, m.p. 2050 °C, and the ions become free to move. Industrially, the need to maintain such a high temperature is avoided by dissolving the aluminium oxide in cryolite (see industrial practice below).

$$Al_2O_3 \rightarrow 2Al^{3+} + 3O^{2-}$$

The aluminium ions drift towards the cathode where they are reduced, Fig. 2.10. The oxygen ions drift towards the anode where they are oxidised.

Cathode reaction

$$2Al^{3+} + 6e^- \rightarrow 2Al$$

Anode reaction

$$3O^{2-} \rightarrow 3O + 6e^- \rightarrow {}^3/_2O_2 + 6e^-$$

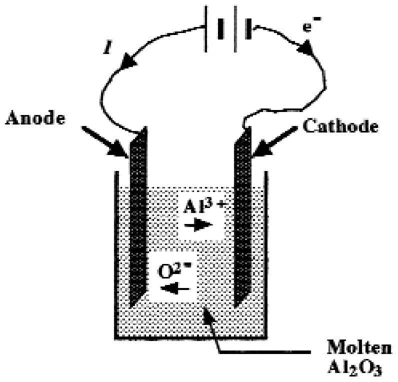


Fig. 2.10 *Electrolysis of molten aluminium oxide*

The electrons for the reduction are supplied by the negative terminal of the battery and the electrons released from oxide ions during the oxidation return to the positive terminal of the battery. Thus, the electron (e^-) flow through the voltameter is from the cathode through the melt back to the anode through the battery, etc. The products are aluminium metal and oxygen gas. The cell reaction is obtained by adding the electrode reactions.

$$Al_2O_3 \rightarrow 2Al + {}^3/_2O_2$$

Industrial practice

Aluminium is the most abundant metal in the earth's crust and is widely distributed in clays. The most common ore of aluminium is bauxite, hydrated aluminium oxide, $Al_2O_3.xH_2O$, an ore which contains significant quantities of iron impurities, giving it a red colour. Commercial grade bauxite contains about 40% aluminium oxide. The gemstones, sapphire, ruby and emerald are all aluminium minerals called corundum and have a chemical formula Al_2O_3. They are second only to diamonds in hardness and good quality rubies, sapphires or emeralds can sometimes exceed diamonds in value. Low quality corundum is used as the abrasive on sandpaper and emery boards.

In industry, the production of aluminium metal from bauxite takes place in two distinct stages:

(i) extraction of pure aluminium oxide from bauxite and

(ii) electrolysis of the alumina to produce aluminium metal.

Production of Aluminium Oxide from Bauxite

The modern industrial process for removing the iron impurities from bauxite, which is the first stage in the extraction of very pure white powdered aluminium oxide, is called the Bayer process. It is named after the Austrian chemist who, in 1889, improved upon an earlier process. The Bayer process is used in the Aughinish alumina plant on the Shannon Estuary where bauxite from Guinea in West Africa is processed into 800 000 tonnes of aluminium oxide annually. The Bayer process may be described in five stages.

1. Mixing

The bauxite is ground to a powder which is then mixed with hot concentrated sodium hydroxide solution.

2. Digestion

The mixture of sodium hydroxide and alumina, an amphoteric oxide, is heated to 250 °C at a pressure of nearly 50 atmospheres to ensure complete reaction which brings the aluminium oxide into solution as sodium aluminate ($NaAlO_2$).

$$Al_2O_3.xH_2O + 2NaOH \rightarrow$$
$$2NaAlO_2 + (x{+}1)H_2O + \text{impurities}$$

3. Clarification

The iron impurities, principally Fe_2O_3, are filtered off as $Fe(OH)_3$ and iron silicates (Fe_2SiO_4). Other impurities removed are titanium and silicon oxides. The solids filtered are referred to as red mud. This 'red mud' is washed and discarded. To date, no economical way of extracting the iron from the red mud has been developed. The filtrate is a tea-coloured solution.

4. Precipitation

By addition of water to the filtrate, the reaction which formed sodium aluminate ($NaAlO_2$) above, is essentially reversed, and the aluminium in solution is precipitated as $Al(OH)_3$ by addition of small particles of $Al(OH)_3$ to the filtrate as 'seeds' to encourage the growth of coarser particles of $Al(OH)_3$.

$$2NaAlO_2 + 4H_2O \xrightarrow{\text{seed}} 2Al(OH)_3 + 2NaOH$$

5. Calcination

Finally the $Al(OH)_3$ is heated strongly, at 1000 °C, to dehydrate it to aluminium oxide (Al_2O_3), a fine white powder.

$$2Al(OH)_3 \xrightarrow{1000\ °C} Al_2O_3 + 3H_2O$$

Three tonnes of bauxite yields approximately one tonne of aluminium oxide and two tonnes of 'red mud' and sand. All of the alumina produced in Ireland is exported.

Electrolysis of Alumina

In 1886 **Charles M. Hall** and **Pierre L.T. Héroult** developed (separately and unaware of each other's work) the extraction of aluminium metal from alumina by electrolysis. The Hall-Heroult process for production of aluminium on an economic industrial scale uses an electrolyte consisting of the mineral cryolite, Na_3AlF_6 and approximately 5-8% pure alumina. The addition of the cryolite to the alumina reduces the operating temperature of the cell from 2050 °C to about 950 °C. Cryolite is a rare mineral, found only in Greenland, and most cryolite used industrially today is synthetically produced. Small amounts of CaF_2, LiF and AlF_3 are added to the electrolyte to reduce the melting point further and thus make the process more efficient.

The voltameter itself is made of steel with a graphite lining which acts as a cathode, Fig. 2.11. Graphite blocks lowered into the electrolyte act as anodes. There are no special features of the cell to keep the aluminium and oxygen products separated after electrolysis as the aluminium metal is more dense than the electrolyte and sinks to the bottom of the voltameter while the oxygen gas rises through the electrolyte at the anodes. The oxygen gas oxidises the graphite anodes to carbon dioxide and the graphite blocks must be lowered more and more into the electrolyte as they are consumed, and they must be replaced approximately every 21 days. The heat evolved in this reaction helps keep the electrolyte molten. A crust of electrolyte forms at the top of the pot.

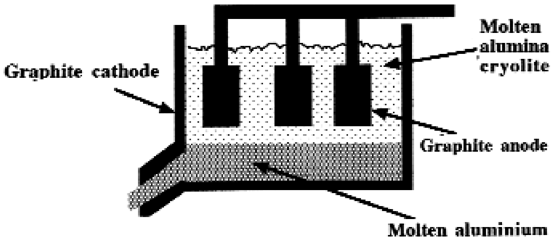


Fig. 2.11 *Electrolysis of alumina*

The cells use currents of about 30 kA each and operate at a potential difference of about 5 V. If the voltage is increased the cryolite starts to electrolyse. In fact a potential difference of 2.1 V across the terminals is theoretically sufficient to electrolyse aluminium oxide. The excess voltage drives a larger current and the heating effect of this current contributes to keeping the electrolyte molten. About 64% of the electrical energy supplied is lost as heat. It is essential, therefore, to locate an alumina electrolysis plant where cheap electricity is available. This means locations such as near a hydroelectric power plant (as in Kitimat, British Columbia, Canada) or a nuclear power plant (as in Angelsea Aluminium Ltd near Holyhead in Wales). An alternative is to seek a location near a coalfield, provided the smelter's being near the aluminium market (e.g. Lynemouth in the UK) offsets the relatively high cost of producing electricity in this way. Approximately two tonnes of alumina yields one tonne of aluminium metal upon smelting.

The molten aluminium, m.p. 660 °C, can be drained off at the base of the voltameter or siphoned off through the electrolyte. The concentration of alumina is not allowed to fall below 2% to maintain the conductivity of the electrolyte.

The principal uses of aluminium depend on its strength, lightness and resistance to corrosion, e.g. as a building material, in car engine and body parts and aircraft bodies, in electrical transmission wires, for packaging, most commonly as foil and beverage cans. Aluminium is second only to iron in the wide range of its uses.

Recycling

The cost of recycling one tonne of aluminium is approximately 5-10% of the cost of the production of one tonne of aluminium from bauxite. The recycling of aluminium is very desirable and more than 30% of the aluminium in use in Europe today is recycled, or secondary, aluminium. The deposit of beverage cans in separate refuse bags in Irish schools and in can banks in community shopping centres and elsewhere are some of the first recycling initiatives to be successfully launched here. Between 40 000 and 50 000 cans are required to produce one tonne of recycled aluminium and over 200 million cans are sold in Ireland every year. A national recycling rate of 15% has been achieved and the current target is to achieve a 25% rate of recovery by the year 2000 in line with the EU Packaging Waste Directive. The Dutch, Swiss and Germans achieve rates of 75% so Ireland has a lot of catching up to do! Even the stay-on tabs that help to open cans conserve a little more aluminium with each recycled can.

There are a number of environmental considerations to be considered in the manufacture of aluminium. During the electrolysis of aluminium oxide, the release of fluoride compounds into the atmosphere must be monitored and controlled. In addition, the consumption of fossil fuels and nuclear fuels in the production of electricity for aluminium smelting is of great environmental significance. Each tonne of aluminium produced requires approximately 13 MWh of electrical energy. Recycling aluminium obviously reduces the consumption of electricity and helps control litter as well as providing employment for those involved in the reprocessing of the aluminium.

Anodising

Aluminium is quite high in the electrochemical series and might therefore be expected to corrode rapidly. In fact, aluminium is quite resistant to corrosion because the oxide of aluminium formed at the surface of aluminium upon exposure to atmospheric oxygen adheres to the metal surface and thus reduces its rate of corrosion. This situation contrasts sharply with the corrosion of iron in which the rust that has formed does not adhere well to the iron - it forms a porous flaky layer which does not provide good protection from atmospheric oxygen. Furthermore, if the outer layer of aluminium oxide is made artificially thicker, it actually becomes completely impermeable to oxygen and provides better protection from corrosion than the thin layer formed naturally. Scratches in aluminium quickly 'heal' when a layer of aluminium oxide reseals the aluminium metal from attack by oxygen. The artificial thickening of the aluminium oxide layer on the surface of aluminium metal is carried out electrochemically and is known as anodising. Nearly all aluminium articles are anodised as part of the manufacturing process to improve their resistance to corrosion and to harden their surfaces so that they are more resistant to wear. The oxide layer is typically thickened from a few millionths of a millimetre to between 0.003 and 0.025 mm by the anodising process.

The article to be anodised is cleaned using an organic solvent to remove grease which would prevent the formation of an aluminium oxide coating. It is then dipped in concentrated sodium hydroxide solution to remove the existing oxide layer and expose fresh metal.

The object to be anodised is made an anode at the centre of an electrochemical cell with an aluminium cathode and dilute sulphuric acid as the electrolyte.

A current is passed through the cell and as a result the water is electrolysed. Oxygen gas is produced at the anode where it reacts with the aluminium metal to produce a sufficiently thick aluminium oxide layer after a period of 20-30 minutes. Hydrogen gas is produced at the cathode.

When the anodised object is removed from the electrochemical cell the oxide layer is quite porous and, if immersed in a suitable dye solution at this stage, it can acquire the colour of the dye solution. It is then placed in boiling water which acts as a sealant and makes the anodised layer impermeable.

Electrolysis in Aqueous Solution

Electrolysis in aqueous solution is quite complicated and its treatment requires consideration of a number of factors.

(i) There are several species present in the electrolyte and each species present has a different ease of reduction and oxidation, depending on its position relative to the other species in the electrochemical series.

(ii) A number of competing reactions may be possible at each electrode, particularly if the concentrations of the species are similar.

(iii) The concentrations of one of the species may be relatively high, promoting the occurrence of its reaction in favour of any others despite relative positions of species in the electrochemical series.

(iv) The electrodes may become involved in reduction or oxidation reactions.

(v) The migration rates of the species towards the electrodes may be quite different, giving different concentrations at the electrodes than in the bulk solution.

The list of reactions in Table 2.2, which may take place in electrolysis reactions in aqueous solutions is given in the order of decreasing standard electrode reduction potentials, i.e. **decreasing ease of reduction at the cathode**. The higher up the list the more likely that reaction is to take place at the cathode in a mixture of species of approximately equal concentrations. The standard electrode reduction potential of each reaction is given. This is a measure of ease of reduction, with the reduction of hydronium ions given an arbitrary value of zero volts in a one molar solution of hydronium ions at one atmosphere pressure. Any species more easily reduced than hydronium ions is given a positive value and any species more difficult to reduce is given a negative value. The closer the electrode potentials the more likely the reactions are to compete with one another.

Standard electrode reduction potentials/V	
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
$2H_3O^+ + 2e^- \rightarrow 2H_2O + H_2$	0.00
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	–0.828
$Na^+ + e^- \rightarrow Na$	–2.71
$K^+ + e^- \rightarrow K$	–2.925

Table 2.2 *Selected species in order of decreasing ease of reduction at a cathode*

In Table 2.3 are listed the reactions which may take place in electrolysis reactions given in the order of **decreasing ease of oxidation at the anode**. The higher up the list the more likely that reaction will take place at the anode in a mixture of species of approximately equal concentrations at the anode. Here, the more negative the electrode potential the more difficult it is to oxidise the species.

Standard electrode oxidation potentials/V	
$I^- \rightarrow I + e^- \rightarrow {}^1\!/_2 I_2 + e^-$	–0.536
$Cu \rightarrow Cu^{2+} + 2e^-$	–0.34
$2OH^- \rightarrow {}^1\!/_2 O_2 + H_2O + 2e^-$	–0.41
$3H_2O \rightarrow {}^1\!/_2 O_2 + 2H_3O^+ + 2e^-$	–1.23
$Cl^- \rightarrow Cl + e^- \rightarrow {}^1\!/_2 Cl_2 + e^-$	–1.36
$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^-$	–2.01
$F^- \rightarrow F + e^- \rightarrow {}^1\!/_2 F_2 + e^-$	–2.87

Table 2.3 *Selected species in order of decreasing ease of oxidation at an anode*

NB. If the concentration of a species at an electrode is very high, this is the one that is

likely to be oxidised or reduced, whatever its position on the lists above relative to other species.

Electrolysis of Dilute Sulphuric Acid (inert Pt electrodes)

The electrolysis of dilute sulphuric acid is carried out in a special demonstration apparatus called a Hofmann voltameter. The electrodes are made of inert platinum and located at the bases of two inverted burettes.

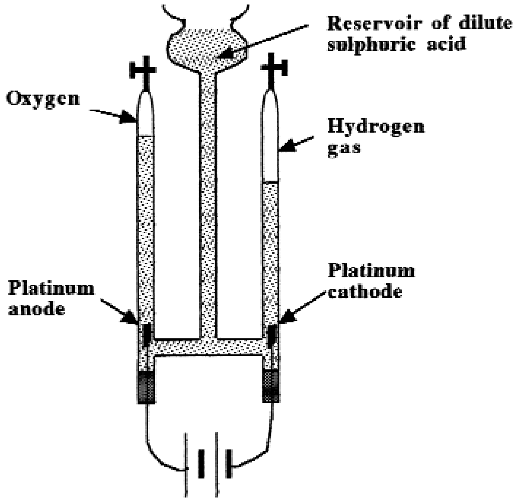


Fig. 2.12 *Electrolysis of dilute sulphuric acid*

In dilute sulphuric acid, the species present are water, H_3O^+ ions from the acid and from the ionisation of water, OH^- ions from the ionisation of water and the counter ions (negative) from the acid. As before, the positive ions migrate to the cathode and the negative ions to the anode. Water is present at both electrodes.

At the cathode water and H_3O^+ ions will be present. If one consults the reactions listed above to see which species is the most easily reduced (highest up the list) one would expect that H_3O^+ would be reduced rather than water. In addition, because of their positive charge, H_3O^+ ions migrate very successfully onto the cathode, increasing the hydrogen ion concentration there. Hence the reaction observed at the cathode is the reduction of hydrogen ions.

$$2H_3O^+ + 2e^- \rightarrow 2H_2O + H_2$$

Hydrogen gas collects above the cathode. To test for hydrogen, open the tap and collect some of the gas in an inverted test-tube - it ignites with a pop when a lighted splint is applied.

At the anode, water, OH^- and SO_4^{2-} ions will be present. The oxidation of sulphate ions is too difficult due to the position of the sulphate ion in the list given above. The hydroxide ion concentration in acidic solution is too low for its oxidation to be able to compete successfully with the oxidation of water. Water is therefore the species oxidised at the anode.

$$3H_2O \rightarrow {}^1/_2O_2 + 2H_3O^+ + 2e^-$$

Oxygen gas collects above the anode. To test for oxygen, open the tap and collect some of the gas in an inverted test-tube. Oxygen re-ignites a glowing splint.

The cell reaction is obtained by adding the cathode and anode reactions. Note that the volume of hydrogen gas collected is double the volume of oxygen gas collected, confirming the composition of water. Note also that the hydrogen ions consumed at the cathode during the reaction are regenerated at the anode.

$$H_2O \rightarrow {}^1/_2O_2 + H_2$$

Electrolysis of Dilute Aqueous Sodium Sulphate (inert Pt electrodes)

The electrolysis of dilute aqueous sodium sulphate may be carried out in a Hofmann voltameter or in a beaker, Fig. 2.13. The Hofmann voltameter allows the gases evolved to be collected and tested. The electrodes are made of platinum, which is inert.

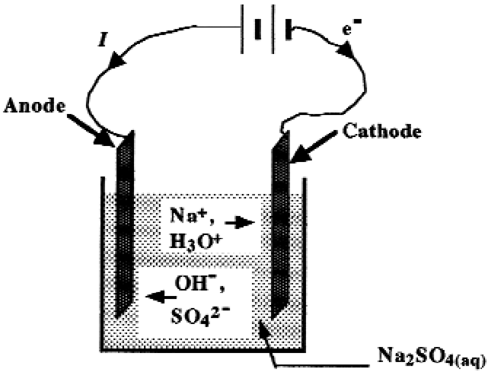


Fig. 2.13 *Electrolysis of dilute aqueous sodium sulphate*

In aqueous sodium sulphate solution, the species present are water, H_3O^+ ions from the ionisation of water, OH^- ions from the ionisation of water and Na^+ and SO_4^{2-} ions from the salt. As before, the positive ions migrate to the cathode and the negative ions to the anode.

At the cathode water, Na^+ and H_3O^+ ions will be present. If one consults the reactions listed above to see which species is the most easily reduced (highest up the list), one would certainly not expect the Na^+ ions to be reduced because of their position on the list. Hydronium ions, H_3O^+, might be expected to be reduced rather than water (consult table above), but as in the case of dilute sulphuric acid described above, the concentration of H_3O^+ ions in aqueous sodium sulphate solution is very low. Hence the reaction observed at the cathode is the reduction of water. Hydrogen gas collects at the cathode.

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

At the anode, water, OH^- and SO_4^{2-} ions will be present. The situation is identical to that encountered at the anode in the case of the electrolysis of dilute sulphuric acid. The oxidation of sulphate ions is too difficult due to the sulphate ion's position on the list given above. Hydroxide ion concentration is too low for its oxidation to be able to compete successfully with the oxidation of water. Water is therefore the species oxidised at the anode. Thus, oxygen gas collects at the anode.

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

The cell reaction is obtained by adding the cathode and anode reactions. Note also that the hydroxide ions produced at the cathode react with the hydrogen ions produced at the anode to make water. As in the electrolysis of dilute sulphuric acid, the reaction that occurs is the electrolysis of water to oxygen and hydrogen gases.

$$H_2O \rightarrow {}^1/{}_2O_2 + H_2$$

This electrolysis can be demonstrated by making up a solution containing 2 g of anhydrous sodium sulphate and sufficient bromothymol blue indicator solution to give an intense green colour in 100 cm^3 boiling water. If the solution is not green, acid or base is added dropwise until it is green. The green solution is poured into a U-tube. Graphite electrodes are inserted into the arms of the U-tube. A potential difference of about 12 V is applied across the electrodes and electrolysis as described above takes place. The U-tube reduces rapid mixing of the electrolyte between the cathode and anode and allows one to observe a yellow colour due to the formation of hydrogen ions at the anode, and a blue colour due to the formation of hydroxide ions at the cathode.

Electrolysis of Dilute Aqueous Potassium Iodide (inert electrodes)

The electrolysis of dilute aqueous potassium iodide may be carried out in a Hofmann voltameter or in a beaker, Fig. 2.14.

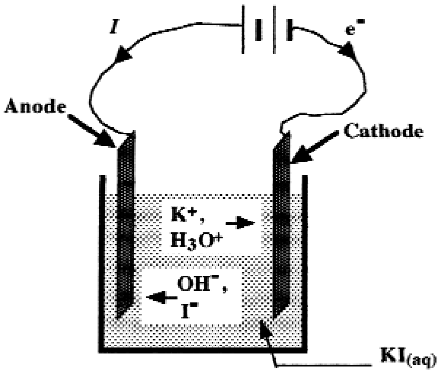


Fig. 2.14 *Electrolysis of dilute aqueous potassium iodide*

In aqueous potassium iodide solution, the species present are water, H_3O^+ ions from the ionisation of water, OH^- ions from the ionisation of water and K^+ and I^- ions from the salt. As before, the positive ions migrate to the cathode and the negative ions to the anode.

At the cathode, water, K^+ and H_3O^+ ions will be present. If one consults the reactions listed above to see which species is the most easily reduced (highest up the list), one would certainly not expect the K^+ ions to be reduced because of their position on the list. Hydronium ions, H_3O^+, might be expected to be reduced rather than water because of their relative positions on the list, but as in the case of dilute sulphuric acid described above, the concentration of H^+ ions in aqueous potassium iodide solution is very low. Hence the reaction observed at the cathode is the reduction of water. Hydrogen gas collects at the cathode.

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

At the anode, water, OH^- and I^- ions will be present. Of these, the species most easily oxidised is the I^- ion. So iodine is formed at the anode and gives the solution a golden brown colour, being soluble in potassium iodide solution.

$$2I^- \rightarrow I_2 + 2e^-$$

The cell reaction is obtained by adding the cathode and anode reactions.

$$2H_2O + 2I^- \rightarrow I_2 + H_2 + 2OH^-$$

This electrolysis can be demonstrated by making up a solution containing 2 g potassium iodide and a few drops of phenolphthalein indicator solution in 100 cm^3 of water. The solution is poured into a U-tube. Graphite electrodes are inserted into the arms of the U-tube. A potential difference of about 9 V is applied across the electrodes and electrolysis as described above takes place. The U-tube reduces rapid mixing of the electrolyte between the cathode and anode and allows one to observe a pink colour appearing at the cathode due to the formation of hydroxide ions, and a golden brown colour appearing at the anode, as iodine is discharged into solution.

Electrolysis of Aqueous Copper Sulphate (active Cu electrodes)

A blue solution of copper sulphate is the electrolyte here. The electrodes in this case are made of copper and participate in the anode and cathode reactions, i.e. they are active electrodes, Fig. 2.15.

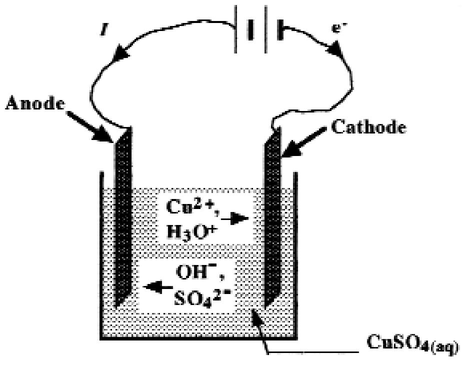


Fig. 2.15 *Electrolysis of aqueous copper sulphate*

In aqueous copper sulphate solution the species present are water, H_3O^+ ions from the ionisation of water, OH^- ions from the ionisation of water and Cu^{2+} and SO_4^{2-} ions from the salt. As before, the positive ions migrate to the cathode and the negative ions to the anode. Copper metal is present as the electrode material itself and may participate in reactions at either the cathode or anode.

At the cathode, copper, water, Cu^{2+} and H_3O^+ ions will be present. If one consults the reactions listed above to see which species is the most easily reduced (highest up the list), one would expect the Cu^{2+} ions to be reduced in preference to all other species, because of their position on the list. Metals are not easily reduced so copper metal from the cathode does not react here. Hence the reaction observed at the cathode is the reduction of copper ions to copper metal, which plates out onto the copper cathode. Copper metal is produced at the cathode.

$$Cu^{2+} + 2e^- \rightarrow Cu$$

At the anode, copper, water, OH^- and SO_4^{2-} ions will be present. The situation is identical to that encountered in the case of the electrolysis of dilute sulphuric acid except for the presence of copper metal. In fact, the copper metal is more easily oxidised than the other species present. Copper from the anode is oxidised to copper ions. As a result the anode dissolves into solution as Cu^{2+}. Copper metal wears away at the anode.

$$Cu \rightarrow Cu^{2+} + 2e^{-}$$

The cell reaction is obtained by adding the cathode and anode reactions.

$$Cu^{2+} + Cu \rightarrow Cu + Cu^{2+}$$

The products of the electrolysis of copper sulphate using inert electrodes are copper metal at the cathode and oxygen gas at the anode.

Industrial practice

There are two methods used to extract copper from copper deposits. Over 50% of copper deposits are sulphides, e.g. $CuFeS_2$, and the copper is recovered by roasting in the presence of air and silica. The sulphur is removed as sulphur dioxide, and the iron as a slag. No reducing agent is required. The second method is a hydrometallurgical one for extraction of copper from its ores and is used for low-grade copper deposits, and copper oxides or carbonates which are unsuitable for smelting. The ore is added to dilute sulphuric acid where copper(II) sulphate is formed. This step is called **leaching**. Then scrap iron is added to the solution where a displacement reaction takes place to deposit copper, as discussed earlier (p. 27). This step is called cementation. The copper is obtained as a fine powder which must then be purified as described below.

$$Cu^{2+} + Fe \rightarrow Cu + Fe^{2+}$$

Purification of copper

Electrolysis is used in the purification of impure copper extracted from its ore by smelting or electrodeposition. The copper obtained from roasting is too impure for the principal application of copper, which is as an electrical conductor. The electrorefined copper has a purity of 99.98% and therefore the low resistivity necessary for electrical conduction. The impure copper is made the anode of an electrolytic cell. The cathode is a thin sheet of ultra-pure copper, and the electrolyte is acidified copper sulphate solution. The electrolysis is carried out at a temperature of 60 °C and at a voltage of approximately 0.3 V. The current density, that is the current flowing per unit surface area of the cathode, is critical to ensure good electrodeposition. A current density of 200 A m^{-2} is suitable. During the electrolysis small quantities of precious metals, including platinum, gold and silver, found associated with the original copper ore are deposited at the base of the cell under the anode. These metals, lower down the electrochemical series than copper, are not oxidised at the anode. These deposits, called ‘anode sludge’ or mud, are recovered and the metals separated. Other less precious elements, e.g. zinc and iron, also impurities in the anode, are easily oxidised and do react at the anode and must be recovered routinely from the electrolyte when their concentrations have built up.

2.4 Electroplating

Electroplating is the transfer of one metal, acting as an anode, onto the surface of another piece of metal, acting as the cathode in an electrolytic cell. A solution of a salt of the metal being transferred is used as the electrolyte. The metal being transferred is usually more precious, or of more pleasing appearance, or more resistant to corrosion, than the metal on to which it is deposited. In some cases, however, the anode and cathode are composed of the same metal and the purpose of the electroplating is then to obtain a larger cathode of pure metal using an impure anode as in the purification of copper described above.

The object to be plated must be thoroughly cleaned to remove any oxides on its surface and to expose the pure metal. It must also be dipped in organic solvents to remove grease that could prevent electrodeposition on to the metal. A complex electrolyte, composed of a mixture of salts of the metal being electrodeposited and organic chemicals, ensures good electrical conductivity and also that the deposit has good appearance and durability. A poor cathode surface with pores and cracks will not plate with a perfectly smooth finish. A suitable current density is chosen to ensure a uniformly thick coat with good adhesion.

In this way, silver medals are sometimes gold-plated, steel framed bicycles are chrome plated, cutlery is nickel plated, etc. Nickel metal is resistant to corrosion and has a good lustrous appearance. It is therefore a good metal for use in electroplating metals that are more prone to corrosion.

Chrome plate gives a very corrosive-resistant bright shiny finish to steel alloy. It was widely used on automobile trim and is used in bathroom fittings. Chrome plate consists of a layer of about 0.3 mm thick of chromium metal deposited over a layer of nickel on the steel.

CHAPTER 3

METALS

3.1 Properties of Metals

There is no single property that sets a metal apart from other types of material. Rather it is a set or range of properties, which distinguishes metals from non-metals.

Metallic Crystals

Crystalline structures are described in section 1.2 of the module *Stoichiometry I*.

The atoms of the metal are held together by a special type of bonding called **metallic bonding**. A metal structure consists of a set of metal cations in a regular geometric array, usually face-centred cubic, body-centred cubic or hexagonal close packed. The valence electrons of each metal atom are shared between all the metal atoms present. These electrons move randomly between all the metal atoms present. Thus, the bonds are not directional and their most important characteristic is the freedom of the valence electrons to move. It is this high degree of electron mobility that is responsible for the high electrical conductivities of metals. The common attraction of the metal cations for the shared electrons holds the structure together and prevents electrostatic repulsions between the metal cations causing the structure to disintegrate. The strength of the metal depends on how many shared or delocalised electrons there are for every positive ion present. Thus the metallic bonding in the alkali metals which contribute one electron each per metal atom to the delocalised electron cloud is less strong than in the first row of transition elements where the 4s and a number of 3d electrons are donated to the electron cloud.

The metallic ions surrounded by the delocalised randomly moving cloud of valence electrons are not, however, themselves randomly arranged. The three crystal structures, (1) face-centred cubic, (2) body-centred cubic and (3) close packed hexagonal, are the most common crystal structures of metallic materials. In aluminium, copper, silver, gold and platinum and several other metals the arrangement of the metal cations is face-centred cubic. The metal cations in iron, sodium and other metals are arranged in a body-centred cubic pattern. In magnesium and zinc there is a hexagonal arrangement of the metal cations. A metal is an element that loses electrons in chemical reactions. Most of the elements are metals.

Properties of Metals

All metals are solid at room temperature, with the exception of mercury, which is a liquid.

Hardness

Hardness is a measure of how difficult it is to deform a sample of a material. To measure hardness, a steel ball or diamond tip is impressed under a stated load into a metal sample and the size of the indentation is measured. The bigger the indentation, the softer the metal. One such test is the Brinell test. This test uses a load of 5000 – 30 000 N applied to a hardened steel ball of diameter 1 – 10 mm for 20 seconds to make an indentation. The diameter of the indentation is measured and hence the curved surface area of indentation is calculated.

$$\text{Brinell hardness number} = \frac{\text{Load applied}}{9.8 \times \text{surface area of indentation}}$$

The unit is kg mm^{-2}.

The size of the indenting ball and the applied force are always such that the same result is obtained from each size ball. On this scale aluminium registers a value of 27, copper wire 110, cast iron 200 and alloy steel 400.

The hardness of non-metallic elements may be also measured using this type of test. In the case of elastic substances, the diameter of the indentation must be measured while the load is applied.

Another way of testing hardness involves comparing how materials suffer abrasion relative to one another. **Friederich Mohs** was a German geologist who devised a simple way of comparing the hardness of minerals. This is called the Mohs scale of hardness and on this scale diamond is assigned a value of 10 because it is the hardest known material and cannot be scratched by any other material. Aluminium oxide is assigned a value of 9 on this scale, which means the only material capable of scratching it is diamond and it is capable of scratching all other minerals. Working down the scale, calcium fluoride has a value of 4. It is scratched by any material with a higher value than it on the scale, but can scratch the minerals with lower values.

In the Vickers test, a diamond cut in the form of a square pyramid having an apex angle of 136° is used and the Vickers hardness number (VHN) is defined as the load/surface area of the impression which can be shown to be given by

$$\text{VHN} = 0.189P/d^2$$

where P is the applied load (N), d is the distance across the diagonal of the indent impression (mm).

Metals vary quite considerably in their hardness, from sodium which can be cut with a knife, to alloys like hardened steel which are used in boring and in machine parts. The hardness of a metal can be altered by the heat treatment it receives. For example, steel immersed suddenly in cold water is hard and brittle. If the quenched steel is then heated to 200 - 300 °C and quenched again it becomes tempered, i.e. becomes hard but malleable. In fact, anywhere that hardness is required, a pure metal is unlikely to be used. Alloying can invariably enhance the hardness of metals. Note that diamond, tungsten carbide (WC) used in drilling, and corundum (Al_2O_3) abrasives are harder than metals. Gold has a value of only 3 on the Mohs scale and is described as soft. For this reason, gold for jewellery is always alloyed with copper.

Lustre

Lustre is the name given to the sheen associated with metals, particularly a freshly exposed metallic surface. Any impurity atoms adsorbed onto the surface will interfere with the regular reflection of light from the metallic surface and dull the lustre. Gold retains its rich yellow lustre permanently. Sodium forms an ugly dull crust on its surface in less than an hour. Silver has the greatest ability of all metals to reflect light, although aluminium reflects ultraviolet radiation better and does not tarnish as easily as silver. The famous chemist **Justus von Liebig** discovered a method for depositing silver on glass to create a mirror in 1835. While his method is still in use, most mirrors are now created in a vacuum in which the aluminium or silver is vaporised onto the surface. Other substances besides metals have the ability to reflect light, particularly crystalline structures that sometimes transmit light as well as reflecting it, e.g. diamond. Metals show little variation in colour - copper is reddish, gold is yellow but all the other metals are subtle shades of silver or grey.

Malleability

Malleability is the ability of a material to be hammered into sheets or to be compressed without fracture. Gold is the most malleable of all metals. Very thin gold foil is used in gold leaf electroscopes, and in Rutherford’s famous experiment that led to the discovery of the nucleus. Away from the laboratory, gold leaf is used to decorate picture frames, statues, buildings, etc. Lead and mild steel are also malleable. However, lead is not ductile.

Ductility

Ductility is the ability of a material to be drawn into wire. It is defined as the strain at fracture. It is usually quoted as a percentage: percentage elongation at fracture. Metals can be considerably elongated before fracture, while most non-metallic materials break, and are described as brittle (e.g. glasses, ceramics and some plastics). The ductility of a material is measured in a tensile-testing machine which pulls a sample, so that the sample gradually elongates under tension, the load and extension being measured continuously. From the load-extension curve, it is possible to measure the strain (i.e. elongation per unit length). Altering the composition of a metal can affect its ductility: for example, the ductility of steel decreases as its carbon content increases. Gold is the most ductile of all metals.

Electrical conductivity

The ability of metals to conduct electricity depends on the availability of 'free' electrons within metallic structures. As described above, the valence electrons of each metal atom are effectively detached from their atoms and are free to move. Under the influence of an applied electrical potential difference between the ends of the metal the electrons will move towards the higher potential. Silver is the best electrical conductor of all the metals but unfortunately suffers from tarnishing, especially in polluted air, forming silver sulphide on its surface. In situations where corrosion is unacceptable, gold is the next best electrical conductor. Good conductors have low resistivity and high conductivity. Resistivity is the resistance of a sample of material of cross section 1 m^2 and one metre long at 20 °C. Conductivity is the reciprocal of resistivity.

Materials other than metals do not tend to be good electrical conductors because their valence electrons are tightly bound to the atoms of the structure and are not delocalised as in a metal. The electrons are not free to travel through the material even under an applied potential difference and so conduction is virtually non-existent (insulators, e.g. glass, plastic) or minimal by comparison to metals (semiconductors, e.g. silicon, germanium).

Heat conductivity

Metals are also good thermal conductors. Again, this is due primarily to the availability of 'free' electrons in the metal lattice. When one end of a piece of metal is heated 'free' electrons at that end gain energy and move away, their place being taken by slower electrons from the cooler end. A second, though less important, mechanism also contributes to thermal conduction in metals. When heat energy is supplied to one end of a piece of metal, the atoms at that end vibrate about their lattice points more vigorously. As a result, adjacent atoms are set in motion about their lattice positions and, in turn, vibrations are transmitted along the metal. Silver is the best heat conductor of all the metals.

Metal Alloys

An alloy is composed of two or more elements, one of which must be a metal, and the alloy itself must exhibit metallic characteristics. The base metal of an alloy is the metal present in the greatest proportion, while other metallic or non-metallic elements present are known as alloying elements. Examples of alloys are brass, which is made up of copper and zinc, and monel which is made of nickel and copper. The elements that make up the alloy are referred to as components. An alloy system is all the alloys you can make from a set of elements, e.g. the Cu-Zn system describes all the alloys you can make from copper and zinc. The composition of an alloy is usually measured in weight %, e.g. lead-tin alloy containing 90% lead and 10% Sn is written 90% Pb - 10% Sn. Gold is alloyed with copper or silver (in the case of 'white gold') in the manufacture of jewellery. The copper makes the alloy harder than the pure metal. Twenty-four carat gold is pure gold. Twenty-two carat gold is 22 parts gold and 2 parts copper. Similarly, 18, 14 or 9 carat gold are 18, 14 and 9 parts gold respectively, with the remainder being copper. Thus, a 22-carat gold ring, worn on the same finger and in contact with a 14-carat gold ring, will gradually wear away becoming thin from its contact with the harder alloy.

Properties of alloys

In general, the physical, chemical and mechanical properties of an alloy are not found by averaging the properties of its component pure metals. However, the following generalisations can be made.

(a) Hardness is generally at its highest for a composition of 50% of each metal, while strength (tensile) increases gradually towards that of the stronger component.

(b) Electrical conductivity is usually lower in alloys than it is in the pure elements, and even very small amounts of alloying elements are sufficient to lower the electrical conductivity drastically.

3.2 Transition Elements

The d-block elements are unambiguously identifiable: **d-block elements are those where the highest energy electron occupies a d sublevel**. They form an obvious block of thirty elements in the middle of the periodic table.

The term 'transition element' is defined differently in different sources. The transition elements are grouped together because they have similar properties, i.e. they all exhibit variable valency, they form coloured compounds and complexes, and frequently have good catalytic properties. We need a definition that identifies the elements with these properties, and excludes those that do not have some or all of these properties.

Sometimes the terms transition elements and d-block elements are taken as synonymous. But not all thirty d-block elements form coloured compounds, e.g. zinc. Mercury and cadmium have fixed valency in their compounds. Therefore, the definition of transition metal does not correctly apply to all of the d-block elements.

The most widely used definition is that transition elements have partially-filled d sublevels. This definition excludes the elements zinc, cadmium and mercury and therefore is more satisfactory than the first. However, not all the remaining twenty-seven elements identified by this definition exhibit variable valency. The elements scandium, yttrium and lanthanum each have a fixed valency of three and therefore do not have one of the important chemical properties associated with transition elements.

The accepted definition of a transition metal is that it is a metal which **forms at least one ion with a partially filled d sublevel.**

The electron configurations of the first row of d-block elements are given in Table 3.1 (p. 45) with the transition elements in bold print. Note that in chromium and copper, the electrons in the two highest energy sublevels are distributed in these sublevels to achieve maximum stability. In chromium, two half-filled sublevels ($4s^1 3d^5$) are more stable than the $4s^2 3d^4$ alternative. Similarly in copper, a half-filled 4s sublevel and a filled 3d sublevel ($4s^1 3d^{10}$) is a more stable configuration than the $4s^2 3d^9$ alternative. In the case of copper, this does not contradict the definition of a transition element as at least one ion (Cu^{2+}) has a partially filled d sublevel.

The common oxidation states for these elements are also given with the most stable oxidation state of each element underlined.

Atomic No	Symbol	Electronic configuration	Oxidation states observed
21	Sc	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^1$	+3
22	Ti	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^2$	+2, +3, +4
23	V	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^3$	+1, +2, +3, +4, +5
24	Cr	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^5$	+1, +2, +3, +4, +5, +6
25	Mn	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^5$	+1, +2, +3, +4, +5, +6, +7
26	Fe	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^6$	+1, +2, +3, +4, +5, +6
27	Co	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^7$	+1, +2, +3, +4, +5
28	Ni	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^8$	+1, +2, +3, +4
29	Cu	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^{10}$	+1, +2, +3
30	Zn	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}$	+2

Table 3.1 *Electronic configurations and observed oxidation states for the first row d-block metals. In each the most common oxidation state of the element is underlined.*

Variable Valency

The electron configurations given for each first row d-block element above, show the electrons conforming to the Aufbau Principle, i.e. the electrons occupy the lowest energy set of orbitals. However, when electrons are lost by d-block elements, the 4s electrons are lost before the 3d electrons. This is because the 3d electrons are strongly stabilised as the nuclear charge increases. This stabilisation of 3d electrons also accounts for the fact that manganese can lose up to seven electrons while iron, cobalt and nickel do not lose all their 3d electrons.

Scandium has no oxidation state other than +3.

Titanium has three possible valencies, 2, 3 and 4, depending on whether it loses both of the 4s electrons, the 4s electrons and one 4d electron or both the 4s and both the 4d electrons.

In a transition metal exhibiting variable valency, one of the valencies occurs more commonly than the others. In titanium compounds the oxidation state of +4 is more common than oxidation states of +2 or +3. In addition, one of the oxidation states is more stable than the others. This is not necessarily the most common oxidation state although in the case of titanium the +4 is also the most stable.

Similarly, vanadium has five possible valencies, 1, 2, 3, 4 and 5, corresponding to the loss of one or both of the 4s electrons, the 4s electrons and one 4d electron, both the 4s and two of the 3d electrons or finally the 4s and all three 3d electrons. Here the +4 is the most stable oxidation state.

For chromium, the most common and most stable oxidation state is +3, and oxidation states up to +6 are known.

The electron configurations of the ions of manganese are given in Table 3.2.

Oxidation states of manganese	Electronic configuration
Mn^+	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^5$
Mn^{2+}	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^0, 3d^5$
Mn^{3+}	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^0, 3d^4$
Mn^{4+}	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^0, 3d^3$
Mn^{5+}	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^0, 3d^2$
Mn^{6+}	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^0, 3d^1$
Mn^{7+}	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^0, 3d^0$

Table 3.2 *Oxidation states of manganese and corresponding electronic configurations*

Electron configurations for the ions of the other transition metals follow a similar pattern, the 4s electrons being lost first. The most stable oxidation state of manganese is +2.

Iron, cobalt and nickel can lose either one or two 4s electrons or the two 4s electrons and one 3d electron. Further 3d electrons are not lost because of the increasing nuclear charge in these elements giving greater stability to electrons in 3d orbitals. In all three elements the +2 oxidation state is the most stable. The electron configuration of Fe^{3+} is clearly more stable than that of the Fe^{2+} ion, but Fe(II) compounds of iron are more effectively stabilised by the atoms, ions or neutral molecules with which the transition metal ion bonds.

Copper is the only first row transition d-block element where the +1 oxidation state occurs in simple binary compounds, e.g. CuCl. The oxidation state of +2 is more common and more stable.

In the case of zinc, the only valency observed is 2, corresponding to the loss of the 4s electrons.

Coloured Compounds and Complexes

Compounds of the transition elements are often coloured. Transition metal compounds are responsible for some of the shades of artists' oils and watercolours. The pigments chrome yellow, raw sienna, cobalt blue and prussian blue contain the compounds $PbCrO_4$, Fe_2O_3, CoO and $KFe[Fe(CN)_6]$, respectively. Manganese dioxide, MnO_2, is used to colour glass or enamels black.

Colour changes in spot tests for chemicals are often due to transition metals changing from one oxidation state to another or taking part in other non-redox reactions. For example, in the test for reducing sugars with Fehling's reagent, the original blue colour is due to $Cu^{2+}_{(aq)}$ and it is reduced to a red precipitate of Cu_2O during a positive test. Furthermore, in the breathalyser test for alcohol, a chromium compound changes colour from orange, Cr(VI), to green, Cr(III), in the presence of alcohol and a spot test for water uses anhydrous $CoCl_2$ which is blue but changes to pink in the presence of water.

Transition metal compounds are coloured because their electronic structures permit the absorption of light from the visible region of the electromagnetic spectrum. As a result, the visible colours not absorbed are transmitted or reflected giving the transition metal compound the colour of the transmitted or reflected light.

Since the transition element has a different electronic structure for each of its oxidation states, then more than one colour is associated with each element. For example, there are green, red, yellow and blue-violet chromium compounds. Furthermore, not all compounds of the same element in the same oxidation state have the same colour since the other atoms, ions or molecules to which the transition metal is bound will also contribute to the electronic properties of the compound. Therefore, while many Cu^{2+} compounds are blue, copper(II) chloride is green.

Compounds of elements, which are not transition elements, generally do not absorb light from the visible part of the spectrum and therefore either transmit all of the light incident on them or reflect it, giving them a colourless or white appearance, respectively. Since the distinguishing feature of the transition elements is the partially-filled d sublevels, it is not unexpected that the absorption of light from the visible part of the spectrum involves the electrons of the d sublevel. The explanation of these d-d electron transitions lies in crystal field theory, which is beyond the scope of this booklet.

However, colour is not exclusive to transition metal compounds and not all transition metal compounds are coloured. A number of non-metal elements are coloured. These include sulphur, carbon in the form of graphite and phosphorus. Many organic compounds are coloured, particularly if there are extended conjugated systems of double bonds (i.e. double bonds separated by a single bond) and aromaticity in the compound, e.g. 2,4-dinitrophenylhydrazones. There are even a number of simple main group substances which are coloured, e.g. yellow PCl_5, and black Sb_2S_3, a pigment used in mascara.

A very important transition metal compound whose usefulness depends on it being non-coloured is titanium oxide, TiO_2, the white pigment used extensively in paints of light shades to give an opaque coat, and in correction fluids for the same reason.

Transition Metals as Catalysts

Many transition elements have catalytic properties. This can be explained in terms of the partially filled d sublevel which is characteristic of such elements. Electrons from the substrate molecule(s) can form temporary bonds with the transition metal atom using d orbitals to do so. Vacant d orbitals may also be used for electron transfers which occur during the reaction. Both of these processes change the mechanism of the original reaction, and if the new mechanism is lower in activation energy, successful catalysis is achieved.

There are many examples of heterogeneous catalysis involving transition metals where a substrate molecule bonds to the solid transition metal surface. This has the effect of increasing its concentration there and therefore leading to an increased rate of reaction if sufficient surface area of metal is provided. By bonding to the metal surface the original bonds of the substrate are weakened and this activates the molecule and makes it more susceptible to rearrangement or reaction with another molecule. Reaction with another molecule is also facilitated by the availability of vacant d orbitals for electron transfers from one molecule to the other. Examples of heterogeneous catalysis by transition metals or transition metal compounds include:

(i) the hydrogenation of unsaturated hydrocarbons over Ni at 200 °C;

(ii) the production of ammonia from hydrogen and nitrogen gases using an iron catalyst;

(iii) nickel oxide, NiO, catalyst in steam reforming of natural gas;

(iv) the use of manganese dioxide, MnO_2, to decompose hydrogen peroxide.

Transition metals and their compounds are also involved in homogeneous catalysis which takes place in solution. Examples include: (i) the use of Co^{2+} as the catalyst in the reaction between sodium potassium tartrate and hydrogen peroxide and (ii) Mn^{2+} ions act as an autocatalyst in the reaction between potassium permanganate [potassium manganate(VII)] and ethanedioic acid.

Again, it is the ability of the transition metal ion to use its partially-filled d sublevel to form a complex with one of the reactants, which is responsible for the change in the overall rate of reaction. The bonds of the substrate molecule are disturbed in making the catalyst-substrate complex and, as a result, the catalyst-substrate complex reacts quickly with the second reactant. Note that catalytic behaviour is not confined to transition metals and their compounds.

3.3 Isolation of Metals

The method employed to extract a metal from its ore is directly related to its position in the electrochemical series. The isolation of the elements potassium, sodium, calcium and magnesium was not achieved until 1808. In modern times, electrolysis remains the most efficient method for obtaining these metals, although in theory, sodium could be obtained by displacement with potassium, etc. The other methods available to chemists for isolating metals from their ores, namely roasting or roasting with a reducing agent, were not sufficient to reduce the ions of these elements within a reasonable time and at reasonable rates of heating. Similarly, the most economic way of producing aluminium is to electrolyse pure alumina. Because of their reactivity, the alkali metals have no everyday household uses. While magnesium has a number of uses in making low-density alloys, in fireworks and in the laboratory, it has few everyday uses.

Metals below aluminium in the electrochemical series are more easily reduced and therefore roasting the metal in the presence of a reducing agent will provide the metal. Examples of metals produced from their ores in this way include iron, zinc and lead. Common reducing agents include hydrogen, coke and the alkali metals. The extraction of iron from its ore is described below as an example of this type of metal winning (extraction). These metals are amongst the most widely used metals with greatest annual production. Iron is the single most widely used metal for construction of machinery, bridges, railways, tools and in steel-reinforced concrete, etc. Lead and zinc are also quite widely used, although their consumption levels are approximately 100 times less than that of iron.

Metals low down in the electrochemical series include copper, silver and gold. To reduce the metal ions to the corresponding metals it is only necessary to provide heat, although further reactions are sometimes necessary to isolate the metal. Gold has a complete resistance to corrosion, which means it does not have to be chemically reduced during its extraction from its ores although it usually has to be physically separated from impurities present. Metals of this type are called the coinage metals as they were originally used as coins and other precious items. Since early civilisations were able to obtain these metals from their ores, they retained their value, as their rates of corrosion were low. Their abilities to retain their value, their association with jewellery and their comparative rarity, keep the cost of these metals, particularly silver and gold, relatively high today.

3.4 Iron

Extraction of Iron using the Blast Furnace

The principal ores of iron are haematite, Fe_2O_3 and magnetite, Fe_3O_4. The iron content of ores can vary from a good 70% to a poor 20%, so ores from different sources are used to give a suitable charge. The iron is extracted from iron ore in a blast furnace, Fig. 3.1. No iron ore occurs to any significant extent in Ireland so there is no blast furnace in this country.

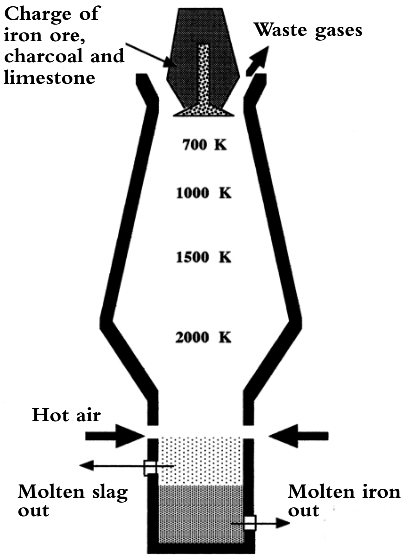


Fig. 3.1 *Extraction of iron*

The charge consisting of iron ore, coke and limestone is added at the top of the blast furnace, which is usually about 30 m high. The tower is lined with firebricks (refractory bricks) to withstand the high temperatures that are present. The tower must be re-lined after every six years approximately. The ore is sintered before addition to the furnace. This means that the crushed ore is mixed with limestone and coke. The mixture is baked and then broken up to give fused sinters of a suitable size.The use of sintered ore distributes material evenly in the furnace and ensures regular and efficient circulation of reducing gas within the furnace. The ore is added via a carriage on tracks, and a hopper, to an arrangement called a double bell. The charge falls on the sloping walls of the upper bell, which is then lowered. The charge slides down the sides of the larger bell and into the space between the bells. The second bell is then lowered and the charge slides down the walls of the smaller bell and into the furnace. This arrangement is to allow the addition of materials to the furnace without the escape of exhaust gases.

As the material falls, different reactions occur at different temperatures at different levels of the tower. The carbon in the coke burns at the high temperatures low in the tower to form CO_2. Hot air is blasted into the lower part of the furnace through nozzles called **tuyeres**. The burning of coke is an exothermic reaction and generates the heat which allows all the other chemical reactions mentioned (all of which are endothermic) to take place. The coke also provides a strong support to hold the charge at the top of the blast furnace, and to allow molten products to trickle down and gases to travel upwards. The following are the main reactions that occur.

1. Burning of coke (occurs in the lower region of the furnace i.e. at high temperature).

$$C + O_2 \rightarrow CO_2$$

2. More CO_2 is formed from the decomposition of the limestone (occurs in the middle to lower regions of the furnace, i.e. at a slightly lower temperature).

$$CaCO_3 \rightarrow CaO + CO_2$$

3. As the CO_2 rises, it reacts with carbon midway in the tower, to yield CO (occurs in the middle region of the furnace).

$$CO_2 + C \rightarrow 2CO$$

   Thus, the coke generates heat, provides a solid support and generates the principal reducing agent.

4. The reduction of iron ore by CO, the principal reducing agent, occurs at the cooler temperatures high in the tower.

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$

Excess CO is removed through waste gas exhaust pipes, the downcomer, at the top of the blast furnace. After scrubbing, this gas is burned in special stoves to generate heat for the air blasted into the tuyeres at the bottom of the furnace, as well as providing heat for the rest of the plant. The lime formed from the decomposition of the limestone reacts with sandy impurities such as SiO_2, to form slag.

$$CaO + SiO_2 \rightarrow CaSiO_3$$

The molten iron and slag trickle to the bottom, **the hearth**, where the less dense slag floats on the molten iron. The iron produced has a melting point of about 1200 °C and is called 'pig iron' and it contains upwards of 3% carbon and traces of silicon, sulphur, phosphorus, and manganese. Though this material is hard, it is brittle and is unsuitable for most uses. Brittle means that the cast iron shows little or no permanent deformation before it breaks. Pig iron gets its name from the shape of the moulds into which it used to be cast. Nowadays the pig iron is usually converted to steel without cooling to a solid and is therefore called 'hot iron'. The slag may be used for road construction.

The modern blast furnace is the centrepiece in an extremely efficient continuous process for the production of iron from its ore. Such a furnace is capable of producing up to 10 000 tonnes of iron per day from about 15 000 tonnes of ore, requiring 4500 tonnes of coke, 14 000 tonnes of hot air and 1000 tonnes of limestone.

The role of carbon is important. Pig iron contains a relatively high percentage of carbon and it is brittle and has few direct applications. If the pig iron from the blast furnace is re-melted, it is known as cast iron. Cast iron has moderate strength and hardness, poor ductility but good ability to acquire a shape in a mould. Cast iron was therefore widely used to make stoves, engines of early cars, lamp posts, post boxes, etc. Melting pig iron and iron oxide together makes wrought iron. As a result the impurities in pig iron are oxidised and the percentage iron content of the metal increases. The Eiffel Tower is constructed of wrought iron, as are gates and railings. However, wrought iron is unsuitable for purposes in which load bearing is required.

Steelmaking

Steel is an alloy of iron and carbon that can contain up to 1.5% carbon but most steels have only 0.1 - 0.25% carbon and, depending on the use of the steel, a number of other metals may be present. We can classify different steels according to the quantity of carbon present in them.

1. Low carbon steel (mild steel): contains less than 0.25%(w/w) C. It is a general purpose steel, for applications where strength is not particularly important, such as nails, car bodies.

2. Medium carbon steel: contains anything from 0.25 to 0.50%(w/w) C. It is employed for components needing a higher strength than that of mild steel coupled with good toughness (i.e. it cannot be brittle).

3. High carbon steel: contains greater than 0.50%(w/w) C. This steel type is hard, but lacks the ductility and toughness of the lower carbon content steels. Therefore, it is often found in applications where wear is the prime consideration, e.g. in cutting tools.

The pig iron from a blast furnace can be converted to steel by injecting oxygen into it using a lance. This is called the **Basic Oxygen Process**. The amount of oxygen added is carefully controlled to bring the carbon content down to the required level. Carbon is converted to carbon dioxide, which escapes. Other impurities in the pig iron are also oxidised at this stage. Sulphur dioxide from any sulphur impurities also escapes. Lime is added to convert other oxides such as SiO_2, SO_3 and P_2O_5 to slag, consisting of $CaSiO_3$, $CaSO_4$ and $Ca_3(PO_4)_2$. This slag floats on the steel and is tapped off separately.

Irish Ispat in Haulbowline, Co. Cork recycles scrap steel, (two-thirds of which is imported), by melting it together with lime using an electric arc to supply the heat. The process is carried out in a steel furnace lined with refractory bricks and possessing two spouts, one low down at the front to pour the processed steel, the second higher up at the back of the furnace for slag. Three graphite electrodes connected to a three-phase power supply are lowered through a water-cooled lid. A water-cooled lance, through which oxygen is blown, is also inserted through the lid. This process for steel production is called the **Electric Arc Process**.

Charging

Scrap steel (about 110 tonnes) is added and melted in the furnace in stages. Five tonnes of lime are added to react with impurities in the steel and separate them as slag.

Melting

When the lid is put in place, the electrodes are lowered to within 15 cm of the surface of the metal; a spark or arc of electricity passes from the electrodes to the metal. Due to the high temperature of the arc (3500 °C) at the tips of the electrodes, the scrap is soon melted.

Analysis and refining

A sample of the molten scrap is analysed for 17 different elements. Oxygen blown into the scrap steel via the water-cooled lance oxidises carbon to carbon monoxide and then to carbon dioxide. Extractors remove the waste gas. The heat generated in the oxidation of carbon helps to keep the contents of the furnace molten. Phosphorus and silicon react with oxygen to give phosphorus pentoxide and silicon dioxide, respectively. These oxides, and also aluminium oxide present in the scrap metal, then react with the lime present, to form slag. Metals, including manganese and vanadium, are added to the steel to increase hardness and strength. Chromium and nickel increase corrosion resistance. Further analysis is carried out to ensure that the impurity levels, particularly those of carbon, have fallen into the acceptable range, depending on customer requirements.

Tapping

The furnace is tilted back and the molten slag floating on top of the refined steel is poured into a trolley. This slag is used in road making. The furnace is tilted forward and the molten steel is poured out into an insulated ladle, from which the steel is allowed to flow directly into casting machines.

In Irish Ispat, casting and rolling produces channels and beams of steel to meet specific customer requirements.

Steel is several times stronger than pig iron and alloying with trace amounts of elements such as nickel and chromium can change its resistance to corrosion. Manganese is used to harden the steel.

Rusting of Iron

Iron does not corrode in dry air, or in water free of oxygen. Iron requires moist air for the familiar rapid corrosion to produce a red/brown flaky product called rust. Corrosion is even faster when salt or acid is present or if the iron is heated. Iron will corrode more rapidly in contact with metals below it in the electrochemical series (e.g. lead or copper) and less rapidly when in contact with metals above it (e.g. magnesium or zinc).

The rusting of iron is an electrochemical process that occurs in tiny electrochemical cells, e.g. a droplet of water on the surface of the metal or in a scratch or crevice. The first stage in the corrosion of iron is the oxidation of Fe to Fe^{2+}, which damages the iron surface. This can be considered the anode reaction.

$$Fe \rightarrow Fe^{2+} + 2e^{-}$$

The electrons lost in this step travel through the water to the edge of the drop, or to dissolved oxygen in the drop, where they cause the reduction of oxygen to hydroxide ions. The reaction that occurs is

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-}$$

The above equation can be considered as the cathode reaction.

The iron(II) ions and the hydroxide ions react to form a precipitate of iron(II) hydroxide.

$$Fe^{2+} + 2OH^{-} \rightarrow Fe(OH)_2$$

Iron(II) hydroxide is rapidly oxidised by air to insoluble rust with a formula which may be written as $Fe_2O_3.H_2O$. This step involves the oxidation of Fe^{2+} to Fe^{3+}. Rust does not adhere to iron and flakes off, exposing fresh iron to further corrosion.

MODULE 10

Some Irish Contributions to Chemistry

SOME IRISH CONTRIBUTIONS TO CHEMISTRY

by Charles Mollan

Introduction

It is not generally recognised that Ireland has a scientific history of which to be proud. The chemistry taught to-day in Ireland's schools is the result of centuries of accumulating knowledge, and Irish scientists have made important contributions over the years.

Of course, science is not bound by the constraints of national boundaries. But it is scientists who make scientific discoveries. The place and circumstances of the birth and childhood of these people will have had a profound effect on their character and initiative. The distinctive Irish contributions to literature are widely recognised, and the Irish background of our literary giants is appreciated internationally. We have made equivalent contributions to science, but little attention has been paid to this aspect of our culture. It is time that we claimed or reclaimed our due credit.

In chemistry, we have a very good place to start, for Robert Boyle (1627-1691), who was born in Lismore in Co. Waterford, is widely described as "the Son of the Earl of Cork(e) and the Father of Chemistry".

Chemistry before Boyle

Of course, no one will claim that chemistry started with Robert Boyle. Applied chemistry has prehistoric roots. Once fire was controlled, cookery (sometimes called the first science), the metallurgical arts, the making of pottery, paints, perfumes, and glass, were developed (Brock 1992,9-11). The seven basic metals, via their associations with the planets, gave their names to the days of the week:

Gold	Sun	Sunday	
Silver	Moon	Monday	
Iron	Mars	Tuesday	(Saxon Tiw = Mars)
Mercury	Mercury	Wednesday	(Saxon Woden = Mercury)
Tin	Jupiter	Thursday	(Saxon Thor = Jupiter)
Copper	Venus	Friday	(Saxon Friff = Venus)
Lead	Saturn	Saturday	

If we visit the National Museum in Dublin we will see how well metallurgy was developed in Ireland from prehistoric times.

Early Irish chemistry had close associations with medicine, and some of the Irish clans had hereditary physicians (Ó Raghallaigh 1941,1-2):

> *The O'Hickeys were hereditary physicians to the O'Briens of Thomond, and the O'Shiels to the Mahoneys of Oriel. O'Callenans migrated from Galway to Cork, and their fame became a proverb, so that, down to the middle of the eighteenth century, it was said of an incurable patient: 'Not even an O'Callenan could save him'. Halley* [Edmond Halley, 1656-1742], *the celebrated astronomer, was descended from an Irish family of hereditary physicians.*

Indeed, it is likely that Robert Boyle developed his interest in chemistry partly as a result of his own poor health. One sickly episode in Boyle's early life was the result of an apothecary's mistake while Robert was at Eton College, an incident about which he wrote (Boyle 1648-9, quoted in Maddison 1969,16):

This Accident made him long after apprehend more the Fisicke than the Disease & was possibly the occasion that made him afterwards so inquisitiuely [to] apply himself to the study of Fisicke, that he may haue the lesse need of them that professe it.

Chemistry did not develop as early as astronomy, physics, or indeed anatomy and physiology, because it presented the early natural philosopher with particularly difficult problems. Chemicals were not generally found in their elemental state, but in complex molecules and mixtures, there were no recognised divisions into organic and inorganic compounds, into solids, liquids and gases, into acids, bases and salts, no concept of purity, and no accepted chemical language (Brock 1992,42).

The burning of wood had been given as evidence of the four elements - fire, air, water, and earth - of which matter was believed to be composed (Boyle 1661,21-22):

If You but consider a piece of green-Wood burning in a Chimney, You will readily discern in the disbonded parts of it the four Elements, of which we teach It and other mixt bodies to be compos'd. The fire discovers it self [sic] in the flame by its own light; the smoke by ascending to the top of the chimney, and there readily vanishing into air, like a River losing it self in the Sea, sufficiently manifests to what Element it belongs and gladly returns. The water in its own form boyling and hissing at the ends of the burning wood betrays it self to more then [sic] one of our senses; and the ashes by their weight, their firiness [sic], and their dryness, put it past doubt that they belong to the Element of Earth.

Thus we will start our account with Boyle, who introduced science to the rigours of the experimental method, and demonstrated that there was a better explanation of chemical phenomena than the fire, air, water, and earth concept, or indeed its rival, which postulated the three elements, mercury, sulphur, and salt.

Robert Boyle (1627-1691)

Robert Boyle was born at Lismore Castle in Co. Waterford, on 25 January 1627, the second youngest of fifteen children of Richard Boyle (1566-1643), the first Earl of Cork, who arrived in Ireland in 1588. His mother was Katheryne Fenton (c.1586-1630), Richard's second wife, whom he married in 1603 (she was 17 and he was 36 at the time). Katheryne (also referred to as Catherine or Katherine) was the Irish-born daughter of Sir Geoffrey Fenton (c.1539-1608), Principal Secretary of State in Ireland from 1580.

Robert was fortunate in having been born, as he put it 'in a Condition that neither was high enuf to proue a Temptation to Lazinesse, nor low enuf to discourage him from aspiring' (quoted in Maddison 1969,3). At Lismore, he was provided with a tutor at an early age, becoming very proficient at Latin and French. His mother had died when he was three, and he was sent to Eton College in England at about eight years of age. He stayed there for four years. After this, he left on an extended European tour, and his party was in Florence when Galileo died in nearby Arcetri in 1642. After his father's death in 1643, Robert returned to a war-torn England, but he managed to keep his head down politically, and occupied himself with chemistry at the manor at Stalbridge in Dorset, the first English estate purchased by his father in 1636.

Robert belonged to a group of thinkers who met together in London to discuss scientific topics. Several members of this group took up residence in Oxford, and Boyle followed them there, after a brief return, in the early 1650s, to his estates in Ireland. At Oxford, he carried out experiments on the nature and properties of the vacuum, using an improved air pump. He demonstrated that sound could not be heard in a vacuum, that a feather fell faster in a vacuum than in air, that a candle was extinguished, and that an unfortunate cat died. We particularly remember Robert Boyle today when we learn

Boyle's law, which states that, at constant temperature, the volume of a fixed mass of gas is inversely proportional to the pressure applied to it ($V \times p$ = constant). He published his results in his 1660 book (second edition 1662) *New experiments physico-mechanical, touching the spring of the air, and its effects.*

Boyle introduced the experimental method by describing procedures and results in sufficient detail so that others could assess and repeat the work at a later date. Contemporary thinkers, like the Dutch physicist Christiaan Huygens (1629-1695) and the German mathematician Gottfried Leibniz (1646-1716), doubted the value of demonstrating by experiment what they, and all 'rational' thinkers, knew to be true by logical reasoning alone. Robert was born into a world in which the theories of Aristotle and the beliefs of alchemy were paramount. When he died, experimental science was firmly established, and much of the credit is due to him.

In 1661, the year after he and others founded the Royal Society, he published his most famous work, whose impressive full title is rarely quoted:

The SCEPTICAL CHYMIST or CHYMICO-PHYSICAL Doubts & Paradoxes, Touching the SPAGYRIST'S PRINCIPLES Commonly Called HYPOSTATICAL, As they are wont to be Propos'd and Defended by the Generality of ALCHYMISTS Whereunto is PRAEMIS'D Part of another Discourse relating to the same Subject

In this book, commonly abbreviated to *The sceptical chymist*, he described many of his recent experiments, including the preparation of hydrogen by the action of mineral acid on steel filings, and new compounds of copper and mercury.

Robert believed that what he called 'corpuscles' were arranged into stable 'primary mixts' such as the metals, and these endured through series of chemical reactions. They would be something like what we now identify as chemical elements (Knight 1992,37). All science could be constructed on the ideas of matter and motion:

Mechanical principles and explanations are for their clearness preferred….the sagacity and industry of modern naturalists and mathematicians having happily applied them to several of those difficult phenomena….that before were or might be referred to occult qualities….when this philosophy is deeplier searched into and farther improved, it will be found applicable to the solution of more and more of the phenomena of nature (quoted in Knight 1992,37).

He introduced many analytical tests, including the use of vegetable dyes as acid-base indicators, and flame tests to detect metals. His tests enabled him to classify substances as acidic, alkaline or neutral. The use of colour reagents was described in his 1663 *Experiments and considerations touching colours.*

In 1668, he moved to London, and remained there - at the home of his sister, Katherine, Lady Ranelagh, in Pall Mall - until his death, devoting time to the affairs of the Royal Society. One of his neighbours in Pall Mall was Nell Gwyn, mistress of Charles II.

Robert had interests beyond productive science. He continued to be attracted to alchemy. He was an extraordinarily devout man, who wrote as much on theology as on natural philosophy, and he paid for translations of the Bible into Irish and Welsh. He even paid for it to be translated into a native American language (Knight 1992,34). Nevertheless, due to his influence, science was changed, and has progressed at an ever-increasing pace since his time.

Irish-born Robert Boyle not only initiated Irish contributions to modern chemistry, but he also played a major role in establishing the international tradition of experimental science, which has so transformed our world. He died in London on 30 December 1691.

Peter Woulfe (c.1727-1803)

Although a much less influential figure, the name of Peter Woulfe has probably been used more in the average chemical laboratory than that of Robert Boyle, for he gave his name to that common item of laboratory glassware, the Woulfe bottle, which he described in a series of distillation experiments in 1767. This vessel, with two or three outlets on top, had a variety of uses, notably to pass a gas through a liquid in order to clean it or to absorb it.

Peter's origins are obscure, but he is reported to have been born near Limerick, descended from a colony of Palatine refugees imported by Queen Elizabeth to save them from persecution in their native Germany (O'Donnell 1976b,47). He appears to have lived mostly in Paris and London, and was elected Fellow of the Royal Society in 1767, when he was described as a 'Gentleman well skilled in Natural Philosophy and particularly Chymistry'. He received the coveted Copley Medal from the Society for his paper 'Experiments on distillation of acids, volatile alkalis, &c', in the Society's *Philosophical Transactions* (1767,517), and he investigated the Cornish tin deposits. He obtained marine ether (ethyl chloride) by distilling hydrochloric acid and alcohol separately and mixing their vapours, and he was the first to prepare picric acid by the action of concentrated nitric acid on indigo (Partington 1962,301).

He was an eccentric, and continued his beliefs in alchemy and transmutation. 'He had long vainly searched for the elixir, and attributed his failures to the want of due preparation by pious and charitable acts' (W.T. Brande, quoted in the *Dictionary of Scientific Biography - henceforth DSB* - Vol.14, 508). Humphry Davy (1778-1829) describes Peter attaching little pieces of paper with prayers on them to his apparatus (personal communication from Professor David Knight - who comments 'we might do so too if we had to cope with his glassware'!)

Peter Woulfe died in London in 1803.

Joseph Black (1728-1799)

If Robert Boyle is called the father of chemistry, another man with Irish roots can be credited as the founder of pneumatic chemistry and modern quantitative chemistry. He is Joseph Black.

Joseph was born in Bordeaux, France, on 16 April 1728, the ninth child of fifteen of John Black, a wine merchant from Belfast, and his wife Margaret Gordon. At the age of twelve, Joseph was sent to school in Belfast, and transferred four years later to Glasgow University, where he studied medicine. There he came under the influence of William Cullen, the first lecturer in chemistry at the University, and the first teacher of chemistry in Scotland to extend the scope of the subject beyond its application to pharmaceutical preparation. Cullen appointed Black to be his assistant in the chemical laboratory (Anderson 1982,7).

In 1752, Black left Glasgow for Edinburgh, where his MD degree thesis was based on the chemical properties of lime water, which was then used medically to dissolve urinary calculi. He studied 'magnesia alba', a basic magnesium carbonate and, in the process, was the first to appreciate the chemical distinction between 'fixed air' (later named carbon dioxide) and 'atmospheric air'. In 1757, he ascertained the effect of fixed air on animals, and its production by respiration, fermentation, and the burning of charcoal. His differentiation of the gas was soon followed by the discovery and investigation of hydrogen, nitrogen, oxygen, chlorine, and nitrogen oxides, by Henry Cavendish, Daniel Rutherford, Joseph Priestley, Antoine Lavoisier, and Wilhelm Scheele, respectively. Black had launched pneumatic chemistry. His work was characterised by the accurate use of the balance, laying the foundation of quantitative chemistry.

In 1756, he was appointed professor of anatomy and botany, and lecturer in chemistry, back at Glasgow, and then professor of medicine. He started his first chemistry course in 1757, and continued the course for ten sessions. It was during this period that he came into contact with James Watt, who developed the separate condenser steam engine. Watt provided him with laboratory apparatus, and eventually they went into partnership. Black's major researches were into the theory of heat, and he was the first to develop the concepts of latent and specific heat.

In 1766, he moved again to Edinburgh, where he was appointed professor of medicine and chemistry. At Edinburgh he concentrated on teaching, and did not emulate his brilliant early research successes.

But he was credited with exceptional lecturing skills. ‘His discourse was so plain and perspicuous, his illustrations by experiment so apposite, that his sentiments on any subject never could be mistaken, even by the most illiterate’ (Dictionary of National Biography - henceforth *DNB* - Vol.II,573). Even if this eulogy is a bit over the top, there is no doubt that he had a powerful effect on the popularisation of chemistry, not only in Scotland, and ‘attendance at his lectures came to be a fashionable amusement’.

He was widely admired in other respects (Anderson 1982,11 and *DNB* Vol.II,573):

He was a striking and beautiful person; tall, very thin and cadaverously pale; his hair carefully powdered, though there was little of it except what was collected into a long, thin queue; his eyes dark, like deep pools of pure water.

He was of most easy approach, affable, and readily entered into conversation, whether serious or trivial. Nor did he disdain elegant accomplishments. In his youth he both sang and played tastefully upon the flute.

None better knew to raise the glowing fire,
And bid the pungent volatiles aspire.
Sound his opinion, and his judgement rare,
Of salts and earths, of sulphur and of air.

(Quoted in Lawrence 1982,1)

Joseph died in Edinburgh on 6 December 1799.

Richard Kirwan (1733-1812)

Another eminent Irish chemist was not always so affable. A noted eccentric in his later years, Richard Kirwan refused to remove his hat at meals or even at court, and received his friends, summer or winter, extended on a couch before a blazing fire. He always ate alone. Flies were his especial aversion. He kept a pet eagle, and was attended by six large dogs (*DNB* Vol.XI,229).

Lady Morgan, a famous Dublin authoress of the time, described him when he first called to visit her (Donovan 1850,cix):

The apparition, which for a moment halted at the threshold, and then moved on in solemn gait, actually made me start. A tall, gaunt figure, wrapped from neck to heel in dark roquelaure, with a large-leafed hat flapped low over the face, presenting the very picture of Guy Fawkes with nothing wanted but his dark lantern: the venerable, but very singular-looking philosopher stood confessed.

This, however, is a very unflattering introduction to one of Ireland’s greatest historic scientists. In contrast, his biographer describes him in 1757 (Donovan 1850,lxxxv):

But a young gentleman of large fortune, handsome person, and pleasing manners, like Kirwan, received such flattering attentions from the Galway families resident in Dublin, that he could scarcely escape the nets spread for him in all directions.

Richard, who had intended to become a priest, gave up the unequal battle and married Anne Blake, whose family had ‘splendidly received him...with French wines and the choicest fruits of the country’.

Kirwan was born at Cloughballymore, Co. Galway, on 1 August 1733, the second son of Martin Kirwan and his wife Mary French. He had the misfortune of losing his father in 1741, when he was eight, and his beloved mother ten years later. Then his older brother was killed in a duel in Dublin in 1755, and his wife died in 1765 (*DNB* Vol.XI,228-9). There would seem to be ample reason for his later eccentricity.

His brother’s untimely death changed his life. Following his early education in Ireland, Richard had entered the University of Poitiers in France in about 1750, and joined the Jesuit noviciate in Paris in 1754. But after his brother was killed, he became heir to the family fortune. Back in Galway, he soon fitted up a laboratory and amassed a library. Following a brief foray into law (he was called to the Irish Bar in 1766), he returned to science, working both in Ireland and in England.

It is claimed that Kirwan was put off chemistry for a while by an apparent snub from Joseph Black (Donovan 1850,lxxxviii):

Dr. Black's discoveries respecting carbonic acid, and the cause of causticity, at this time occupied universal attention. Mr. Kirwan wrote him several letters containing observations on his views, but Black made no reply. So disappointed was Kirwan at this rather uncourteous treatment, that he relinquished his chemical inquiries, and did not resume them until he subsequently abandoned the profession of the law. He and Dr. Black afterward became the best friends.

Richard lived in London from 1769 to 1772, and again from 1777 to 1787, after which, because of his real or imagined state of health, he resided in Dublin for the rest of his life.

While in London, he had become a Fellow of the Royal Society in 1780, and was awarded its prestigious Copley medal in 1782 for his work on chemical affinity (*DSB* Vol.7,388):

Chymical affinity or attraction is that power by which the invisible particles of different bodies intermix and unite with each other so intimately as to be inseparable by mere mechanical means.

His most famous publication was called *An essay on phlogiston and the constitution of acids,* which appeared in 1787. Its impact can be seen in that it was translated into French in 1788 by Marie Anne Pierette Paulze, wife of Antoine Lavoisier (1743-1794), and it achieved a second English edition in 1789. It was thought that this mysterious phlogiston was lost when something burnt. Kirwan identified it with 'inflammable air' (hydrogen), contrasting it with Black's 'fixed air' (carbon dioxide). Careful quantitative analysis revealed that Kirwan was incorrect and that something (oxygen) was added on burning, rather than lost, for the result was a gain in weight not a loss. Donovan 1850,xcv records:

Kirwan's work was an obstacle which it was necessary to remove; and of such magnitude was it considered, that it was not only translated into French, but partitioned amongst no less than five of the most eminent chemists which France could at that time boast of, in order that they might reply to his arguments: these were Lavoisier, Berthollet, Morveau, Fourcroy, and Monge; and, truth to say, never was a refutation more complete.

Lavoisier published his classic *Traité élementaire de chimie* in 1789, the same year in which William Higgins (see below) published his *A comparitive view of the phlogistic and anti-phlogistic theories,* which sided with Lavoisier against Kirwan. In one of Lavoisier's experiments (Higgins 1814,2-3):

He confined mercury and oxygen, of ascertained weights, in an apparatus calculated for the purpose, and exposed the mercury to the heat of 700° of Fahrenheit: in time the whole of the oxygen united to the mercury, and converted it into a red oxide which weighed more than the mercury in the simple metallic state: this additional weight corresponded with the weight of the oxygen absorbed. When this oxide was exposed to a red heat, the whole of the oxygen was expelled in its gaseous state, without any change whatever, and the mercury was reduced to its metallic lustre and fluidity.

To his credit, Richard, 'with a candour which only belongs to superior minds, publicly acknowledged the subversion of the phlogistic hypothesis'.

Kirwan, then, is best remembered in the history of chemistry for encouraging Lavoisier into print. It was Lavoisier who gave the name oxygen (oxygine) to 'eminently respirable air'. Chemistry took a giant leap forward through his introduction of a new way of approaching chemistry (*DSB* Vol.8,81). Sadly, Lavoisier soon lost his need for oxygine, for he was sent to the guillotine in 1794. Joseph Lagrange is recorded as stating: 'It took them only an instant to cut off that head, and a hundred years may not produce another like it' (*DSB* Vol.8,85).

Madame Lavoisier, who had married her first husband when she was only 14 (Brody 1987,19) later married Sir Benjamin Thompson, Count Rumford (1753-1814), an American who had come to Ireland in 1796. However, in contrast to her first marriage, this second union 'turned out to be a complete disaster', and Madame Lavoisier Rumford (as she insisted on being called) is reported on one occasion as having poured boiling water over Rumford's flowers in the garden (Brody 1987,21). While in Ireland Rumford introduced many improvements into workhouses and hospitals. He was especially interested in the cooking of food and heating of houses, and he worked in the premises of the Dublin Society (later the Royal Dublin Society), which had been set up in 1731 with the purpose of 'improving husbandry, manufactures and other useful arts and sciences'. Impressed with that organisation, he founded the Royal Institution in Albemarle Street in London in 1799 (Berry 1915,225).

In addition to his more academic contributions to chemistry, Richard Kirwan had a particular interest in applied chemistry, writing about coalmines, and the analysis of the coal they produced, about manures used in agriculture, in which he pointed out the importance of mineral salts, and about the alkaline substances used in the bleaching of linen, and the colouring matter of linen-yarn (Philbin 1985,276). In the introduction to the latter study, he refers to the 'contradictory testimonies' of the principal bleachers, who were 'little acquainted with the general agency of the instruments' which they employed, and he commented (*Transactions of the Royal Irish Academy,* 1790,4):

> *This task, which I have imposed upon myself solely with a view to the utility of the public, requires no ingenuity, and might have been long ago well executed by others, if chymistry, which has so many votaries of the highest rank in the most civilised parts of Europe, had been more known and cultivated in this country, which perhaps of all others stands most in need of its assistance.*

But Kirwan's abilities in chemistry, so widely acknowledged internationally in his day, were not his only claims to fame. He also made important contributions to mineralogy and meteorology.

He published his *Elements of mineralogy* in 1784, the first systematic work on the subject in English. In the preface to this work, he contrasts the neglect of the science in England (where he was living at the time) with the situation in Continental Europe (quoted in Philbin 1985,278):

> *Chymistry, the parent of mineralogy, is cultivated by the most enlightened nations in Europe and particularly in France, with a degree of ardour that approaches to enthusiasm.*

His *Elements* was translated and published in Paris within a year (Burns 1985,15), and a second English edition was published in two volumes in 1794 and 1796, with translations also into German and Russian. Richard was the prime mover in persuading the Dublin Society to purchase the Leskean cabinet of 7331 specimens of minerals in 1792, the total cost to the Society being about £1350. The collection had been built up by Nathaniel Gottfried Leske, professor of natural history at Marburg, in 1782 to 1787, and it was enlarged, revised and described by Ludwig Karsten after Leske's death. Kirwan subjected it to a rigorous examination, and corrected errors. He pronounced it 'one of the most perfect monuments of mineralogical ability extant' (Berry 1915,156-7).

In meteorology, Kirwan published *An estimate of temperature of different latitudes* in 1787, collecting data from 42 places, from Lapland to the Falkland Islands, from Peking to Philadelphia (Dixon 1987,54). He used his own and earlier weather summaries to predict seasonal weather with great success, and was reputed to have been consulted as a weather-prophet by half the farmers in Ireland! (*DNB* Vol.XI,229). Between 1788 and 1808 he published 38 memoirs in the *Transactions of the Royal Irish Academy*, many of them dealing with meteorology. They included an essay on the variations of the barometer, and the description of a new anemometer, as well as several 'synoptical views' on the state of the weather (Donovan 1850,xcvi-xcvii). Many of his ideas anticipated twentieth century concepts, such as the air mass idea, with air masses classified as polar, extra-tropical, intra-tropical, supra-terrene and supra-marine (Dixon 1987,54).

His reputation was such that a Kirwanian Society was set up in Dublin during his lifetime (Donovan 1850,xciv). On the death of Lord Charlemont in 1799, Richard was elected President of the Royal Irish Academy, a position he retained until his death in Dublin on 1 June 1812. He was an honorary member of the Academies of Stockholm, Uppsala, Berlin, Dijon and Philadelphia. He asked that 'he should be buried with as little expense, and in as private a manner as possible', but his reputation was such that 'there were between 800 and 900 gentlemen' in his funeral procession to St George's Church, 'followed by a numerous train of carriages of the nobility and gentry' (Donovan 1850,cxv). His portraits can still be seen at the Royal Irish Academy and at the Royal Dublin Society, and the latter body retains his elegant double burning glass, which it purchased from his Executors in 1812 (Mollan 1995b,212).

Bryan Higgins (c.1741-1818)

Where the Kirwans belonged to the landed tribes of Galway, the Sligo branch of the O'Higgins clan were a bardic family with traditions going far back into old Gaelic times. As the bards declined in importance with the ruin of native chieftainry, some of them turned to medicine for a surer livelihood. The Colooney [sic] branch of the O'Higgins clan shared this progressive attitude, with their medical tradition producing two major chemists as the eighteenth century drew to a close (O'Donnell 1976a,48).

Bryan Higgins was born at Collooney, Co. Sligo, the third son of a successful physician, also Bryan, and he took an MD degree from Leiden University. He married an heiress, Jane Welland of London, about 1770 and, in 1774, opened his school of practical chemistry in Greek Street, Soho, near Josiah Wedgwood's London showrooms. His idea was that the pupils at the school, who included noblemen and gentlemen, 'might have uncommon advantages, at the same time that my apparatus might be enlarged, and my experiments conducted at common expense' (*DSB* Vol.6,382).

Apart from his courses in chemistry, of which he published the syllabus on three occasions, he had a practical turn of mind. He took a patent for a cheap form of cement in 1779, and he resided in Spanish Town Jamaica between 1797 and 1799, where he advised on the manufacture of sugar and rum (DNB Vol.IX, 817-8). He also developed a considerable business in the manufacture and supply of reagents and chemicals. In 1786, he published his best known work *Experiments and observations relating to acetous acid, fixable air, dense inflammable air, oil & fuels, the matter of fire and light, metallic reduction, combustion, fermentation, putrefaction, respiration, and other subjects of chemical philosophy.* His writings 'reveal a powerful mind actively grappling with some of the leading theoretical problems of the day' (*DSB* Vol.6,384). He died in Walford, Staffordshire, in 1818.

William Higgins (1763-1825)

William Higgins, who was also born in Collooney, Co. Sligo, was the second son of physician Thomas Higgins, elder brother of Bryan. Little of William's early life is known, but he was sent to work with his uncle, Bryan, in London about 1782 (Wheeler 1960,viii,2&58). He became a lecturer-assistant at Oxford from 1786 to 1788, working with Thomas Beddoes (1760-1808), before returning to London. Dr Beddoes' wife was a sister of Irish novelist, Maria Edgeworth (1767-1849) (Ó Raghallaigh 1941,1). Her father, Richard Lovell Edgeworth (1744-1817) had four wives and twenty-two children, of whom nineteen survived infancy, and they turn up all over the place. Another, for example, was the wife of Irish astronomer, Thomas Romney Robinson (1793-1882) who, in 1850, invented the familiar four-cup anemometer for measuring wind speed.

In 1792, William was appointed chemist at the Apothecaries' Hall in Dublin with a generous salary of '£200 a year, apartments, coals and candles' (*DSB* Vol.6,385). In 1795, he became Professor of Chemistry and Mineralogy to the Dublin Society (later the Royal Dublin Society). There he had charge of the impressive Leskean collection of minerals which was purchased by the Society in 1792 thanks largely to the inspiration of Richard Kirwan (*see above*).

However, knowing of his already established reputation as a chemist, the Society ordered also (quoted in Berry 1915,355-6):

> *That from Mr. Higgins' extensive skill at chymistry he be directed from time to time to make such experiments on dyeing materials and other articles, wherein chymistry may assist the arts as may occur; and that, for that purpose, a small chymical apparatus should be procured and erected in the repository, under the direction of Mr. Higgins.*

William remained at the Society until his death. While at the Dublin Society he acted also as chemist to the trustees of the linen and hempen manufacturers of Ireland, publishing his *Essay on bleaching* in 1799 (*DSB*, Vol.6,385). He was called to London in 1802 by His Majesty's Revenue, 'as a person of skill and ability to assist in ascertaining an hydrometer which shall hereafter be made use of to judge the strength of spirits subject to excise or import duty' (Berry 1915,357). He thus represented one of the first examples of a new kind of chemist - the professional chemist. Earlier practitioners had largely been either gentlemen of means or university academics (usually of medicine).

Before his appointment to the Apothecaries' Hall, William had entered the fray in the battle between the phlogistonists, led by Richard Kirwan, and the anti-phlogistonists, led by Antoine Lavoisier and, with considerable self-confidence, he persuasively argued the case against the phlogistic theory, thereby challenging his widely respected countryman, some thirty years his senior. He did this in his book *A comparative view of the phlogistic and antiphlogistic theories*, published in 1789, with a second edition in 1791.

In this book, Higgins hit on the idea of using arbitrary affinity numbers to reinforce his arguments. He sought to explain the mechanisms of possible reactions between ultimate particles of, for example, sulphur and oxygen by using diagrams of the reacting particles and the affinity forces between them (*DSB* Vol.6,386). By 1789, the case against phlogiston had been largely won, but Higgins' *Comparative view* took on an added significance, since he claimed with great vigour that the book introduced the chemical atomic theory, and in so doing anticipated John Dalton (1766-1844), to whom the credit was being given, although the latter did not publish his *A new system of chemical philosophy* until 1808. It has been accepted that William's arguments contained among their unstated assumptions ideas on combination proportions which were later made explicit in the atomic theory (*DSB* Vol.6,386). But his claims to priority over Dalton have not been upheld. He died in Dublin on or around 30 June 1825.

William James MacNevin (1763-1841)

William James MacNevin was the eldest son born, on 21 March 1763, to a minor family of the old Irish landed gentry who lived at Ballynahowna, near Aughrim, in Co. Galway. He was taught at the local hedge school, before being despatched, at the age of 11, to his uncle, Baron William Kelly MacNevin, who was Dean of Medicine at the University of Prague and one of the physicians to Empress Maria Theresa. After studying medicine at Prague, William junior went on to graduate at the University of Vienna in 1783. He returned to Dublin in 1784, where he became a United Irishman in 1797. He was imprisoned in '98, but submitted to banishment for life and, after briefly joining Napoleon's army in France, he emigrated to America, arriving in New York in 1805, appropriately enough, on the 4th of July. In 1808, he was appointed Professor of Midwifery at the College of Physicians and Surgeons in New York, becoming Professor of Chemistry in 1811. For many years he was co-editor of the *New York Medical and Philosophical Journal,* and he was a member of the American Philosophical Society. O'Donnell (1976b,48) writes:

> *The new professor was responsible for the introduction of Continental [European] chemistry to an America still relatively untutored in this skill. He analysed local minerals and New Jersey waters, thereby stimulating research on calcium and barium derivatives then much in the scientific news. He was instrumental in introducing proper text-books, likewise continuously stressing the importance of chemistry in the agricultural potential of his new but undeveloped world.....He took Dalton's part in the*

Higgins controversy [over the priority for the discovery of the atomic theory].....*He died acclaimed as 'the father of American chemistry, one who raised the subject to a science and prepared it for future illimitable extension'.*

William died in New York on 12 July 1841.

Richard Chenevix (1774-1830)

To this day, there remains a tendency for scientists to consider that their latest hypotheses are 'true', since they are apparently confirmed by their experiments. Thus Richard Kirwan is still frequently looked down upon because he took the 'wrong' side in the phlogiston debate, while Antoine Lavoisier is lauded because he took the 'right' side. But it is no disgrace for a scientist to be proved wrong. The whole essence of science is to postulate hypotheses, but these are not, in essence, right - they remain the best interpretation of experimental results until a better explanation is found. And it will be recalled that Kirwan accepted the superiority of the anti-phlogiston theory when experiments demonstrated more and more clearly that the latter resulted in a better interpretation of the experimental facts. Kirwan was doing precisely what scientists ought to do. His hypothesis may have been wrong, but his science was right. How many eighteenth century hypotheses have survived intact until today?

This aside was inspired by the words of another Irish chemist who got it wrong (quoted in Cottington 1991,142):

The philosopher, indeed, will feel no humiliation in being forced to correct or to extend his knowledge; and will not altogether disbelieve a fact, because he can adduce no parallel instance, or because it is not in unison with his received opinion. Such conduct would be an insurmountable barrier against the progress of science.

Richard Chenevix was born at Ballycommon, near Dublin, of Huguenot stock. His family had come to Ireland on the revocation of the Edict of Nantes (*DSB*, Vol.3,232, *DNB*, Vol.IV,185). (The Edict had been signed by Henry IV of France in 1598, giving a large measure of religious liberty to the protestant Huguenots, but it was revoked by Louis XIV in 1685, thus depriving French protestants of all religious and civil liberty - *Encyclopaedia Britannica* - henceforth *EB* - 1968,Vol.15,1169).

Richard junior was educated at the University of Glasgow, and soon established a reputation as an analytical chemist, taking a particular interest in metals and minerals. He published *Remarks upon chemical nomenclature, according to the principles of the French neologists* in 1802, a pioneering contribution. In 1803, he won the Copley medal of the Royal Society, to which he had been elected Fellow in 1801 'for his various chemical papers printed in the *Philosophical Transactions'*. He was also a Member of the Royal Irish Academy and a Fellow of other learned societies on the Continent. In addition to his scientific activities, he was an author of novels, a playwright, and a poet.

Richard is best remembered in the history of chemistry for his role in the discovery of palladium (Cottington 1991,141-6). William Hyde Wollaston (1766-1828) had, anonymously, published a handbill in 1803, announcing for sale a 'new noble metal', which he called 'new silver' or palladium. Chenevix obtained a sample of the metal, carried out some tests, and proceeded to buy out the entire stock. He believed that the announcement was a hoax, and the palladium was an alloy of platinum and mercury. He claimed to be able to synthesise palladium from the other two metals. However, he was wrong, and palladium was established as a new metal. Richard left England for France in about 1804, and he remained there for the rest of his life. He died in Paris on 5 April 1830.

Josias Christopher Gamble (1776-1848)

An Irishman with an entrepreneurial turn of mind was Josias Gamble. He was born in Enniskillen, Co. Fermanagh, and trained for the Presbyterian ministry at the University of Glasgow, where he learned his chemistry (Brock 1992,276). But, like Richard Kirwan, he abandoned the cloth for science. In his case, he did become ordained, around 1799, and ministered to his flocks in Enniskillen and Belfast, being transferred to the latter in 1804 (O'Donnell 1976b,48). But he became very interested in the technicalities of the flax industry, gave up his ministry, and set up in Dublin as a manufacturer of bleaching powder and sulphuric acid.

When the British Government repealed the tax on salt in 1823, thus making economic Leblanc's 1787 process for manufacturing soda (sodium carbonate), Gamble moved his Dublin works to Liverpool to be near the Cheshire salt deposits. Soda was an essential raw material for the manufacture of soap, glass and paper, and in bleaching and dyeing operations. Previously it had been extracted from the Mediterranean barilla plant, or from sea kelp. But, since it was known that common salt (sodium chloride) and soda shared the same base, industrial methods were derived to convert one into the other. In the Leblanc process, common salt was converted into sodium sulphate by heating with concentrated sulphuric acid, and the sulphate was then heated with carbon and chalk (calcium carbonate) to form soda and calcium sulphide.

In England, Josias became a leading chemical industrialist. He died at St Helen's on 27 January 1848. Today's multinational firm, Proctor & Gamble, descendant of Josias' business, has a manufacturing facility in Nenagh, Co. Tipperary.

Aeneas Coffey (1780-1852)

Although not a chemist, Aeneas Coffey deserves a passing mention, for he invented a new patent still in 1831. Purification by distillation is, of course, a key technology in many chemical plants, and Coffey's still, the first heat exchanger, was a considerable improvement on previous methods, incorporating as it did some of the features of the modern fractionating column. Indeed, it was invented for the production of whiskey, but it worked so efficiently that it removed the very constituents which give the drink its character, and came to be used rather for the production of industrial spirits (Davis 1985a,22-23).

Aeneas was the son of Andrew Coffey, City Engineer at Dublin City Waterworks. It is not clear whether Aeneas was born in Dublin or Calais, but his early years were spent in France. He returned to Dublin around 1800, and worked at the Excise Department, where he became Surveyor for Dublin in 1809, and then took charge of operations against illicit distilling in Donegal. In the Inishowen peninsula (the birth-place of the author's mother!), he was beaten up until he was supposed to be dead, but he survived, and became Inspector General of Excise in 1819. In 1824, he retired, and set up his own distillery in Dublin (Rothery 1968,54-58).

His still made use of the outgoing hot vapour from the distillation to heat the incoming liquid awaiting distillation, thus saving on fuel by heat exchange. The still could be run continuously, contrasting with previous practice of distillation in batches. It could produce a spirit with a 95% alcohol content and with few other volatile components. Aeneas died at Bromley, England, on 26 November 1852.

In passing, attention can be drawn to another Irish-based chemist who made important contributions to distillation. He was Sydney Young (1857-1937), who was born in Lancashire, but who was professor of chemistry at Trinity College, Dublin, from 1903-1928, becoming President of the Royal Irish Academy from 1921-1926. An accomplished glassblower, who made his own fractionating columns (some of them preserved in the TCD Chemistry Department), he was, at the beginning of the twentieth century 'regarded as the foremost authority in the world on distillation' (Davis 1990, 46-47).

Edmund Davy (1785-1857)

So far (apart from Sydney Young just mentioned), the chemists we have considered have been born in Ireland, or have belonged to Irish families living abroad. But some immigrants carried out valuable chemical work while they resided in Ireland. One of these was Edmund Davy, cousin of the famous Sir Humphry Davy (1778-1829), Director of the Royal Institution in London. Sir Humphry had created a dramatic impression on those who were interested in science in Ireland through two courses of lectures he gave at the Dublin Society (later the Royal Dublin Society) in 1810 and 1811. He was paid the remarkable sums of 500 guineas for the first series, and £750 for the second, together with the thanks of the Society for having 'materially increased the spirit of philosophical research in Ireland' (quoted in Berry 1915,161). Indeed Humphry emerged as a great admirer of the Irish, and was a keen supporter of Catholic Emancipation 'unusual for prominent men of science in Great Britain' (personal communication from Professor David Knight). Edmund had been an assistant to his famous cousin at the Royal Institution, and we can assume with some confidence that his connections with Humphry got him his job in Ireland.

Edmund was born in Penzance, where he received his early education, moving to the Royal Institution in 1804. He remained there for eight years, becoming Superintendent of the mineralogical collection. In 1813, he was elected Professor of Chemistry and Secretary of the Royal Cork Institution, which had been constituted in 1802. He spent thirteen years in Cork, before being appointed Professor of Chemistry at the Royal Dublin Society (as it had become) in 1826.

He described an electrolytic method for the detection of arsenic, mercury, lead, and copper in poisoning, worked on the corrosion of iron by seawater, and on 'nicotin', which had been discovered in tobacco in 1809 by Louis Vauquelin (1763-1829). In a more exotic study, he showed that the excrement of a boa constrictor was almost entirely uric acid, and he invented a hydrometer for detecting the adulteration of skimmed milk with water (Partington, 1964,74-5).

It was in the laboratory of the Royal Dublin Society that Edmund first prepared acetylene, his most important legacy to chemical history. He was trying to make potassium by heating a mixture of 'calcined cream of tartar' (potassium carbonate) and charcoal (carbon). Some of the resulting black lumps (potassium carbide) reacted slowly with water to give a gas, which he called 'bicarburet of hydrogen' (acetylene), among whose properties he noted one which became of great practical relevance:

When kindled in contact with air, it burns with a bright white flame, apparently denser, and of greater splendour, than that of olefiant gas, under similar circumstances.

Edmund died in Dublin on 5 November 1857.

Another much used form of lighting also has Irish connections. Thomas Drummond (1797-1840) was born in Edinburgh and entered the Royal Engineers in 1815 (*DNB* Vol.VI,41-45). In 1816, he invented limelight, and it was used to great effect, from 1825, in the Ordnance Survey of Ireland. When calcium (lime) is heated to incandescence in jets of oxygen and hydrogen, it produces a brilliant light which can be directed and focused (*EB* 1968 Vol.21,90). Drummond's light was used widely in the theatre, and being at the centre of attention is still referred to as being 'in the limelight'. Thomas was Under Secretary at Dublin Castle from 1835-1840, and is particularly remembered for telling the landlords, in 1838, that 'property has its duties as well as its rights'.

James Murray (1788-1871)

The intimate early connection between medicine and chemistry, so often encountered in this article, is well illustrated by the life and work of James Murray. He was born in Derry, the eldest son of Edward Murray, and set out on a medical career, completing his studies in Edinburgh in 1807. He set up a medical practice in Belfast in 1808 and, in 1812, he developed a medicine which has stood the test of time like few others - the well-known milk of magnesia. He dissolved magnesium carbonate in water through which carbon dioxide had been bubbled (Garvin 1993,10). In 1817 he published a paper 'Danger of using solid magnesia, and on the great value in a fluid state for internal use'. He patented the process and set up a commercial manufacturing plant in Belfast.

James carried out trials on the use of waste chemicals from his plant as fertilisers, and is credited with the first production of superphosphate (calcium sulphate and dihydrogen calcium phosphate) for this purpose.

In 1843, he published *Trials and effects of chemical fertilisers with various experiments in agriculture,* but he sold out his patent to his main competitor, John Bennet Lawes, in 1846.

Meanwhile, he had moved to Dublin, and was appointed resident physician to the Lord Lieutenant in 1831. He was knighted in 1832, and he served three incumbents over the next ten years. Among his medical publications were: *Electricity as a cause of cholera and other epidemics..., Dissertation on heat and humidity...,* and *Medical effects of atmospheric pressure.*

Following his death on 10 December 1871, his obituary in *The Irish Times* (10:12:1871) recorded:

> *A most perfect tolerance in matters of creed and party distinguished him. He was himself a Catholic, and a supporter of what is still called the Liberal party; but his friendship and benevolence were as wide as the fraternity of man.*

James Muspratt (1793-1886) and
James Sheridan Muspratt (1821-1871)

Another man of Irish birth achieved much greater success in industrial chemistry. He was James Muspratt, who is regarded as the founder of the British chemical industry (Brock 1992,276).

James was born in Dublin on 12 August 1793, the son of Evan Muspratt and Sarah Mainwaring. He was educated at a commercial school in Dublin and then apprenticed to a wholesale chemist and druggist, called Mitcheltree. Sadly, his father died in 1810 and his mother a year later. He then spent a few adventurous years in Europe, during the Peninsular war, and only escaped being captured by the French in Madrid in 1812 by walking a hundred miles in two days while suffering from a fever (*DNB* Vol.XIII,1330). He enlisted as a midshipman, took part in the blockade of Brest, deserted, and returned to Dublin in 1814.

In 1818, he came into a modest inheritance and started to manufacture yellow prussiate of potash (potassium ferrocyanide) by fusing animal horn and blood with potassium carbonate in iron vessels. This was then used to prepare the valuable pigment, prussian blue, by precipitation with ferric chloride (Brock 1992,276). James also made chlorine and bleaching powder for the linen industry. Like Josias Gamble before him (see above), he moved to Liverpool, where he began to manufacture sulphuric acid. As was the case with Josiah, the repeal of the salt tax in 1823 enabled him to launch his soda business and, indeed, the two went into a brief partnership at St Helens in 1828 for a couple of years. A by-product of the Leblanc process is hydrochloric acid, and Musspratt got into trouble with his neighbours because of the damage done by the acid fumes from his works. In the end, he had to close them, opening new and successful ones in Widnes and Flint. He retired in 1857, and died at Seaforth Hall, near Liverpool, on 4 May 1886.

James had married Julia Connor in Dublin in 1819, and they had ten children, four of his sons becoming chemists. The best known is James Sheridan Muspratt, who was born in Dublin on 8 March 1821, and who studied chemistry in the Andersonian University in Glasgow, and at University College, London. His father had visited Justus von Liebig (1803-1873) at Giessen and, after a failed venture in America, J.S. joined Liebeg in 1843. He carried out useful work on the sulphites, and also investigated toluidine and nitraniline, which were first prepared by himself and August Hofmann (1818-1892). After travelling for some years in Germany, he returned to England, where he founded the Liverpool College of Chemistry, a private institution for the training of chemists (*DNB* Vol.XIII,1331). From 1854-1860, he was engaged in publishing his best known work, *Chemistry, theoretical, practical, and analytical, as applied and relating to the arts and manufactures,* which was printed in 36 parts before being bound into two large volumes.

> *Each fascicule of 32 pages craftily ended in the middle of an entry, so that the subscriber had the incentive to purchase the next monthly part....Muspratt's Chemistry was perhaps distinctive in its uncompromising emphasis on the practice of chemical technology* (Brock 1992,275).

The work achieved several English and German editions, and was also translated into Russian. Harvard awarded Muspratt an honorary doctorate for his achievement. Among a considerable volume of his other publications were his *Outlines of qualitative analysis* (1849, 1850) and his translation of K.F. Plattner's *The use of the blowpipe* (1845, 1850). In 1857, he succeeded to a share in his father's business. He died in West Derby, Liverpool, on 3 April 1871.

James Apjohn (1796-1886)

James Apjohn was born in Limerick on 1 September 1796, the son of a tax-collector, Thomas Apjohn, and he attended Tipperary Grammar School before going up to Trinity College Dublin, where he graduated in medicine in 1821 (Anderson 1990,16-17). After a brief period as lecturer in science at the Royal Cork Institution, he became lecturer in chemistry at the Park Street Medical School in Dublin (Wheeler 1953,65). Following this, he had a variety of posts, and Cocker records (1978,66):

> *Apjohn must have held a record for multiple appointments. In the period from 1828-1881, he held the professorship of chemistry in the College of Surgeons School (1828-1850), the professorship of applied chemistry in Trinity College (1844-1881), the professorship of mineralogy (1845-1881), and the university professorship of chemistry (1850-1874).*

The professorships in applied chemistry and mineralogy were in the engineering school, which had been founded in 1841.

He had wide interests, publishing 48 scientific papers between 1821 and 1871. Among these interests were the specific heats of gases, and he also carried out important work on the tables of conversion of wet and dry bulb hygrometer readings into humidity, the results of which he published in 1835. Indeed, the common Mason hygrometer could with more justice be called the Apjohn hygrometer, since the relevant 1836 paper by the surgeon John Abraham Mason from Pentonville has been described by a noted meteorological historian as 'absurdly pompous' (Knowles-Middleton 1969,126).

When the British Association for the Advancement of Science, which had been founded in 1831, had its first meeting in Dublin in 1835, Apjohn was President of Section B, which dealt with chemistry. This meeting was important in the history of chemistry because it was agreed during it that the symbols for the elements – still used today – should be those proposed by J.J. Berzelius (1779-1848), in spite of objections from, for example, John Dalton (Knight 1998b,214). Basically, the symbol for each element was the first letter of the Latin name, with the second letter used in cases where more than one element had the same first letter.

From the late 1830s, Apjohn's interests developed towards mineralogical chemistry. The name *Apjohnite* was given to a manganese alum from South Africa, which he described in 1838. Another of the minerals which he described was a yellow-green garnet, which was called Jellettite, after a later Trinity Provost, John Jellett (1817-888), who had found it in Switzerland (Anderson 1990,17).

Apjohn performed many other analyses on minerals, and he investigated inorganic compounds, including complexes of potassium iodide. He became a fellow of the Royal Society in 1853. He published an inorganic chemistry textbook, *Manual of the metalloids,* in 1864, second edition 1865. Relating to his medical training, he contributed to articles in the *Cyclopaedia of practical medicine* between 1833 and 1835. It is recorded that Charles Dickens based his account of the death of Krook in Bleak House on Apjohn's description of spontaneous combustion. Apjohn also checked the chemical processes described in the first edition of the *British Pharmacopoeia* of 1864 (Anderson 1990,17). He died in Co. Dublin on 2 June 1886.

Robert John Kane (1809-1890)

Robert Kane was the second son of John Kean and Eleanor Troy. He was born in Dublin on 24 September 1809, and spent his early years at 48 Henry Street. He has an interesting and colourful family background.

John Kean was a member of the United Irishmen and was involved in the '98 rebellion, after which he was obliged to go on the run. He fled to Paris. While there, he took the opportunity to study chemistry and, when things had quietened down at home, he changed his name to Kane, and set up business in Dublin as a lime-burner. His business soon prospered, and he manufactured bleaching powder and sulphuric acid, reputedly the first firm in Britain or Ireland to set up and work a Gay-Lussac Tower for the latter purpose (Wheeler 1944,6).

Robert's mother was the sister of the famous Archbishop John Thomas Troy of Dublin (1739-1823), who is remembered for denouncing the Whiteboys, condemning the '98 rising, supporting the 1801 Union, preaching the duty of obedience to the established government, and agreeing that only those loyal to the government should be promoted to Irish bishoprics (Boylan 1978,355-6). He laid the foundation stone of the pro-Cathedral in Marlborough Street in 1815.

Since John and Eleanor had married in 1797, we can assume that the household was the scene of many a debate on the merits or demerits of the British presence in Ireland, and can hope, for the sake of family peace, that Eleanor took the side of her husband rather than that of her brother.

It is hardly surprising that Robert developed an interest in chemistry, and he also showed an interest in mineralogy, having at an early age purchased a mineral collection, in which he found an arsenide of manganese, consequently named *Kaneite*. In 1829, he became a licentiate of the Apothecaries Hall in Dublin, which qualified him to practise medicine. He became a clinical clerk in the Meath Hospital, where he assisted the famous Irish medics Robert Graves (1796-1853) and William Stokes (1804-1878).

The year 1831 was something of an *annus mirabilis* for the young Kane. In that year he published his first book *Elements of practical pharmacy,* and he was appointed to the chair of chemistry by the Apothecaries' Company. He was also elected to the Royal Irish Academy. Like Kirwan before him, he went on to become President of the Academy from 1877 to 1882. Finally, he founded the *Dublin Journal of Medical and Chemical Science* (DJMCS). This became the *Irish Journal of Medical Science* in 1922, and is still being published in 1999. The 'boy professor' turned his attention to chemistry, and never practised as a doctor.

During this time he was an undergraduate at Trinity College, but his other interests delayed his graduation, and it was not until 1835 that he earned his BA. Meanwhile he was publishing actively, with about twenty papers between 1832 and 1837, half of them in the journal which he had founded. One of them, on 'The theory of the ethers', in DJMCS in 1833, is of particular importance in the history of chemistry, for in it he was the first to propose what came to be known as the ethyl radical ($C_2H_5^{\bullet}$). He called it ethereum. He worked on wood spirit and devised a method of purifying methyl alcohol by combining it with calcium chloride. Another important achievement was his preparation, in 1837, of the cyclic trimethyl benzene (mesitylene - C_9H_{12}), by reacting acetone with concentrated sulphuric or hydrochloric acid (Partington 1964,347&355). He studied essential oils and the colouring matters of berries and lichens - the latter work winning for him the Royal Medal of the Royal Society in 1841. He also carried out important work on the combination of ammonia with metallic salts, for which he won the Cunningham Medal of the Royal Irish Academy in 1843. The President of the Academy at the time was Ireland's most famous mathematician, Sir William Rowan Hamilton (1805-1865) and, in his presentation speech (Wheeler 1944,11), he referred to:

that combination of genius and industry which has already caused the researches of Kane to influence in no slight degree the progress of chemical science and has won for him a European reputation.

Meanwhile, Kane had been appointed Lecturer (1834) and then Professor (1839) of Natural Philosophy at the Royal Dublin Society, where he worked for 13 years. And he was appointed an Editor of the *Philosophical Magazine* in 1840, an office he retained for the rest of his life. He wrote a book entitled *Elements of chemistry* (1842, second edition 1849), which was a great international success.

It is recorded that, on one occasion, Robert received by mistake from his publisher the proofs of a book called *The Irish flora*, by Katherine Baily, and he was so impressed that he found out her address and returned the proofs personally. Whether or not it was love at first sight is not recorded, but Robert and Kathleen were married in 1838, and had a very happy marriage, with nine children to prove it (Wheeler 1944,13).

Notwithstanding his remarkable contributions to chemistry, it is not as a chemist that Robert is chiefly remembered in Ireland. Instead it is for his book *The Industrial resources of Ireland* (1844, second edition 1845). In the preface to the first edition he noted:

In other countries it has been the most anxious care of Government, and of those intrusted with the superintendance of education, to ascertain the nature and amount of their means of promoting industry, and extending the employment of the people...If similar zeal and intelligence were manifested in developing the resources of this country, there would be no fear of the result.

Kane's call to action was very well received on its publication and has proved inspirational since, though it is only recently that successive Governments have begun to make adequate responses.

Having thus passed on from his earlier chemical studies, Robert was in 1845 appointed Director of a newly established Museum of Economic Geology, which shared offices at 51 St Stephen's Green (now the headquarters of the Office of Public Works) with the Irish Geological Survey. In the same year, the Queen's Colleges at Belfast, Cork and Galway were set up, and Kane became the first President of the Cork College. He resigned his professorships at the Apothecaries' Hall and at the Royal Dublin Society, and received a knighthood in 1846.

Meanwhile, however, the potato blight had hit Ireland, and Kane was involved in both the scientific studies aimed at eliminating it or reducing its impact, and in administrative arrangements. But neither activity led to much amelioration of the horrendous impact of the great famine.

However, in 1847, Kane's recommendation that the scope of the Museum of Economic Geology should be extended to embrace manufactures as well as geology was accepted, and it became the Museum of Irish Industry. It included illustrations of the manufacture of metals, and models of chemical plant, such as those relating to the manufacture of sulphuric acid and soda (Wheeler 1944,22-3).

Wheeler (1944,40) sums up Robert's career in the words:

Kane is one of the most distinguished of our Irish chemists; few before or since have achieved the same international reputation; few can point to the same number of fundamental discoveries. His great book still influences Irish thought, while in the Museum of Irish Industry and later in the Royal College of Science, he first gave Irish youth an opportunity of obtaining higher training in technology - without which no industrial revival is possible.

His wide interests can be illustrated further by the fact that he was working on a translation into Spanish of *Ivanhoe* when he died in Dublin in his eightieth year, on 16 February 1890.

Thomas Andrews (1813-1885)

Thomas Andrews was born in Donegall Square, Belfast, on 19 December 1813, the son of Thomas Andrews, a linen merchant, and Elizabeth Stevenson. After schooling in Belfast he went, at the age of 15, to Glasgow University and, after two years, to Paris, where he studied under Jean-Baptiste Dumas (1800-1884) – who had another famous pupil in Louis Pasteur. He then read classics and medicine at Trinity College Dublin, and transferred to Edinburgh University, where he obtained his MD in 1835 (*DSB* Vol.1,160).

Back in Belfast, he set up a medical practice, and also became the first Professor of Chemistry at the

Belfast Academical Institution (‘Inst’) which he himself had attended as a schoolboy. He was elected a Member of the Royal Irish Academy in 1839, and was an original Member of the Chemical Society on its foundation in 1841 (Davis 1977,311). In 1845 he gave up both his medical practice and his teaching to become the first Vice-President of the newly formed Queen’s College. When teaching started in 1849, he became Professor of Chemistry, and the same year he was elected Fellow of the Royal Society. He remained as Professor of Chemistry at Queen’s until his retirement in 1879.

He carried our accurate experiments on heats of neutralisation, heats of formation of metallic halides, heats of reaction of salt solutions, heats of formation of oxides and chlorides, and of water, and latent heats of evaporation (Partington 1964,609). He was the first to use a ‘bomb-calorimeter’ - a closed metal vessel in which a mixture of gases could be electrically exploded. He demonstrated that ozone was a form of oxygen.

But his major contribution to the history of chemistry was his identification, in 1861, of a critical temperature for gases, above which they could not be liquefied by pressure alone. His work was, in a sense, a continuation of that of Robert Boyle, since he demonstrated that Boyle’s law does not describe the behaviour of gases under extreme conditions. His results could be represented by a three dimensional surface, which added a temperature co-ordinate to those of pressure and volume. He trapped samples of gas in heavy capillary tubes above mercury, and subjected them to different pressures over a range of temperatures. The curves increasingly departed from those expected for an ‘ideal gas’ until, below the critical point, liquefied gas began to appear under pressure. He was thus able, for the first time, to distinguish between a gas and a vapour; the terms had been used loosely and interchangeably before this. A gas becomes a vapour when its temperature is reduced below its critical point, after which it can be liquefied. Thus carbon dioxide, whose critical point is 31°C, is actually a vapour at room temperature, not a gas (Mills 1995,70). Thomas wrote in 1871 (*DSB*, Vol.1,161):

We may yet live to see, or at least we may feel with some confidence that those who come after us will see, such bodies as oxygen and hydrogen in the liquid, perhaps even in the solid state.

How true this was. Liquid and solid gases have had dramatic impacts on subsequent scientific and technological development.

His critical state apparatus, made for him by J.A. Cumine of Belfast, is on display in the Science Museum in London, and the chemistry department at The Queen’s University of Belfast retains several examples of his experimental apparatus (Mollan 1995b,396&177-9).

Thomas had wider interests (Garvin 1993,16-17):

He was concerned about the higher education of women and of working-class people. He suggested the creation of a department of Celtic at Queen’s because he believed that the Irish language should be represented in the university. He wrote an article entitled ’Suggestions for checking the hurtful use of alcoholic beverages by the working classes’, which proposed that no public house should have a licence to sell alcohol unless it could provide cooked meals for its customers.

He was offered a knighthood, but is recorded as having declined on the grounds of ill-health (Garvin 1993,17). He died in Belfast on 26 November 1885.

Maxwell Simpson (1815-1902)

Maxwell Simpson, born at Beech Hill in Co. Armagh on 15 March 1815, the son of Thomas Simpson, was the youngest in a family of nine. His early education was at a well-known private school, run by Dr Henderson of Newry in Co. Down, which was also attended by future Young Irelanders, John Martin and John Mitchell. Maxwell studied arts and medicine in Trinity College Dublin, between 1832 and 1837, but did not complete the medical course. He moved to London, but made trips to Paris, where he was inspired to adopt chemistry for his career following a lecture by Jean Baptiste Dumas (Reilly 1953,160).

After working in the laboratory of Thomas Graham in the University of London, he returned to Dublin in 1845, and married his childhood sweetheart, Mary Martin, sister of John, and daughter of Samuel Martin of Langthorne in Co. Down. It is recorded (Reilly 1953,160): 'Throughout his chemical career, Simpson owed much to the enthusiasm and encouragement of his wife'. They had six children, but only two survived their father (*DNB* 1901-1911,320).

In order to take up the position of Professor of Chemistry at the Medical School of Park Street, Dublin, he needed to hold a medical degree, which he soon completed at Trinity College in 1847. When Park Street closed, he held a similar position in the Peter School or 'Original' School of Medicine. In order to learn the continental system of teaching chemistry, he and his family moved to Marburg in 1851, where he worked in the laboratory of Adolph Kolbe (1818-1884). He then moved on to Heidelberg, where Robert Bunsen (1811-1899) was professor. After returning to Dublin, he left again, this time for Paris in 1857, where he worked in the laboratory of Charles-Adolphe Wurtz (1817-1884). He became a Fellow of the Chemical Society in 1857, and was Vice-President from 1872 to 1874 (*DNB* 1901-1911,320).

Returning to Dublin in 1859 or 1860, Maxwell fitted up a laboratory at his home at 33 Wellington Road and, during the next seven years, most of his finest work was done there. He became a Fellow of the Royal Society in 1862. After again working in Paris in 1867, and then in London, he received his first full-time chemical appointment at the age of 57, when he was appointed Professor of Chemistry at Queen's College, Cork, in 1872, a post which he held until 1891 (Reilly 1953,162):

> *Simpson's prestige as a scientific enquirer, well known in the chemical world of England, France and Germany, added valuable impetus to chemical thought in the South of Ireland. In his 20-year term as professor in Cork, the firm foundations of an excellent chemical teaching and research department were laid under his stimulating guidance.*

But what were the achievements which had led to Simpson's international chemical prestige? His chief contribution was in the study of the aliphatic organic compounds. He established the structure of glycerine, he investigated the behaviour of cyanides of divalent and trivalent compound radicals with hot caustic potash, and was the first to synthesise succinic acid from ethylene cyanide (published in 1860). He also synthesised other di-basic and tri-basic acids. His work clarified the picture of the structure of the oxalic acid series. He studied the synthesis of halogen derivatives of the olefins, many of which he was the first to prepare (Reilly 1953,166-7).

He is remembered also for introducing, in 1854, an improved method of determining nitrogen in organic compounds, which could be used in cases in which the compounds were difficult to burn. He used cupric and mercuric oxides to convert the carbon to carbon dioxide, and the hydrogen to water. The resulting CO_2 and nitrogen were collected over mercury, the CO_2 absorbed with caustic potash, and the resulting nitrogen measured. His method, in its refined form, could obtain results within half of one percent of theoretical predictions, and it remained a standard technique for more than a generation (Reilly 1953,164). He also standardised the hypobromite method for determining urea (Partington 1964,488). He died in London on 26 February 1902.

John Tyndall (1820-1893)

> *Tyndall was a true son of the nineteenth century's passion for self help and improvement. Born to relative poverty in an obscure Irish village, he became one of the most respected figures in London at the height of her cultural splendour* (Burchfield 1981,1).

John Tyndall, born in Leighlinbridge in Co. Carlow on 2 August 1820, is chiefly remembered as a physicist and populariser of science, achieving great fame as Director of the Royal Institution in London, where he was the successor to Michael Faraday. But he has claims in the history of chemistry also, for he is credited as a founder of the discipline of chemical physics 'the elusive borderline between chemistry and physics' (McCabe 1981,93).

John had studied in Marburg under the great German chemist, Robert Bunsen (1811-1899) - who gave his name to the ubiquitous Bunsen burner, and who, with Gustav Kirchhoff (1824-1887), introduced the use of spectroscopy for chemical analysis in 1860. John is recorded as commenting: ‘Chemistry is beginning to be more beautiful as I attain a clearer vision of it as a science’ - a view which will surely bring back memories of their own maturing in the subject to many readers of this article.

His first major study was of ‘magne-crystalline action’ - the behaviour of crystalline bodies between the poles of a magnet, and he progressed to the study of glaciers, then to the effect of solar radiation and heat on atmospheric gases. He explained why the sky is blue - due to scattering of light by dust particles, refuted the idea of spontaneous generation, and established the principle of discontinuous heating for sterilisation (*DSB* Vol.13,522):

This formidable capacity to move from electromagnetism through thermodynamics and into bacteriology was the hallmark of Tyndall’s genius. No less formidable were his talents in describing, with charm and lucidity, the phenomena of physics to large audiences.

In his *Contributions to molecular physics in the domain of radiant heat* (1872) - one of his many books - he commented (p. 425):

I wish to draw the attention of chemists to a form or method of experiment which, though obvious, is unknown, and which, I doubt not, will in their hands become a new experimental power. It consists of subjecting the vapours of volatile liquids to the action of concentrated sunlight, or to the concentrated beam of the electric light.

How right he was.

Tyndall’s lectures and writings could be controversial, none more so than his Presidential Address to the British Association for the Advancement of Science, which was meeting in Belfast in 1874. In this, he outlined his objections to ecclesiastical suppression of scientific knowledge, and his view that science should ‘wrest from theology the entire domain of cosmological theory’. He was responding, among other things, to a document dated November 1873 (Tyndall 1876,549):

It is a Memorial addressed by Seventy of the Students and Ex-students of the Catholic University of Ireland, to the Episcopal Board of the University; and it constitutes the plainest and bravest remonstrance ever addressed by Irish laymen to their spiritual pastors and masters. It expresses the profoundest dissatisfaction with the curriculum marked out for students of the University; setting forth the extraordinary fact that the lecture-list for the faculty of Science, published a month before they wrote, did not contain the name of a single Professor of the Physical or Natural Sciences.

He commended their courage (p. 552):

Though moulded for centuries to an obedience unparalleled in any other country, except Spain, the Irish intellect is beginning to show signs of independence; demanding a diet more suited to its years than the pabulum of the Middle Ages.

Tyndall, unsurprisingly, had by his remarks made many enemies within Ireland and beyond. But he had supporters too. W.K. Sullivan, the lay Professor of Chemistry at the Catholic University (*see next biography*), had commented (Murphy 1995,100):

[The bishops] *wish to impose upon University Students the discipline which in my opinion is even unsuited to a Seminary.....As a scientific man, I cannot consent to see young Catholics - my own sons - deprived of the means of competing with their Protestant fellow-countrymen. As a layman, I cannot consent to allow the office of teacher to become among Catholics the exclusive privilege of priests.*

John Tyndall died in Hindhead, Surrey, on 4 December 1893.

William Kerby Sullivan (1822-1890)

William Kerby Sullivan was one or Robert Kane's employees in the Museum of Irish Industry, and was in charge of the chemical department, which had a role similar to that played by the present State Laboratory.

William was born in Dripsey, Co. Cork, where his father was the proprietor of a paper mill, and he was educated in Cork by the Christian Brothers before going to study chemistry under the great German chemist Justus von Liebig (1803-1873) at Giessen (Murphy 1995,97). Robert Kane had also spent time with Liebig in 1836, where he went to study new analytical techniques in organic chemistry (Philbin 1985,286). Sullivan later became a Professor at the Catholic University (established in 1854) and at the Royal College of Science (established in 1867), and he succeeded Kane as President of Queen's College Cork, a post he held from 1873 until his death in Cork on 12 May 1890. He made a greater commitment to the latter post than did Kane, for Sullivan actually lived in Cork during his term of office, moving to a President's house which 'was in a state of some neglect...since Kane had only been intermittently resident at best' (Murphy 1995,102). Sullivan worked with Kane on the destructive distillation of peat and on the growing of sugar beet, which later, of course, became an important industry in Ireland.

Following the setting up of a new Department of Science and Art, the Museum evolved to a 'Museum of Irish Industry and Government School of Science applied to Mining and the Arts', with Sullivan as the Professor of Chemistry. Practical courses were arranged, at a time when chemistry to degree standard in the Queen's Colleges involved no practical work (Wheeler 1944,25). The Museum further evolved into the Royal College of Science in 1867, and its magnificent new home in Merrion Street was declared open by King George V in 1911 (O'Brien 1994,238). This, in turn, was incorporated into the Science and Engineering Faculties of University College Dublin in 1926, until the premises were taken over in 1989 to become Government Buildings. Guarding the entrance, then as now, are statues of the Honourable Robert Boyle, the Father of Chemistry, and of Sir William Rowan Hamilton, Ireland's greatest mathematician.

James Bell (1824-1908)

James Bell was born in Altamagham, Co. Armagh. After private education, followed by the study of mathematics and chemistry at University College, London (UCL), he joined, in 1846, the Inland Revenue Department in Somerset House, which was closely associated with UCL. He rose to become the Principal of the Chemical Section there from 1874-1894. He married Ellen Reece in 1858, and they had one son, William James, who later became Sir William Bell and was alderman of London County Council from 1903 to 1907.

James made his scientific reputation by elaborating methods for analysing foodstuffs, being elected to fellowship of the Royal Society in 1884, and becoming President of the Institute of Chemistry from 1888 to 1891. He wrote *The Analysis and adulteration of foods* in three parts between 1881 and 1883, which was translated into German. He also published *The chemistry of tobacco* in 1887 (*DNB* 1901-1911,136). He died at Hove on 31 March 1908.

Charles Alexander Cameron (1830-1921)

Although remembered mainly for his contributions to public health in Ireland, Charles Cameron had a life-long interest in chemistry, an interest which he demonstrated early by setting up a little chemical laboratory in his childhood bedroom. He nearly blew himself up when he inadvertently prepared nitrogen trichloride, frightening his neighbours with the resulting explosion (Davis 1977,312-3 - the rest of the biographical sketch is taken from this reference).

Charles was born in Dublin and, at the age of sixteen, went to work at an apothecary's laboratory, soon acquiring a good knowledge of pharmaceutical chemistry. In 1852, a private society, the Dublin Chemical Society, was set up, and Cameron, then a twenty-two year old medical student, was elected its Professor of Chemistry. The Society set up a laboratory and lecture room at 64 Capel Street. It lasted for ten years, until the Royal College of Science started to provide teaching in chemistry. Charles also lectured on chemistry to the Mechanics' Institute. He became Professor of Chemistry and Natural Philosophy in the Dublin School of Medicine in 1856, and then Lecturer in Chemistry in the Original School of Medicine in Peter Street. From there he moved to the Royal College of Surgeons in 1868, as Professor of Political Medicine and Hygiene and, in 1875, succeeded James Emerson Reynolds (see below) as Professor of Chemistry. He served as President of the College in 1886.

He published on agricultural chemistry, and on the analysis of milk, water and drugs, and was the author of twelve books. Following the passing of the Adulteration of Food Act, 1860, he was appointed Public Analyst for Dublin, a post he held for fifty-eight years, becoming also Dublin Medical Officer for Health in about 1874. He was Analyst for thirty-three counties and boroughs, and was President of the Society for Analytical Chemistry from 1893-1894.

In 1877, he became an original Member of the Institute of Chemistry of Great Britain and Ireland, and was the only original Member to serve on the first committee of the Irish Section when it was founded in November 1918. Charles was knighted in 1885 for his efforts to improve the housing of Dublin's workers, and was made a Freeman of the City of Dublin in 1911.

Cornelius O'Sullivan (1841-1907)

An Irishman, who was the first chemist to be appointed to a brewery firm, has been given credit as the 'founder of the modern science of bio-chemistry' (Ó Raghallaigh 1941,23). He was Cornelius O'Sullivan, who was born in Bandon in Co. Cork on 20 December 1841, the son of James O'Sullivan and Elizabeth Morgan (*DNB* 1901-1911,59).

Cornelius was educated in local private schools and, in 1862, after obtaining first place in relevant exams in inorganic and organic chemistry, he won a scholarship to the Royal School of Mines in London. There he came under the influence of August Hofmann (1818-1892), whom Cornelius followed to Berlin as his assistant in 1865.

The first firm of brewers to appoint a chemist was Bass & Co., of Burton-on-Trent, and Cornelius got the job in 1866 on the recommendation of Hofmann. He remained in Burton for the rest of his life, becoming head brewer in 1894. Remembering his origins, he returned each year to fish in Cork. 'Somewhat bohemian' in appearance, he was once mistaken for a trespasser and poacher in the grounds of Queen's College, Cork, but was rescued by the chemistry professor, Maxwell Simpson, thus avoiding being handed over to the police (Ó Raghallaigh 1941,24).

He published work on the chemistry of brewing, sugar, starch, amylans, cereals, enzyme action, the action of diastase on starch, and the chemistry of the gums. He elucidated the distinct character of maltose, and his 'voluminous writings on the technology of brewing' (*Concise DNB*, 2260) included *On maltose* (1876) and *Presence of Raffinose in barley* (1886). With his exact methods of analysis, he put brewing on a scientific basis, becoming a fellow of the Royal Society in 1885 (Davis 1977,313-4).

O'Sullivan was awarded the Longstaff Medal of the Chemical Society in 1884, the medal being accompanied by a 'purse of gold'. In presenting the medal, the president, William Henry Perkin (1838-1907) said (quoted in Davis 1977,314):

It gives me great pleasure to present to you the Longstaff Medal awarded to you for the important and laborious researches on the carbohydrates. The methods you have used for the purpose of getting an insight into the complicated structures of many of these compounds, by gradually breaking down the molecule and examining the resulting products, have thrown much light on their constitution. The methods of determining starch, and the investigation of α- and β-amylan, the constituents of some cereals, are also subjects of considerable interest and utility. It is hoped that this recognition of your labours may encourage you in *your work, and that, ere long, we may receive fresh communications from you.*

Cornelius died at Burton-on-Trent on 8 January 1907.

Some other Irish chemists made useful contributions to the science of brewing. The younger brother of Cornelius O'Sullivan, James, followed his brother to Bass & Co. He published papers on the germination of barley, hydrolytic functions of yeast, hydrolysis and estimations of sugar, enzymes, maltose, and the rate of alcoholic fermentation. He became head brewer on the death of his brother (Ó Raghallaigh 1941,24).

John Heron graduated in engineering from Queen's College Cork in 1871, but then took up chemistry, studying under Sir Edward Frankland at the Royal College of Chemistry in London. He then became assistant chemist at Worthington's Brewery at Burton and held other related posts, before setting up as a brewer's analyst and consultant in 1895. He was the first President of the Institute of Brewing (1890-1891), and was London Secretary of the Society of Chemical Industry from 1892-1898. His work on the use of the polarimeter in brewing analysis was significant, and he carried out investigations into malt analysis, the influence of mineral salts in the extraction of hops, and the determination of brewer's extract (Ó Raghallaigh 1941,25).

James Emerson Reynolds (1844-1920)

Ireland has claim to another significant world first in the history of chemistry - for the very first person with the title 'Professor of Analytical Chemistry' was James Emerson Reynolds, who was given this title, at his own request, by the Royal Dublin Society, in 1872 (Crowley 1981,177).

James was born in Booterstown, Co. Dublin, on 8 January 1844, the only son of Dr James Reynolds, who kept a medical hall. On leaving school, he became assistant to his father, and he fitted up a small laboratory at his home where he carried out research on his own initiative, publishing his first paper 'On the oleaginous matter formed on dissolving different kinds of iron in dilute acids' in *Chemical News*, in 1861, when he was only seventeen. He qualified as a Licentiate in Medicine of the Edinburgh College of Physicians and Surgeons in 1865, but gave up his medical practice on his father's death to devote himself to chemistry.

In 1867, he was appointed Keeper of Minerals at the National Museum in Dublin and, the following year, Analyst to the Royal Dublin Society (RDS). In the Society's laboratories, he made his most important contribution to the history of synthetic chemistry, for he prepared thiourea, the sulphur equivalent of urea, by heating ammonium thiocyanide (*DNB* 1912-1921,455-6):

His discovery was not due to chance. The existence of thiourea was indicated by theory, but its isolation had already baffled the skill of such distinguished chemists as Liebig and Hofmann in Germany. This discovery, described in the Journal of the Chemical Society of London for 1869 [xxii,1], attracted much attention and was quickly republished in several continental periodicals. It at once established Reynolds's position as one of the most promising of the younger British chemists.

Note here the use of the term 'British', which is strictly correct because the synthesis was carried out in the 'British Isles', and is a higher compliment than would have been the case if 'Irish' had been substituted. But the unqualified use of British has resulted in the devaluation of the many Irish (and, indeed, English, Scottish and Welsh) contributions to the development of science and technology. In this article, we are reclaiming them!

The original crystals of thiourea, prepared by Reynolds, are preserved in the Chemistry Department of Trinity College (Mollan 1995b,240). James also devised a test for acetone - which became well known - based on the colloidal derivative it forms with mercuric oxide. He retained a life-long interest in silicon and organo-silicon compounds (Davis 1977,314).

While still at the RDS, he was appointed Professor of Chemistry at the Royal College of Surgeons in

Dublin in 1870, but relinquished both posts to become Professor of Chemistry at Trinity College in 1875, the successor to James Apjohn. He then wrote his *Experimental chemistry for junior students*, published in 1882 in four small volumes, which introduced for the first time the concept of students verifying for themselves the fundamental laws of chemistry by carefully tested quantitative experiments. It achieved several editions, and was translated into German (*DNB* 1912-1921,456). In the introduction, he writes (Reynolds 1885,1):

CHEMISTRY has for its object the discovery of the laws which govern the composition of all material things, and the action of one kind of matter upon another in all cases involving change in composition. This knowledge is acquired by experiment, accurate observation of the phenomena presented during experiment, and careful reasoning upon the result. The following pages contain numerous illustrations of the application of this experimental method of inquiry in the study of chemistry.

James was elected a Fellow of the Royal Society in 1880, and was a Vice-President of the Society from 1901 to 1902. He was president of the Society of Chemical Industry in 1891, and of the Chemical Society from 1901 to 1903 (DNB 1912-1921,456). He resigned his chair and moved to London in 1903, where he continued to work, mainly on silicon compounds, in the Davy-Faraday Laboratory at the Royal Institution. He died in Kensington on 18 February 1920.

Walter Noel Hartley (1846-1913)

Irish scientists have made important contributions to the development of spectroscopy, but an account of the history of chemistry is not the right place to describe the achievements of such Irish-born scientists as Sir George Gabriel Stokes (1819-1903), George Johnstone Stoney (1826-1911), George Francis FitzGerald (1851-1901), Sir Joseph Larmor (1857-1942), and Thomas Preston (1860-1900), because they were physicists concerned with the theory of spectra, rather than chemists using the technique. The achievements in medical spectroscopy of the Sligo-born doctor, Charles McMunn (1852-1911), who published the first description of the respiratory pigment now known as cytochrome (Coakley 1992,225-232), do not really qualify either, nor do the improved spectroscopes made by the famous Dublin firm of optical instrument makers, the Grubbs of Observatory Lane in Rathmines (Mollan 1995b,482).

With all this distinction in the field, it turns out that the most eminent of ‘Irish’ chemical spectroscopists was actually born in England, at Lichfield, on 3 February 1846, but he was Professor of Chemistry at the Royal College of Science for over thirty years from 1879, and he married an Irish woman, the authoress Mary Laffan from Blackrock, in 1882. His name was Walter Hartley.

Walter studied at Edinburgh University, in Germany, Manchester and London, before becoming senior demonstrator at King’s College, London, in 1871, where he began his career as a spectroscopist, transferring to Dublin in 1879. He was the first to establish that there were relationships between the wavelengths of the spectral lines of the elements and their positions in the periodic table, work which he published in 1883 (Burnett 1990,38-9 - most of the information in this biography is taken from this reference).

His main topic of investigation, while he worked in Dublin, was the relationship between the structure and spectra of a wide variety of organic compounds. He was interested in applied science, studying, for example, dyes of particular relevance to the Irish textile industry, and substances relating to the brewing, distilling, and steel-making industries. One of his papers, published in *the Scientific Proceedings of the Royal Dublin Society* (Vol.4,485-90,1885) was on the subject of the colouring matters employed in the illuminations of the Book of Kells. He also demonstrated that the deep-sea animal, the sea cucumber, contained a variety of chlorophyll.

He realised that some colourless organic compounds were absorbing radiation of a higher frequency than dyes - in the ultraviolet - and his ultraviolet spectroscope, with its attached camera, is preserved in the Science Museum in London. It was made, in part, by the Dublin firm of instrument makers, Yeates & Son, of Grafton Street (Mollan 1995b,423). Perhaps the most formidable of the many scientific instruments on display in the newly renovated 'National Science Museum' at St Patrick's College, Maynooth, is Hartley's 'giant' spectroscope, made, in this case, by Adam Hilger of London (Mollan 1994,25-29).

Walter became a Fellow of the Royal Society in 1884, received the Longstaff Medal of the Chemical Society in 1906, and was knighted in 1911. He died in Aberdeenshire, Scotland, on 11 September 1913.

Hugh Ryan (1873-1931)

Hugh Ryan was born at Dolla near Nenagh in Co. Tipperary on 15 September 1873, the son of shopkeeper and farmer, John Ryan, and his wife Sarah Quinn. He attended as a boarder at what is now Blackrock College, and was a noted sportsman there. He studied chemistry and physics in Queen's College Galway, and took first place in both the bachelor's and master's degree examinations of the Royal University in these subjects in 1895 and 1897. He then studied in the University of Berlin under the famous Emil Fischer (1852-1919), returning to the Catholic University Medical School in Dublin in 1899 where, having obtained the necessary DSc of the Royal University, he became Professor of Chemistry. On the foundation of the National University of Ireland in 1908, he was appointed Professor of Chemistry in University College Dublin, a post he retained until his death. He was the key player in the foundation, in 1922, of the Chemical Association of Ireland, which evolved into today's Institute of Chemistry of Ireland (see Ryan 1997).

Although known as a supporter of the anti-Treaty side, he was nevertheless appointed, while retaining his professorship in UCD, to the newly created post of State Chemist in 1924. In spite of his very demanding duties he built up an active research team, his work ranging from investigations of sugar derivatives, through waxes, to natural dyes, particularly the flavanoids (Philbin 1985,294). He died at Booterstown, Co. Dublin, on 27 March 1931.

One of his collaborators was Thomas Dillon, grandson of W.K. Sullivan *(see above*). Dillon became Professor of Chemistry at University College Galway in 1919, where he set up a research team which carried out important work on carbohydrates, particularly those found in seaweeds.

James Drumm (1896-1974)

An Irish chemist who put his training to great practical use was James Drumm, a pioneer in electrically powered transportation. Born in Dundrum, Co. Down, on 25 January 1896, he went to school in St Macartan's College, Monaghan, and graduated in 1917 from University College Dublin in Prof. Hugh Ryan's Department of Chemistry (Casey 1988,29). After some years working in industry, he returned to UCD to work on batteries, and his patented Drumm Cell, an alkaline battery, was fitted to a demonstration rail coach in 1930. Following the success of the tests, Dáil Éireann financed the building of two 'Drumm Trains', which entered service on the Dublin to Bray line in 1932. In 1939 two more trains were built. Between their introduction and the end of their working lives in 1949, the four trains between them are estimated to have travelled over 1 000 000 miles (Flynn 1996,94). A combination of the arrival of the diesel engine and the high price of nickel meant that the battery trains were not replaced.

In the Drumm cell, the positive plates were made of nickel oxide mixed with graphite, and the negative plates were very pure nickel. The electrolyte was a composite of potassium and lithium hydroxide and zinc oxide (Scott 1985,74).

Drumm was the first to import stainless steel into Ireland, and he developed techniques for working with it. He also developed a method for producing the oxygen-free nickel needed for his batteries. He died in Dublin on 18 July 1974,

John Desmond Bernal (1901-1971)

Born near Nenagh, Co. Tipperary, on 10 May 1901, J.D. Bernal had a colourful career. Initially educated locally, he went on to boarding school in England and then up to Cambridge University. In his Natural Science Tripos, he studied chemistry, physics, geology and mineralogy, and then concentrated on crystallography (Johnston 1999). He worked with William Bragg (1862-1942) in the Royal Institution in London, where he designed the X-ray photogoniometer subsequently produced commercially as the standard tool in the discipline. He returned to Cambridge in 1927 where, for the next decade, he worked on the structure of liquids and solids, identifying the type of helical structures which subsequently led to the discovery of DNA. In 1938 he was appointed to the Chair of Physics at Birkbeck College, London. He built up the crystallography group at Birkbeck, occupying the Chair from 1964 up to his retirement in 1968. He supervised work by Rosalind Franklin, who subsequently contributed to the DNA work for which Watson and Crick received the Nobel Prize. He is credited as the founding father of molecular biology (*DSB* Vol.2,18).

John Desmond Bernal was a defiantly unconventional figure who dazzled almost everybody with whom he came into contact. His brilliant capacity to develop original perspectives on almost any topic - science, politics, aesthetics, morality - earned for him the nick-name 'Sage' when he was still an undergraduate. The name stuck. (Ferry 1998,77).

He evolved from being 'a passionate Irish nationalist and even more passionate and fervent Catholic' (*DSB* Vol.2,16), to becoming a Marxist, a believer in free love, and later an adviser to Lord Mountbatten, Chief of Combined Operations. He helped plan the invasion of Europe, and he landed on the Normandy beaches on the afternoon of D-day (6 June 1944), luckily surviving the experience (Goldsmith 1980,110). Later, however, he was a founder member of the World Peace Council, and was awarded the Lenin Prize for Peace.

Some of his many publications included: *The world, the flesh and the devil* (1929); *The Social function of science* (1939); *Marx and science* (1952); *World without war* (1958); and *The origin of life* (1967). *The social function of science* is considered as the founding text for the scientific study of science itself in a social context (Johnston 1999). Sage died in London on 15 September 1971.

Kathleen Lonsdale (1903-1971)

Kathleen Lonsdale was born in Newbridge, Co. Kildare, on 28 January 1903, the tenth child of Harry Yardley, the postmaster there, and his wife, Jessie Cameron. Hers was a very poor family, and four of her six brothers died in infancy. The girls were tougher, though Kathleen herself suffered from rickets as a child, and never grew tall. Kathleen's mother was a 'considerable character', a Baptist, with an independent mind, and the marriage was not too happy. The family moved to Essex in 1908, and Kathleen attended classes in physics, chemistry and higher mathematics at the County High School for Boys in Ilford, the only girl from the girls' school to do so. Anxious to progress, she entered Bedford College for Women in London at the age of sixteen, and came first in the honours BSc exam in 1922 (Hodgkin 1975,449 - most of this biography is taken from this source). Indeed she obtained the highest mark for ten years in her final examination in London University (Ferry 1998,201). She made good use of her small size by coxing the Bedford College eight, and she was also secretary of the Music Society (*DNB* 1971-1980,517).

She was immediately offered a place in the research team of William Bragg, one of her examiners, then at University College London, where she began her work on X-ray diffraction in crystals of organic molecules. By an odd coincidence, the first compound she began to measure was succinic acid, the dibasic acid which had first been synthesised by Maxwell Simpson (*see above*). In 1923 she transferred, with Bragg, to the Royal Institution, but her marriage to Thomas Lonsdale resulted in a move to Leeds, where he was working. She considered giving up science to become a good wife and mother, but Thomas would have none of it. He had not married, he said, to get a free housekeeper. Indeed, he served the additional useful function of cutting her unruly hair! So, while they had their three children, she progressed in her career. It was at Leeds that she made her most memorable contribution to chemical history, for she showed, by her analysis of hexamethylbenzene, in 1929, that the benzene ring was flat.

Her return to London interrupted her experimental work but, in 1931, Bragg offered her £200 to get help at home so that she could work with him. She calculated that it would cost £277 to replace her at home - so he came up with £300! Using a large electromagnet she studied diamagnetic anisotropy, and she was able to provide experimental verification of the postulated delocalisation of electrons and the existence of molecular orbitals - results of considerable importance to theoreticians (*DNB* CD-ROM).

After the war, in 1946, she was appointed reader in crystallography at University College, London, and was Professor of Chemistry there from 1949 to 1968, developing her own research school, which dealt with a wide variety of topics, including solid state reactions, pharmacological compounds, and the constitution of bladder and kidney stones. While at UCL, she edited three volumes of *International tables for X-ray crystallography* (1952,1959,1962), the standard work in the field.

Meanwhile, she had become a Quaker and thus a pacifist, and this led to her imprisonment in 1943 for refusing to register for civil defence duties, and then refusing to pay the £2 fine - ‘Do the police come for one or do I just have to go to prison myself?’ Following her internment, she wrote to the Governor suggesting how conditions for the prisoners could be improved, and she later became a prison visitor.

She got out of prison in time to attend a 1943 scientific meeting at The Dublin Institute for Advanced Studies. This was chaired by Nobel Prizewinner Erwin Schrödinger (1887-1961) – who worked at the Institute from 1940-1956, and became an Irish citizen in 1948 – and was attended by Eamon de Valera. While in Ireland she visited her birthplace at Newbridge.

In 1945, she broke new ground for women, by being the first of her sex to be admitted Fellow of the 285-year-old Royal Society. To be strictly accurate, Kathleen and the biochemist Marjorie Stephenson were together elected to Fellowship on 22 March 1945. They were ‘admitted’ on 17 May, and, as the letter ‘L’ comes before ‘S’ in the alphabet, Kathleen was first. Had she remained single (with her birth surname Yardley), she would have been second!

Kathleen was created a Dame Commander of the Order of the British Empire in 1956 - her pacifism presumably forgiven. She was the first woman President of the British Association for the Advancement of Science in 1968, and she received many other honours. She died in London on 1 April 1971.

Vincent Barry (1908-1975)

Born in Cork on 17 May 1908, Vincent Barry was educated in North Monastery Christian Brothers School, and University College Dublin, where he graduated in chemistry in 1928. The next year he became assistant to the Professor of Chemistry - Thomas Dillon - at University College Galway. His work on sugars at Galway led to the establishment of an industry based on seaweed (Davis 1985b,76).

From 1943, Barry worked on the chemotherapy of tuberculosis as a fellow of the Medical Research Council of Ireland and, in 1950, became director of the Council’s new laboratories located at Trinity College Dublin (Philbin 1985,297). Hundreds of compounds were synthesised and tested over the next two decades for the treatment of tuberculosis, cancer and leprosy. Several proved effective, the most useful being clofazimine which has proved of great value in the treatment of leprosy. Author or co-author of about 170 papers, Barry was awarded the Boyle Medal of the Royal Dublin Society in 1969, and was President of the Royal Irish Academy from 1970-1973. He died in Dublin on 4 September 1975.

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Note: ***DNB*** stands for *Dictionary of national biography*, and ***DSB*** for *Dictionary of scientific biography* – see entries under **Dictionary** below. ***EB*** stands for *Encyclopaedia Britannica* – in this case details of the reference are given in the text.

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Internet for Girls: World Wide Resources List	http://www.sdsc.edu/~woodka/resources.html
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