

Reaction Kinetics

Dr Claire Vallance
First year, Hilary term

Suggested Reading

Physical Chemistry, P. W. Atkins
Reaction Kinetics, M. J. Pilling and P. W. Seakins
Chemical Kinetics, K. J. Laidler
Modern Liquid Phase Kinetics, B. G. Cox

Course synopsis

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1. Introduction

Chemical reaction kinetics deals with the rates of chemical processes. Any chemical process may be broken down into a sequence of one or more single-step processes known either as *elementary processes*, *elementary reactions*, or *elementary steps*. Elementary reactions usually involve either a single reactive collision between two molecules, which we refer to as a *bimolecular* step, or dissociation/isomerisation of a single reactant molecule, which we refer to as a *unimolecular* step. Very rarely, under conditions of extremely high pressure, a *termolecular* step may occur, which involves simultaneous collision of three reactant molecules. An important point to recognise is that many reactions that are written as a single reaction equation in actual fact consist of a series of elementary steps. This will become extremely important as we learn more about the theory of chemical reaction rates.

As a general rule, elementary processes involve a transition between two atomic or molecular states separated by a potential barrier. The potential barrier constitutes the *activation energy* of the process, and determines the rate at which it occurs. When the barrier is low, the thermal energy of the reactants will generally be high enough to surmount the barrier and move over to products, and the reaction will be fast. However, when the barrier is high, only a few reactants will have sufficient energy, and the reaction will be much slower. The presence of a potential barrier to reaction is also the source of the temperature dependence of reaction rates, which we will cover in more detail in Section 19.

The huge variety of chemical species, types of reaction, and the accompanying potential energy surfaces involved means that the timescale over which chemical reactions occur covers many orders of magnitude, from very slow reactions, such as iron rusting, to extremely fast reactions, such as the electron transfer processes involved in many biological systems or the combustion reactions occurring in flames.

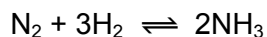
A study into the kinetics of a chemical reaction is usually carried out with one or both of two main goals in mind:

1. Analysis of the sequence of elementary steps giving rise to the overall reaction. i.e. the *reaction mechanism*.
2. Determination of the absolute rate of the reaction and/or its individual elementary steps.

The aim of this course is to show you how these two goals may be achieved.

2. Rate of reaction

When we talk about the rate of a chemical reaction, what we mean is the rate at which reactants are used up, or equivalently the rate at which products are formed. The rate therefore has units of concentration per unit time, $\text{mol dm}^{-3} \text{s}^{-1}$ (for gas phase reactions, alternative units of concentration are often used, usually units of pressure – Torr, mbar or Pa). To measure a reaction rate, we simply need to monitor the concentration of one of the reactants or products as a function of time. There is one slight complication to our definition of the reaction rate so far, which is to do with the stoichiometry of the reaction. The stoichiometry simply refers to the number of moles of each reactant and product appearing in the reaction equation. For example, the reaction equation for the well-known Haber process, used industrially to produce ammonia, is:



N_2 has a stoichiometric coefficient of 1, H_2 has a coefficient of 3, and NH_3 has a coefficient of 2. We could determine the rate of this reaction in any one of three ways, by monitoring the changing

concentration of N_2 , H_2 , or NH_3 . Say we monitor N_2 , and obtain a rate of $-\frac{d[\text{N}_2]}{dt} = x \text{ mol dm}^{-3} \text{ s}^{-1}$. Since for every mole of N_2 that reacts, we lose three moles of H_2 , if we had monitored H_2 instead of N_2 we would have obtained a rate $-\frac{d[\text{H}_2]}{dt} = 3x \text{ mol dm}^{-3} \text{ s}^{-1}$. Similarly, monitoring the concentration of NH_3 would yield a rate of $2x \text{ mol dm}^{-3} \text{ s}^{-1}$. Clearly, the same reaction cannot have three different rates, so we appear to have a problem. The solution is actually very simple: the reaction rate is defined as the rate of change of the concentration of a reactant or product *divided by its stoichiometric coefficient*. For the above reaction, the rate (usually given the symbol v) is therefore

$$v = -\frac{d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$$

Note that a negative sign appears when we define the rate using the concentration of one of the reactants. This is because the rate of change of a reactant is negative (since it is being used up in the reaction), but the reaction rate needs to be a positive quantity.

3. Rate laws

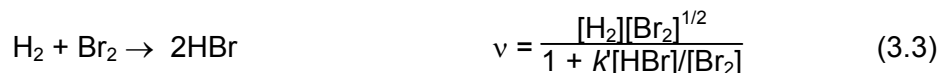
The rate law is an expression relating the rate of a reaction to the concentrations of the chemical species present, which may include reactants, products, and catalysts. Many reactions follow a *simple rate law*, which takes the form

$$v = k [\text{A}]^a [\text{B}]^b [\text{C}]^c \dots \quad (3.1)$$

i.e. the rate is proportional to the concentrations of the reactants each raised to some power. The constant of proportionality, k , is called the *rate constant*. The power a particular concentration is raised to is the *order* of the reaction with respect to that reactant. Note that the orders do not have to be integers. The sum of the powers is called the *overall order*. Even reactions that involve multiple elementary steps often obey rate laws of this kind, though in these cases the orders will not necessarily reflect the stoichiometry of the reaction equation. For example,



Other reactions follow *complex rate laws*. These often have a much more complicated dependence on the chemical species present, and may also contain more than one rate constant. Complex rate laws *always* imply a multi-step reaction mechanism. An example of a reaction with a complex rate law is

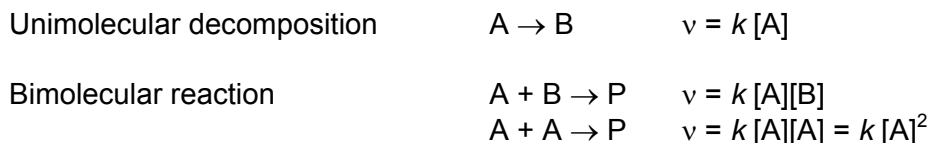


In the above example, the reaction has order 1 with respect to $[\text{H}_2]$, but it is impossible to define orders with respect to Br_2 and HBr since there is no direct proportionality between their concentrations and the reaction rate. Consequently, it is also impossible to define an overall order for this reaction.

To give you some idea of the complexity that may underlie an overall reaction equation, a slightly simplified version of the sequence of elementary steps involved in the above reaction is shown below. We will return to this reaction later when we look at chain reactions in Section 17.



As well as having rate laws for overall reactions, we can of course also write down individual rate laws for elementary steps. Elementary processes always follow simple rate laws, in which the order with respect to each reactant reflects the *molecularity* of the process (how many molecules are involved). For example,



Multi-step processes may follow simple or complex rate laws, and as the above examples have hopefully illustrated, the rate law generally does not follow from the overall reaction equation. This makes perfect sense, since the overall reaction equation for a multi-step process is simply the net result of all of the elementary reactions in the mechanism. The 'reaction' given in the overall reaction equation never actually takes place! However, even though the rate law for a multi-step reaction cannot immediately be written down from the reaction equation as it can in the case of an elementary reaction, the rate law *is* a direct result of the sequence of elementary steps that constitute the reaction mechanism. As such, it provides our best tool for determining an unknown mechanism. As we will find out later in the course, once we know the sequence of elementary steps that constitute the reaction mechanism, we can quite quickly deduce the rate law. Conversely, if we do not know the reaction mechanism, we can carry out experiments to determine the orders with respect to each reactant (see Sections 7 and 8) and then try out various 'trial' reaction mechanisms to see which one fits best with the experimental data. At this point it should be emphasised again that *for multi-step reactions, the rate law, rate constant, and order are determined by experiment*, and the orders are not generally the same as the stoichiometric coefficients in the reaction equation.

A final important point about rate laws is that *overall* rate laws for a reaction may contain reactant, product and catalyst concentrations, *but must not contain concentrations of reactive intermediates* (these will of course appear in rate laws for individual elementary steps).

4. The units of the rate constant

A point which often seems to cause endless confusion is the fact that the units of the rate constant depend on the form of the rate law in which it appears i.e. a rate constant appearing in a first order rate law will have different units from a rate constant appearing in a second order or third order rate law. This follows immediately from the fact that the reaction rate always has the same units of concentration per unit time, which must match the overall units of a rate law in which concentrations raised to varying powers may appear. The good news is that it is very straightforward to determine the units of a rate constant in any given rate law. Below are a few examples.

- (i) Consider the rate law $v = k[H_2][I_2]$. If we substitute units into the equation, we obtain

$$(\text{mol dm}^{-3} \text{ s}^{-1}) = [k] (\text{mol dm}^{-3}) (\text{mol dm}^{-3})$$

where the notation $[k]$ means 'the units of k '. We can rearrange this expression to find the units of the rate constant, k .

$$[k] = \frac{(\text{mol dm}^{-3} \text{ s}^{-1})}{(\text{mol dm}^{-3}) (\text{mol dm}^{-3})} = \text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$

- (ii) We can apply the same treatment to a first order rate law, for example $v = k [\text{CH}_3\text{N}_2\text{CH}_3]$.

$$(\text{mol dm}^{-3} \text{ s}^{-1}) = [k] (\text{mol dm}^{-3})$$

$$[k] = \frac{(\text{mol dm}^{-3} \text{ s}^{-1})}{(\text{mol dm}^{-3})} = \text{s}^{-1}$$

(iii) As a final example, consider the rate law $v = k [\text{CH}_3\text{CHO}]^{3/2}$.

$$(\text{mol dm}^{-3} \text{ s}^{-1}) = [k] (\text{mol dm}^{-3})^{3/2}$$

$$[k] = \frac{(\text{mol dm}^{-3} \text{ s}^{-1})}{(\text{mol dm}^{-3})^{3/2}} = \text{mol}^{-1/2} \text{ dm}^{3/2} \text{ s}^{-1}$$

An important point to note is that *it is meaningless to try and compare two rate constants unless they have the same units.*

5. Integrated rate laws

A rate law is a differential equation that describes the rate of change of a reactant (or product) concentration with time. If we integrate the rate law then we obtain an expression for the concentration as a function of time, which is generally the type of data obtained in an experiment. In many simple cases, the rate law may be integrated analytically. Otherwise, numerical (computer-based) techniques may be used. Four of the simplest rate laws are given below in both their differential and integrated form.

Reaction	Order	Differential form	Integrated form
$A \rightarrow P$	zeroth	$\frac{d[A]}{dt} = -k$	$[A] = [A]_0 - kt$
$A \rightarrow P$	first	$\frac{d[A]}{dt} = -k[A]$	$\ln[A] = \ln[A]_0 - kt$
$A + A \rightarrow P$	second	$\frac{1}{2} \frac{d[A]}{dt} = -k[A]^2$	$\frac{1}{[A]} = \frac{1}{[A]_0} + 2kt$
$A + B \rightarrow P$	second	$\frac{d[A]}{dt} = -k[A][B]$	$kt = \frac{1}{[B]_0 - [A]_0} \ln \frac{[B]_0[A]}{[A]_0[B]}$

In the above $[A]_0$ and $[B]_0$ represent the initial concentrations of A and B i.e. their concentrations at the start of the reaction.

6. Half lives

The half life, $t_{1/2}$, of a substance is defined as the time it takes for the concentration of the substance to fall to half of its initial value. Note that *it only makes sense to define a half life for a substance not present in excess at the start of the reaction.* We can obtain equations for the half lives for reactions of various orders by substituting the values $t = t_{1/2}$ and $[A] = \frac{1}{2} [A]_0$ into the integrated rate laws from Section 5. We obtain

$$\text{Zeroth order reaction} \quad t_{1/2} = \frac{[A]_0}{2k} \quad (6.1)$$

$$\text{First order reaction} \quad t_{1/2} = \frac{\ln 2}{k} \quad (6.2)$$

$$\text{Second order reaction} \quad t_{1/2} = \frac{1}{k[A]_0} \quad (6.3)$$

7. Determining the rate law from experimental data

A kinetics experiment consists of measuring the concentrations of one or more reactants or products at a number of different times during the reaction. We will review some of the experimental techniques used to make these measurements in Section 8. In the present section, we will look at the methods that allow us to use the experimental data to determine the reaction orders with respect to each reactant, and therefore the rate law.

(i) Isolation method

The isolation method is a technique for simplifying the rate law in order to determine its dependence on the concentration of a single reactant. Once the rate law has been simplified, the differential or integral methods discussed in the following subsections may be used to determine the reaction orders.

The dependence of the reaction rate on the chosen reactant concentration is isolated by having all other reactants present in a large excess, so that their concentration remains essentially constant throughout the course of the reaction. As an example, consider a reaction $A + B \rightarrow P$, in which B is present at a concentration 1000 times greater than A. When all of species A has been used up, the concentration of B will only have changed by 1/1000, or 0.1%, and so 99.9% of the original B will still be present. It is therefore a good approximation to treat its concentration as constant throughout the reaction.

This greatly simplifies the rate law since the (constant) concentrations of all reactants present in large excess may be combined with the rate constant to yield a single *effective rate constant*. For example, the rate law for the reaction considered above will become:

$$v = k [A]^a [B]^b \approx k [A]^a [B]_0^b = k_{\text{eff}} [A]^a \quad \text{with} \quad k_{\text{eff}} = k [B]_0^b \quad (7.1)$$

When the rate law contains contributions from a number of reactants, a series of experiments may be carried out in which each reactant is isolated in turn.

(ii) Differential methods

When we have a rate law that depends only on the concentration of one species, either because there is only a single species reacting, or because we have used the isolation method to manipulate the rate law, then the rate law may be written

$$v = k[A]^a \quad (7.2)$$

$$\log v = \log k + a \log [A] \quad (7.3)$$

A plot of $\log v$ against $\log [A]$ will then be a straight line with a slope equal to the reaction order, a , and an intercept equal to $\log k$. There are two ways in which to obtain data to plot in this way.

1. We can measure the concentration of the reactant $[A]$ as a function of time and use this data to calculate the rate, $v = -d[A]/dt$, as a function of $[A]$. A plot of $\log v$ vs $\log [A]$ then yields the reaction order with respect to A.
2. We can make a series of measurements of the initial rate v_0 of the reaction with different initial concentrations $[A]_0$. These may then be plotted as above to determine the order, a . This is a commonly used technique known as the *initial rates method*.

(iii) Integral methods

If we have measured concentrations as a function of time, we may compare their time dependence with the appropriate integrated rate laws. Again, this is most straightforward if we have simplified the rate law so that it depends on only one reactant concentration. The differential rate law given in Equation (7.2) will give rise to different integrated rate laws depending on the value of a , some of which were given in Section 5. The most commonly encountered ones are:

Zeroth order integrated rate law: $[A] = [A]_0 - kt$
A plot of $[A]$ vs t will be linear, with a slope of $-k$.

First order integrated rate law: $\ln[A] = \ln[A]_0 - kt$
A plot of $\ln[A]$ vs t will be linear with a slope of $-k$.

Second order integrated rate law: $\frac{1}{[A]} = \frac{1}{[A]_0} + 2kt$
A plot of $\frac{1}{[A]}$ vs t will be linear with a slope of $2k$.

If none of these plots result in a straight line, then more complicated integrated rate laws must be tried.

(iv) Half lives

Another way of determining the reaction order is to investigate the behaviour of the half life as the reaction proceeds. Specifically, we can measure a series of successive half lives. $t = 0$ is used as the start time from which to measure the first half life, $t_{1/2}^{(1)}$. Then $t_{1/2}^{(1)}$ is used as the start time from which to measure the second half life, $t_{1/2}^{(2)}$, and so on.

Zeroth order $t_{1/2} = \frac{[A]_0}{2k}$

Since at $t_{1/2}^{(1)}$, the new starting concentration is $\frac{1}{2}[A]_0$, successive half lives will decrease by a factor of two for a zeroth order reaction.

First order $t_{1/2} = \frac{\ln 2}{k}$

There is no dependence of the half life on concentration, so $t_{1/2}$ is constant for a first order reaction.

Second order $t_{1/2} = \frac{1}{k[A]_0}$

The inverse dependence on concentration means that successive half lives will double for a second order reaction.

8. Experimental techniques

Experimental techniques have been developed to monitor reactions over timescales varying from hours or days all the way down to a few femtoseconds ($1 \text{ fs} = 10^{-15} \text{ s}$). While it is relatively simple to monitor the kinetics of a slow reaction (occurring over minutes to hours or longer), highly specialised techniques are required in order to study fast reactions, some of which will be considered here.

Whatever the details of the experimental arrangement, any kinetics experiment essentially consists of mixing the reactants and initiating reaction on a timescale that is negligible relative to that of the reaction, and then monitoring the concentration(s) of one or more reactants and/or products as a

function of time. Because rate constants vary with temperature (see Section 19), it is also important to determine and control accurately the temperature at which the reaction occurs.

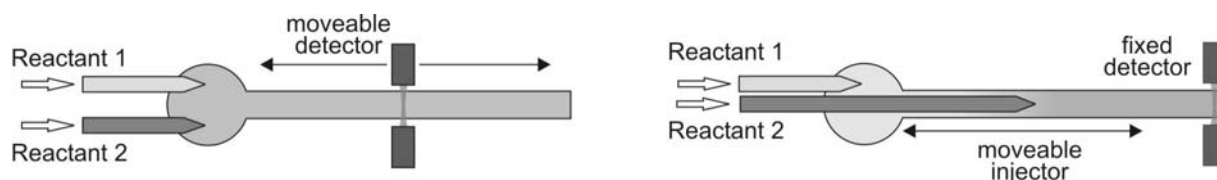
Most of the techniques we will look at are *batch techniques*, in which reaction is initiated at a single chosen time and concentrations are then followed as a function of time after initiation. We will also consider one or two examples of *continuous techniques*, in which reaction is continuously initiated and the time dependence of the reaction mixture composition is inferred from, for example, the concentrations in different regions of the reaction vessel. The continuous flow method outlined in the next section is an example of such a technique.

(i) Techniques for mixing the reactants and initiating reaction

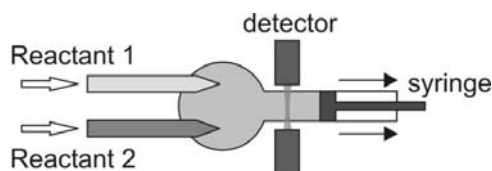
For slow reactions, occurring over minutes to hours, reaction is usually initiated simply by mixing the reactants together by hand or with a magnetic stirrer or other mechanical device. For fast reactions, a wide range of techniques have been developed.

Flow techniques

Flow techniques are typically used to study reactions occurring on timescales of seconds to milliseconds. In the simplest flow method, shown schematically on the left below, reactants are mixed at one end of a flow tube, and the composition of the reaction mixture is monitored at one or more positions further along the tube. If the flow velocity along the tube is known, then measurements at different positions provide information on concentrations at different times after initiation of reaction. In a variation on this method, shown on the right below, the detector may be in a fixed position, but a moveable injector may be used to inject one of the reactants into the flow tube at different positions relative to the detector in order to study the time dependence of the reaction mixture composition. Reactions of atomic or radical species may be studied using the discharge flow method, in which the reactive species is generated by a microwave discharge immediately prior to injection into the flow tube.



Continuous flow methods have the disadvantages that relatively large quantities of reactants are needed, and very high flow velocities are required in order to study fast reactions. These problems may be avoided by using a *stopped flow technique*. In this method, a fixed volume of reactants are rapidly flowed into a reaction chamber and mixed by the action of a syringe fitted with an end stop (see figure below). The composition of the reaction mixture is then monitored spectroscopically as a function of time after mixing at a fixed position in the reaction chamber. Experimental systems may be designed to allow measurements to be made on very small sample volumes, making the stopped flow method popular for the study of biochemical kinetics e.g. enzyme action (see Section 15).



All flow techniques share the common problem that contributions from heterogeneous reactions at the walls of the flow tube can complicate the experiments. These can be minimised by coating the inner surface of the flow tube with an unreactive substance such as teflon or halocarbon wax, and the relative contributions from the process under study and reactions involving the walls may be quantified by varying the diameter of the flow tube (and therefore the ratio of volume to surface area).

Flash photolysis and laser pump probe techniques

In flash photolysis, reaction is initiated by a pulse of light (the 'flash') that dissociates a suitable precursor molecule in the reaction mixture to produce a reactive species, thereby initiating reaction. The concentration of the reactive species is then monitored as a function of time, usually spectroscopically using absorption spectroscopy or fluorescence techniques (see later). The shortest timescale over which reactions may be studied using this technique is determined by the duration of the 'flash'. Originally, the flash was provided by a discharge lamp, with durations in the region of tens of microseconds to several milliseconds. However, in most modern experiments the flash is provided by a laser pulse, typically with a duration of a few nanoseconds ($1 \text{ ns} = 10^{-9} \text{ s}$). For studying extremely fast reactions, such as some of the electron transfer processes involved in photosynthesis, laser pulses as short as a few tens of femtoseconds ($1 \text{ fs} = 10^{-15} \text{ s}$) may be used.

Flash photolysis has the advantage that because reactants are produced from well-mixed precursors, there is no mixing time to reduce the time resolution of the technique. Also, because the reactants are generated and monitored in the centre of the reaction cell, there are no wall reactions to worry about as there are in flow methods.

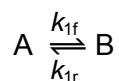
Pulse radiolysis is a variation on flash photolysis in which a short pulse of high energy electrons (10^{-9} to 10^{-6} s in duration) is passed through the sample in order to initiate reaction.

For very fast processes, the 'pump-probe' technique is often used, in which pulsed lasers are employed both to initiate reaction (the 'pump') and to detect the products via a pulsed spectroscopic technique (the 'probe'). The time separation between the two pulses can be varied either electronically or with an optical delay line down to a resolution of around 10 femtoseconds (10^{-14} s)

Relaxation methods

If we allow a chemical system to come to equilibrium and then perturb the equilibrium in some way, the rate of relaxation to a new equilibrium position provides information about the forward and reverse rate constants for the reaction. Since a system at chemical equilibrium is already well-mixed, relaxation methods overcome the mixing problems associated with many flow methods.

As an example, we will investigate the effect of a sudden increase in temperature on a system at equilibrium, an experiment known as a 'temperature jump'. Consider a simple equilibrium



where k_{1f} and k_{1r} are the rate constants for the forward and reverse reactions at the initial temperature T_1 . The rate of change of A is

$$\frac{d[A]}{dt} = -k_{1f}[A] + k_{1r}[B]$$

At equilibrium, the concentration of A is constant, and so

$$k_{1f}[A]_{\text{eq},1} = k_{1r}[B]_{\text{eq},1}$$

We now increase the temperature suddenly by a few degrees. This is often done by discharging a high voltage capacitor through the solution ($\sim 10^{-7}$ s), or by employing a UV or IR laser pulse or microwave discharge. After the temperature jump, the concentrations of A and B are initially at the values $[A]_{\text{eq},1}$ and $[B]_{\text{eq},1}$, but the system is not at the equilibrium composition for the higher temperature. The system relaxes back to the new equilibrium concentrations $[A]_{\text{eq},2}$ and $[B]_{\text{eq},2}$ at a

rate determined by the new higher-temperature rate constants k_{2f} and k_{2r} . The new concentrations are given by

$$k_{2f}[A]_{\text{eq},2} = k_{2r}[B]_{\text{eq},2}$$

If we define $x = [A] - [A]_{\text{eq},2}$ as the deviation of the concentration from its new (higher temperature) equilibrium value (note that the deviation of $[B]$ from its equilibrium value must therefore be $-x$), then during the relaxation the concentrations change as follows

$$\begin{aligned} \frac{d[A]}{dt} &= -k_{2f}[A] + k_{2r}[B] \\ &= -k_{2f}([A]_{\text{eq},2} + x) + k_{2r}([B]_{\text{eq},2} - x) \\ &= -(k_{2f} + k_{2r})x \quad (\text{since } k_{2f}[A]_{\text{eq},2} = k_{2r}[B]_{\text{eq},2}) \end{aligned}$$

Since the rate of change of $[A]$ is the same as the rate of change of x , we can integrate the rate law to give

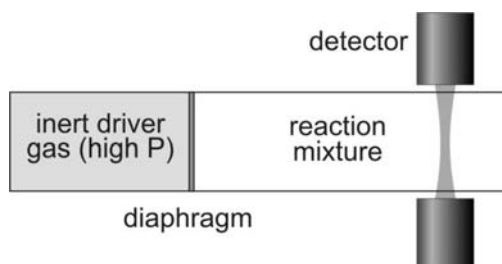
$$x = x_0 \exp(-t/\tau) \quad \text{with} \quad \frac{1}{\tau} = k_{2f} + k_{2r}$$

We see that the rate at which the concentrations relax to their new equilibrium values is determined by the sum of the two new rate constants. The new equilibrium constant is given by the ratio of the two rate constants, $K = k_{2f}/k_{2r}$, so together a measurement of the rate of relaxation and the equilibrium constant allows the individual reaction rate constants for the forward and reverse reaction to be determined.

The details of the kinetic equations change for more complicated reactions, but the basic principle of the technique remains the same.

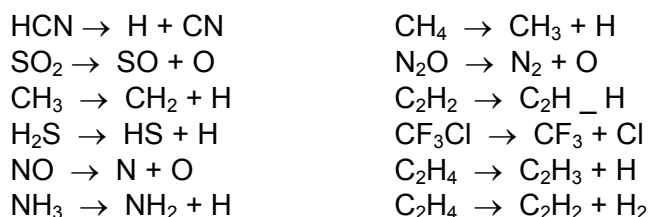
Shock tubes

The shock tube method provides a way of producing highly reactive atomic or radical species through rapid dissociation of a molecular precursor, without the use of a discharge or laser pulse. The method is based on the fact that a very rapid increase in pressure (the shock) causes rapid heating of a gas mixture to a temperature of several thousand Kelvin. Since most dissociation reactions are endothermic, at high temperatures their equilibria are shifted towards products. A rapid increase in temperature therefore leads to rapid production of reactive species (the dissociation products) initiating the reaction of interest. A shock tube (shown schematically below)



essentially consists of two chambers separated by a diaphragm. One chamber contains the appropriate mixture of reactants and precursor, the second an inert gas at high pressure. To initiate reaction, the diaphragm is punctured and a shock wave propagates through the reaction mixture. The temperature rise can be controlled by varying the pressure and composition of the inert gas. The composition of the reaction mixture after initiation is monitored in real time, usually spectroscopically.

The shock tube approach is often used to study combustion reactions. Suitable precursors for such studies, together with the radical species obtained on dissociation using argon as the shock gas include:



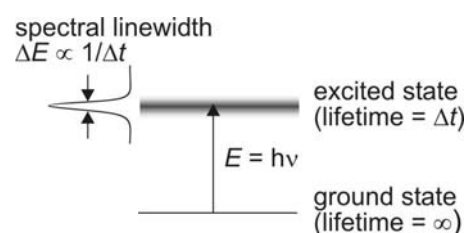
The method does have some major drawbacks, not least of which is the fact that the rapid heating is not selective for a particular molecules, and is likely to lead to at least partial dissociation of all of the species in the 'reactants' chamber. This leads to a complicated mixture of reactive species and often a large number of reactions occurring in addition to the reaction under study. Modelling the kinetics of such a system is often challenging, to say the least. Also, because each experiment is essentially a 'one off', no signal averaging is possible, and signal to noise levels are often low. Compare this with laser pump-probe methods, in which hundreds or even thousands of traces may be averaged to obtain good signal to noise.

Lifetime methods

In quantum mechanics, you learnt about the Heisenberg uncertainty principle, which relating the uncertainty in position and momentum, $\Delta x \Delta p \geq h/4\pi$. A similar uncertainty principle relates energy and time.

$$\Delta E \Delta t \geq h/4\pi \quad \text{or, since } E = h\nu, \quad \Delta \nu \Delta t \geq 1/4\pi$$

The result of this relationship is that an atomic or molecular state has an uncertainty ΔE in its energy that is related to its lifetime Δt . The lifetime of most ground states is effectively infinite, so that the uncertainty in their energy is negligible. However, excited states are short-lived, and their energy is therefore 'fuzzy'. Since photons corresponding to any energies within this uncertainty ΔE may be absorbed, this leads to spectral lines having a finite width known as the *natural linewidth*.



Kinetic processes involving excited states reduce their lifetime and cause further broadening. Many such processes have first order kinetics, for and in these cases the rate constant is simply equal to the reciprocal of the lifetime, $k = 1/\Delta t$. As a consequence, first order rate constants may be determined from measurements of spectral linewidths, provided that other sources of line broadening are absent. Lifetime techniques cover a broad range of timescales, from around 10^{-15} s in photoelectron spectroscopy to around 1 s in NMR.

(ii) Techniques for monitoring concentrations as a function of time

For slow reactions, the composition of the reaction mixture may be analysed while the reaction is in progress either by withdrawing a small sample or by monitoring the bulk. This is known as a *real time analysis*. Another option is to use the *quenching method*, in which reaction is stopped a certain time after initiation so that the composition may be analysed at leisure. Quenching may be achieved in a number of ways. For example:

- sudden cooling
- adding a large amount of solvent
- rapid neutralisation of an acid reagent
- removal of a catalyst
- addition of a quencher

The key requirement is that the reaction must be slow enough (or the quenching method fast enough) for little reaction to occur during the quenching process itself.

Often, the real time and quenching techniques are combined by withdrawing and quenching small samples of the reaction mixture at a series of times during the reaction.

The composition of the reaction mixture may be followed in any one of a variety of different ways by tracking any chemical or physical change that occurs as the reaction proceeds. e.g.

- For reactions in which at least one reactant or product is a gas, the reaction's progress may be followed by monitoring the pressure, or possibly the volume.
- For reactions involving ions, conductivity or pH measurements may often be employed.
- If the reaction is slow enough, the reaction mixture may be titrated.
- If one of the components is coloured then colourimetry may be appropriate.
- Absorption or emission spectroscopy are common (more on these later)
- For reactions involving chiral compounds, polarimetry (measurement of optical activity) may be useful.
- Other techniques include mass spectrometry, gas chromatography, NMR/ESR, and many more.

Fast reactions require a fast measurement technique, and as a consequence are usually monitored spectroscopically. A few commonly used techniques are outlined below.

Absorption spectroscopy – Beer Lambert Law

Also known as *spectrophotometry*, absorption spectroscopy is widely used to track reactions in which the reactants and products have different absorption spectra. A monochromatic light source, often a laser beam, is passed through the reaction mixture, and the ratio of transmitted to incident light intensity, I/I_0 , is measured as a function of time. The quantity $T = I/I_0$ is known as the transmittance, and may be related to the changing concentration of the absorbing species using the Beer Lambert law.

$$T = \frac{I}{I_0} = 10^{-\epsilon cl} \quad \text{or} \quad T = \frac{I}{I_0} = e^{-\alpha cl}$$

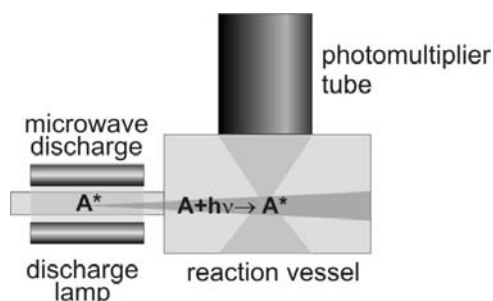
You may come across the Beer Lambert law in either of the forms above, or in log form

$$\log(I/I_0) = -\epsilon cl \quad \text{or} \quad \ln(I/I_0) = -\alpha cl$$

In the above equations, c is the concentration of the absorbing species and l is the path length through the sample. ϵ and α are known as the molar absorption coefficient and molar extinction coefficient, and are a measure of the strength of the spectral absorption. The quantity ϵcl is called the *absorbance*, A . Note that $A = -\log T$. You may also see this quantity referred to as the *optical density*.

Resonance fluorescence

Resonance fluorescence is a widely used technique for detecting atomic species such as H, N, O, Br, Cl or F. The light source is a discharge lamp filled with a mixture of helium and a molecular precursor for the atom of interest. A microwave discharge inside the lamp dissociates the precursor and produces a mixture of ground state and excited state atoms. The lamp then emits radiation at characteristic frequencies as the excited state atoms emit photons to relax down to the ground state. This radiation may be used to excite atoms of the same species present in a reaction mixture, and monitoring the intensity of radiation emitted from *these* atoms as they relax back to the ground state provides a measure of their concentration in the reaction mixture. To ensure that the detected light originates from atoms in the reaction mixture and not the lamp, the detector – usually a photomultiplier tube – is placed at right angles to the direction in which radiation exits the lamp.



Laser-induced fluorescence

In laser-induced fluorescence a laser is used to excite a chosen species in a reaction mixture to an electronically excited state. The excited states then emit photons to return to the ground state, and the intensity of this fluorescent emission is measured. Because the number of excited states produced by the laser pulse is proportional to the number of ground state molecules present in the reaction mixture, the fluorescence intensity provides a measure of the concentration of the chosen species.

(iii) Temperature control and measurement

For any reaction with a non-zero activation energy, the rate constant is dependent on temperature. The temperature dependence is often modelled by the *Arrhenius equation*, which will be treated in more detail in Section 18.

$$k = A \exp(-E_a/RT)$$

where E_a is the activation energy for the reaction, and A is a constant known as the pre-exponential factor.

This temperature dependence means that in order to measure an accurate value for k , the temperature of the reaction mixture must be maintained at a constant, known value. If activation energies are to be measured as part of the kinetic study, rate constants must be measured at a series of temperatures. The temperature is most commonly monitored using a thermocouple, due to its wide range of operation and potential for automation; however, standard thermometers are also commonly used.

There are numerous ways in which the temperature of a reaction mixture may be controlled. For example, reactions in the liquid phase may be carried out in a temperature-controlled thermostat, while reactions in the gas phase are usually carried out inside a stainless steel vacuum chamber, in which thermal equilibrium at the temperature of the chamber is maintained through collisions of the gas molecules with the chamber walls. High temperatures up to 1300 K may be obtained using conventional heaters. Low temperatures may be achieved by flowing cooled liquid through the walls of the reaction vessel, and very low temperatures may be reached by using cryogenic liquids such as liquid nitrogen (~77 K) or liquid helium (~4 K). Extremely low temperatures (down to a few Kelvin), such as those relevant to reactions in interstellar gas clouds, may be obtained by preparing the reactant gases in a supersonic expansion (see Section 9 of the Properties of Gases handout).

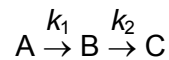
9. Complex reactions

In kinetics, a 'complex reaction' simply means a reaction whose mechanism comprises more than one elementary step. In the previous sections we have looked at experimental methods for measuring reaction rates to provide kinetic data that may be compared with the predictions of theory. In the following sections, we will look at a range of different types of complex reactions and the rate laws that may be predicted from their kinetic mechanisms. Disagreement of a predicted rate law with the experimental data is enough to rule out the corresponding proposed mechanism, while agreement inspires some confidence that the proposed mechanism is the correct one. It should be noted though that agreement between the predicted and measured kinetics is not always enough to assign a mechanism. The proposed mechanism must be able to account for all other properties of the reaction, which may include quantities such as the product distribution, product stereochemistry, kinetic isotope effects, temperature dependence, and so on.

The types of complex mechanisms that we will cover are: consecutive (or sequential) reactions; competing reactions; pre-equilibria; unimolecular reactions; third order reactions; enzyme reactions; chain reactions; and explosions.

10. Consecutive reactions

The simplest complex reaction consists of two consecutive, irreversible elementary steps e.g.



An example of such a process is radioactive decay. This is one of the few kinetic schemes in which it is fairly straightforward to solve the rate equations analytically, so we will look at this example in some detail. We can see immediately that the following initial conditions hold.

$$\begin{aligned} \text{at } t = 0, \quad [A] &= [A]_0 \\ [B] &= 0 \\ [C] &= 0 \end{aligned}$$

$$\text{with at all times} \quad [A] + [B] + [C] = [A]_0.$$

Using this information, we can set up the rate equations for the process and solve them to determine the concentrations of [A], [B], and [C] as a function of time. The rate equations for the concentrations of A, B, and C are:

$$(1) \quad \frac{d[A]}{dt} = -k_1[A]$$

$$(2) \quad \frac{d[B]}{dt} = k_1[A] - k_2[B]$$

$$(3) \quad \frac{d[C]}{dt} = k_2[B]$$

Integrating (1) gives

$$[A] = [A]_0 \exp(-k_1 t).$$

Substituting this into (2) gives $\frac{d[B]}{dt} + k_2[B] = k_1[A]_0 \exp(-k_1 t)$, a differential equation with the solution

$$[B] = \frac{k_1}{k_2 - k_1} \{ \exp(-k_1 t) - \exp(-k_2 t) \} [A]_0$$

Finally, since $[C] = [A]_0 - [B] - [A]$, we find

$$[C] = \left(1 + \frac{k_1 \exp(-k_2 t) - k_2 \exp(-k_1 t)}{k_2 - k_1} \right) [A]_0$$

We will consider two special cases for a pair of sequential reactions:

Case 1: $k_1 \gg k_2$

In this case, all of the A initially present is rapidly converted into B, which is then slowly used up to form C. Since k_2 becomes negligible in comparison with k_1 , the equation for [C] becomes

$$[C] = \{ 1 - \exp(-k_2 t) \} [A]_0$$

i.e. the rate of production of C (and therefore the overall rate of the two-step reaction) becomes independent of k_1 (apart from at the very beginning of the reaction). In other words, the second step is the *rate determining step*.

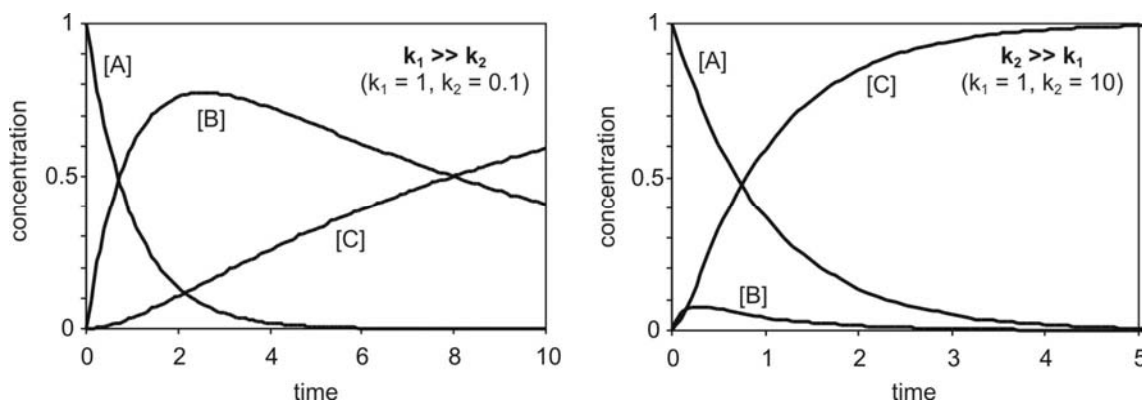
Case 2: $k_2 \gg k_1$

In this case, B is consumed as soon as it is produced, and since k_1 becomes negligible in comparison with k_2 , the equation for [C] simplifies to

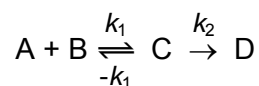
$$[C] = \{1 - \exp(-k_1 t)\} [A]_0$$

i.e. the overall rate now depends only on k_1 , and the first step is rate determining.

The way in which the concentrations of A, B and C vary with time for each of the two cases considered above is shown in the figures below.

**11. Pre-equilibria**

A situation that is only slightly more complicated than the sequential reaction scheme described above is



The rate equations for this reaction are:

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = -k_1[A][B] + k_{-1}[C]$$

$$\frac{d[C]}{dt} = k_1[A][B] - k_2[C]$$

$$\frac{d[D]}{dt} = k_2[C]$$

These cannot be solved analytically, and in general would have to be integrated numerically to obtain an accurate solution. However, the situation simplifies considerably if $k_{-1} \gg k_2$. In this case, an equilibrium is reached between the reactants A and B and the intermediate C, and the equilibrium is only perturbed very slightly by C 'leaking away' very slowly to form the product D.

If we assume that we can neglect this perturbation of the equilibrium, then once equilibrium is reached, the rates of the forward and reverse reactions must be equal. i.e.

$$k_1[A][B] = k_{-1}[C]$$

Rearranging this equation, we find

$$\frac{k_1}{k_{-1}} = \frac{[C]}{[A][B]} = K$$

The equilibrium constant K is therefore given by the ratio of the rate constants k_1 and k_{-1} for the forward and reverse reactions. The rate of the overall reaction is simply the rate of formation of the product D, so

$$v = \frac{d[D]}{dt} = k_2[C] = k_2K[A][B]$$

The reaction therefore follows second order kinetics, with an effective rate constant $k_{\text{eff}} = k_2K$. Note that this rate law will not hold until the equilibrium between A, B and C has been established, and so is unlikely to be accurate in the very early stages of the reaction.

12. The steady state approximation

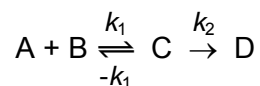
Apart from the two simple examples described above, the rate equations for virtually all complex reaction mechanisms generally comprise a complicated system of coupled differential equations that cannot be solved analytically. In state-of-the-art kinetic modelling studies, fairly sophisticated software is generally used to obtain numerical solutions to the rate equations in order to determine the time-varying concentrations of all species involved in a reaction sequence. However, very good approximate solutions may often be obtained by making simple assumptions about the nature of reactive intermediates.

Almost by definition, a reactive intermediate R will be used up virtually as soon as it is formed, and therefore its concentration will remain very low and essentially constant throughout the course of the reaction. This is true at all times apart from at the very start of the reaction, when [R] must necessarily build up from zero to some small non-zero value, and at the very end of the reaction in the case of a reaction that goes to completion, when [R] must return to zero. During the period of time when [R] is essentially constant, because $d[R]/dt$ is so much less than the rates of change of the reactant and product concentrations, it is a good approximation to set $d[R]/dt = 0$. This is known as the steady state approximation.

Steady state approximation: if a reactive intermediate R is present at low and constant concentration throughout (most of) the course of the reaction, then we can set $d[R]/dt = 0$ in the rate equations.

As we shall see, applying the steady state approximation has the effect of converting a mathematically intractable set of coupled differential equations into a system of simultaneous algebraic equations, one for each species involved in the reaction. The algebraic equations may be solved to find the concentrations of the reactive intermediates, and these may then be substituted back into the more general equations to obtain an expression for the overall rate law.

As a simple example, let us look at the same reaction scheme as in the preequilibrium of Section 11, but now take the case where $k_2 \gg k_{-1}$, so that C is now a reactive intermediate and there is no stable equilibrium between A, B and C. The reaction equation is



We can apply the steady state approximation (SSA) to C, to obtain

$$\frac{d[C]}{dt} = 0 = k_1[A][B] - k_{-1}[C] - k_2[C]$$

This may be solved to give [C] in terms of the reactant concentrations [A] and [B].

$$[C] = \frac{k_1}{k_{-1} + k_2} [A][B]$$

The overall rate is the rate of formation of the product, D, giving

$$v = \frac{d[D]}{dt} = k_2[C] = \frac{k_1 k_2}{k_{-1} + k_2} [A][B]$$

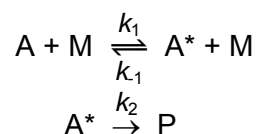
In the limiting case where k_{-1} is much smaller than k_2 , we can neglect k_{-1} in the denominator and the rate becomes simply $k_1[A][B]$ i.e. the rate of the overall reaction is the same as the rate of the first elementary step. This is not all that surprising. If k_2 is much larger than k_{-1} and k_1 then as soon as the $A + B \rightarrow C$ step has occurred, C is immediately converted into products, and there is virtually no chance for the reverse $C \rightarrow A + B$ reaction to occur. The initial elementary step is rate determining, and therefore dominates the kinetics.

We will come across many more applications of the SSA in the next few sections. In general, the steps required in order to use the SSA to obtain an overall rate law for a complex reaction are:

1. Write down a steady state equation for each reactive intermediate.
2. Solve the set of equations to obtain expressions for the concentrations of each intermediate in terms of the reactant and product concentrations. A couple of hints:
 - (i) If the equation contains only one reactive intermediate, it may simply be rearranged to give the concentration of that intermediate in terms of reactant and product concentrations. This can often be substituted into other equations to obtain the corresponding expressions for other reactive intermediates.
 - (ii) If the equations depend on more than one reactive intermediate, and share terms, look for sums or differences of the equations that will simplify matters. Often a SSA problem that initially appears extremely complicated becomes trivial when you simply add together two of the steady state equations.
3. Write down an expression for the overall rate (usually the rate of change of one of the products). This will generally involve the concentrations of one or more reactive intermediates.
4. Substitute your expressions from step 2 into your overall rate equation to obtain an overall rate equation that depends only on reactant and product concentrations. *Concentrations of reactive intermediates must not appear in the final rate law.*

13. 'Unimolecular' reactions – the Lindemann-Hinshelwood mechanism

A number of gas phase reactions follow first order kinetics and apparently only involve one chemical species. Examples include the structural isomerisation of cyclopropane to propene, and the decomposition of azomethane ($\text{CH}_2\text{N}_2\text{CH}_3 \rightarrow \text{C}_2\text{H}_6 + \text{N}_2$, with experimentally determined rate law $v = k[\text{CH}_3\text{N}_2\text{CH}_3]$) The mechanism by which these molecules acquire enough energy to react remained a puzzle for some time, particularly since the rate law seemed to rule out a bimolecular step. The puzzle was solved by Lindemann in 1922, when he proposed the following mechanism for 'thermal' unimolecular reactions¹.



¹ Unimolecular reactions, and indeed many other types of reaction, may also be initiated photochemically by absorption of a photon. You will cover photochemical reactions in second and third year courses.

The reactant, A, acquires enough energy to react by colliding with another molecule, M (note that in many cases M will actually be another A molecule). The excited reactant A* then undergoes unimolecular reaction to form the products, P. To determine the overall rate law arising from this mechanism, we can apply the SSA to the excited state A*.

$$\frac{d[A^*]}{dt} = 0 = k_1[A][M] - k_{-1}[A^*][M] - k_2[A^*] \quad (13.1)$$

Rearranging this expression yields the concentration [A*].

$$[A^*] = \frac{k_1[A][M]}{k_{-1}[M] + k_2} \quad (13.2)$$

The overall rate of reaction is then

$$v = \frac{d[P]}{dt} = k_2[A^*] = \frac{k_1 k_2 [A][M]}{k_{-1}[M] + k_2} \quad (13.3)$$

At first sight, this does not look very much like a first order rate law! However, consider the behaviour of this rate law in the limits of high and low pressure.

High pressure

At high pressure there are many collisions, and collisional de-excitation of A* is therefore much more likely than unimolecular reaction of A* to form products. i.e. $k_{-1}[A^*][M] \gg k_2[A^*]$. In this limit, we can neglect the k_2 term in the denominator of Equation (13.3), and the rate law becomes:

$$v = \frac{k_1 k_2}{k_{-1}} [A] \quad (13.4)$$

which is first order, with a first order rate constant $k_{\text{uni}} = k_1 k_2 / k_{-1}$. This mechanism therefore explains the observed first order kinetics at reasonable pressures, when the unimolecular step is rate determining.

Low pressure

At low pressures there are few collisions, and A* will generally undergo unimolecular reaction before it undergoes collisional de-excitation. i.e. $k_2 \gg k_{-1}[A^*][M]$. In this case, we can neglect the $k_{-1}[M]$ in the denominator of Equation (13.3), and the rate law is now

$$v = k_1[A][M] \quad (13.5)$$

We see that at low pressures the kinetics are second order. This is because formation of the excited species A*, a bimolecular process, is now the rate determining step.

Often, the rate law for such reactions is written

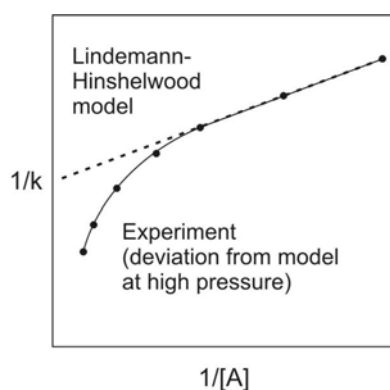
$$v = k[A] \quad \text{with} \quad k = \frac{k_1 k_2 [M]}{k_{-1}[M] + k_2} \quad (13.6)$$

k is the first order rate constant that would be observed experimentally in the high pressure case. If experimental measurements of the rate constant as a function of pressure (equivalent to [M]) are available, the Lindemann-Hinshelwood mechanism may be tested. Taking the reciprocal of our expression for k gives

$$\frac{1}{k} = \frac{k_{-1}}{k_1 k_2} + \frac{1}{k_1 [M]} \quad (13.7)$$

A plot of $1/k$ against $1/[M]$ should therefore be linear, with an intercept of $k_{-1}/(k_1 k_2)$ and a slope of $1/k_1$. An example of such a plot is shown below. Usually there is a reasonable fit between theory and experiment at low pressure, but a pronounced deviation at high pressure, with experimental

values of k being larger than the values predicted by the Lindemann-Hinshelwood mechanism, as shown below.



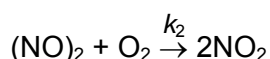
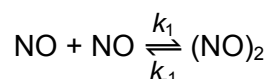
It turns out that while the general idea of a collisional activation process is correct, the true mechanism of 'unimolecular' reactions is slightly more involved. The principal failing of the Lindemann-Hinshelwood mechanism is that it assumes that *any* excited reactant A^* will undergo unimolecular reaction to produce products. In practice, however, excitation is generally required in a degree of freedom that is coupled to the reaction coordinate in some way e.g. vibrational excitation in a bond that breaks during the reaction. More sophisticated theories of unimolecular reactions have been developed which take this and other factors into account, and provide much better agreement with experiment.

14. Third order reactions

A number of reactions are found to have third order kinetics. An example is the oxidation of NO, for which the overall reaction equation and rate law are given below.



One possibility for the mechanism of this reaction would be a three-body collision (i.e. a true termolecular reaction). However, such collisions are exceedingly rare, and certainly too unlikely to explain the observed rate at which this reaction proceeds. An added complication is that the rate of this reaction is found to decrease with increasing temperature, an indication of a complex mechanism. An alternative mechanism that leads to the same rate law is a two step process involving a pre-equilibrium.



The overall rate is

$$v = \frac{1}{2} \frac{d[\text{NO}_2]}{dt} = k_2 [(\text{NO})_2] [\text{O}_2]$$

However, from the pre-equilibrium, we have

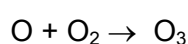
$$K = \frac{[(\text{NO})_2]}{[\text{NO}]^2} \quad \text{so} \quad [(\text{NO})_2] = K[\text{NO}]^2$$

and the overall rate is

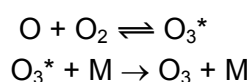
$$v = k_2 K [\text{NO}]^2 [\text{O}_2]$$

i.e. third order, as required.

A very common situation in which third order kinetics are observed are reactions in which two reactants combine to form a single product. Such reactions require a so-called 'third body' to take away some of the excess energy from the reaction product. An example is the formation of ozone



As written, this reaction would barely occur. To understand the reason for this we need to turn to some basic classical mechanics, namely the fact that energy and momentum must both be conserved in the reactive collision. To demonstrate the problem, consider the somewhat contrived situation in which the O and O₂ initially have equal and opposite momenta, and collide head-on to react (the following arguments apply equally well to any other situation, but are clearest to see in this case). Since total momentum must be conserved, and initially the total momentum is zero (because the momenta of the O and O₂ exactly cancel each other out), the final momentum of the O₃ product must be zero i.e. the product must be stationary. Now consider conservation of energy. Since we are forming a bond, the reaction is exothermic, so by conservation of energy, the total kinetic energy possessed by the O₃ product must be the sum of the reaction exothermicity and the kinetic energies of the reactants. We have already determined that conservation of momentum requires the O₃ to be stationary, so all of this kinetic energy must go into vibrational motion of the O₃. Highly vibrationally excited molecules are extremely unstable, and the O₃ will very quickly fall apart back into reactants. The only way for the O₃ to survive is for it to transfer some of its vibrational energy to another molecule M (known as a third body) in a collision. The energy may end up as internal excitation (rotation or vibration) of M, or simply as kinetic energy as the two molecules fly away from each other after the collision. The actual mechanism is therefore

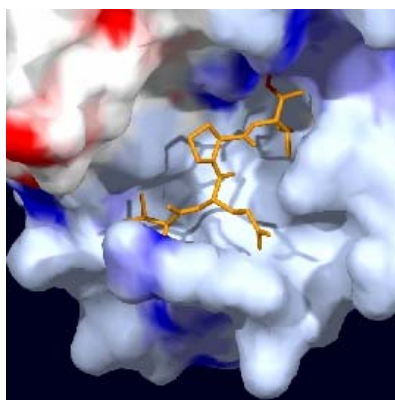


The overall reaction is usually written $\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$.

Note that a third body is *only* required for reactions in which a single product is formed from two or more reactants, since this is the only time that conservation of momentum forces a large amount of energy into the product. If two products are formed, they can both carry away almost arbitrary amounts of energy as kinetic energy while still conserving the total momentum.

15. Enzyme reactions – the Michaelis-Menten mechanism

An enzyme is a protein that catalyses a chemical reaction by lowering the activation energy. Enzymes generally work by having an *active site* that is carefully designed by nature to bind a particular reactant molecule (known as the *substrate*). An example of a substrate bound at the active site of an enzyme is shown on the left (stolen from <http://www.csb.gu.se/neutze/elastase.html>). The activation energy of the reaction for the enzyme-bound substrate is lower than for the free substrate molecule, often due to the fact that the interactions involved in binding shift the substrate geometry closer to that of the transition state for the reaction. Once reaction has occurred, the product molecules are released from the enzyme.



Virtually every chemical reaction in biology requires an enzyme in order to occur at a significant rate (enzyme-catalysed reactions are millions of times faster than the corresponding uncatalysed reactions), and each enzyme is specific to a particular reaction. Many drugs work by binding to a carefully targeted enzyme in place of the normal substrate molecule, thereby inhibiting enzyme activity and slowing the reaction rate. Enzyme kinetics is an extremely important and complex field, but the basic kinetics of a simple enzyme catalysis process may be modelled quite simply, as follows.

In an enzyme-catalysed reaction, a substrate S is converted to products P in a reaction that is catalysed by an enzyme E. For many such reactions, the rate is found experimentally to follow the *Michaelis-Menten equation*

$$v = \frac{v_{\max}[\text{S}]}{K_{\text{M}} + [\text{S}]} \quad (15.1)$$

The constant K_M is called the *Michaelis constant*, and v_{\max} is the maximum rate, which is found to be linearly proportional to the total enzyme concentration.

$$v_{\max} = k_{\text{cat}}[E]_0 \quad (15.2)$$

The constant of proportionality k_{cat} is known as the turnover number, and represents the maximum number of molecules of substrate that each enzyme molecule can convert into products (or ‘turn over’) per second. We shall see later that this occurs when the substrate is present in large excess.

Any kinetic model for enzyme catalysis must explain the fact that the rate depends on the enzyme concentration $[E]$, even though there is no net change in its concentration over the course of the reaction. The simplest trial mechanism involves formation of a bound enzyme-substrate complex ES, followed by conversion of the complex into the products plus free enzyme (which may then go on to catalyse further reaction).



This mechanism is a somewhat special case of applying the steady state approximation. Usually a good rule of thumb is that in order for the SSA to be valid, the concentration of the reactive intermediate (in this case ES) must be much less than the concentration of the reactants. In this case $[ES]$ is not much less than the free enzyme concentration $[E]$. However, because $[E]$ is regenerated in the second step of the mechanism, both $[E]$ and $[ES]$ change much more slowly than $[S]$ and $[P]$ so the SSA is valid. Applying the SSA to $[ES]$, we have

$$\frac{d[ES]}{dt} = 0 = k_1[E][S] - k_{-1}[ES] - k_2[ES] \quad (15.4)$$

Solving for the concentration of the complex, $[ES]$, we obtain

$$[ES] = \frac{k_1[E][S]}{k_{-1} + k_2} \quad (15.5)$$

If the total enzyme concentration is $[E]_0$, then the amount of free enzyme must be $[E] = [E]_0 - [ES]$. Substituting this into the above equation gives

$$[ES] = \frac{k_1([E]_0 - [ES])[S]}{k_{-1} + k_2}, \text{ which rearranges to give } [ES] = \frac{k_1[E]_0[S]}{k_{-1} + k_2 + k_1[S]} \quad (15.6)$$

The overall rate of reaction is then found from the rate of formation of product, P.

$$v = \frac{d[P]}{dt} = k_2[ES] = \frac{k_2 k_1 [E]_0 [S]}{k_{-1} + k_2 + k_1 [S]} = \frac{k_2 [S] [E]_0}{K_M + [S]} = k [E]_0 \quad (15.7)$$

$$\text{where } k = \frac{k_2 [S]}{K_M + [S]} \text{ and } K_M = \frac{k_2 + k_{-1}}{k_1} \text{ is called the Michaelis constant.}$$

We have chosen these particular combinations of rate constants in order to get our rate equation into the same form as the Michaelis-Menten equation. The two equations now agree if $k_2 = k_{\text{cat}}$.

We can see from the above treatment that the rate of enzyme-catalysed reaction (enzymolysis) depends linearly on the enzyme concentration, but in a more complicated way on the substrate concentration. The dependence on $[S]$ simplifies under certain conditions.

1. When $[S] \gg K_M$, then $v = k_2[E]_0 = k_{cat}[E]_0$ and the overall rate is independent of the substrate concentration. This is because there is so much substrate present that its concentration remains essentially constant as the reaction proceeds. Under these conditions, the rate of reaction is a maximum ($v = v_{max}$) and the enzyme is saturated with substrate.
2. When $[S] \ll K_M$, the reaction rate is $v = (k_2/K_M) [E]_0[S]$, and the rate is first order in both $[E]_0$ and $[S]$.

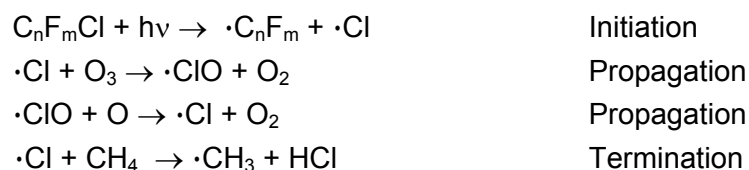
To determine k_2 and K_M from experimental rate data, we invert the expression for k .

$$k = \frac{k_2[S]}{K_M + [S]} \quad \text{becomes} \quad \frac{1}{k} = \frac{K_M}{k_2[S]} + \frac{1}{k_2}$$

A plot of $1/k$ against $1/[S]$ has a slope of K_M/k_2 and an intercept of $1/k_2$. Therefore, $K_M = (\text{slope})/(\text{intercept})$ and $k_2 = 1/(\text{intercept})$. This is called a Lineweaver-Burke plot. Usually, the initial rates method is used to measure k , since this method is not susceptible to complications that may arise from secondary reactions of the products.

16. Chain reactions

Chain reactions are complex reactions that involve *chain carriers*, reactive intermediates which react to produce further reactive intermediates. The elementary steps in a chain reaction may be classified into *initiation*, *propagation*, *inhibition*, and *termination* steps. As an example, consider the infamous reaction by which chlorofluorocarbons (CFCs) destroy ozone:



Initiation step

Reaction is initiated either thermally or photochemically. The first reactive intermediates/chain carriers (in this case a $\cdot Cl$ radical) are produced.

Propagation step

Reaction of a radical leads to formation of another radical – another reactive intermediate. In the first propagation step above, $\cdot Cl$ reacts to form $\cdot ClO$; in the second step $\cdot ClO$ reacts to form $\cdot Cl$.

Termination step

Chain carriers are deactivated. Often this occurs through radical-radical recombination, reaction with walls, or reaction with another molecule to create an inactive product.

Some chain reactions involve *inhibition steps*, in which product molecules are destroyed. Inhibition steps are also sometimes referred to as *retardation* or *de-propagation* steps.

The *chain length* in a chain reaction is defined as the number of propagation steps per initiation step, or alternatively as the rate of propagation divided by the rate of initiation. Chain lengths can be very long – in the above example a single $\cdot Cl$ radical can destroy around 10^6 molecules of ozone.

$$\text{chain length, } n = \frac{v(\text{propagation})}{v(\text{initiation})} = \frac{v(\text{propagation})}{v(\text{termination})}$$

The above reaction is an example of a *cyclic chain reaction*. The $\cdot\text{Cl}$ essentially acts as a catalyst and is continuously regenerated until it is removed by a termination step. It is also possible to have *non-cyclic chain reactions*, involving many reactive species and elementary steps. Non-cyclic chain reactions can have extremely complicated kinetic mechanisms.

Chain reactions in which each propagation step produces only one reactive intermediate are called *linear chain reactions* (as opposed to *branched chain reactions*, which we will cover in Section 18). We will look at some examples of linear chain reactions in the following section.

17. Linear chain reactions

The hydrogen-bromine reaction has become the 'benchmark' system for illustrating the kinetics of linear chain reactions, and we will use this reaction as our main example. We will also compare the kinetics of the hydrogen-bromine reaction with the analogous reactions of chlorine and iodine. Some further examples of chain reactions may be found in the lecture course problems.

The hydrogen – bromine reaction

The kinetics of the reaction between H_2 and Br_2 were determined experimentally by Bodenstein around 100 years ago. The overall reaction has the equation



Bodenstein determined the following rate law for the reaction:

$$\frac{d[\text{HBr}]}{dt} = k [\text{H}_2][\text{Br}_2]^{1/2} \quad (17.2)$$

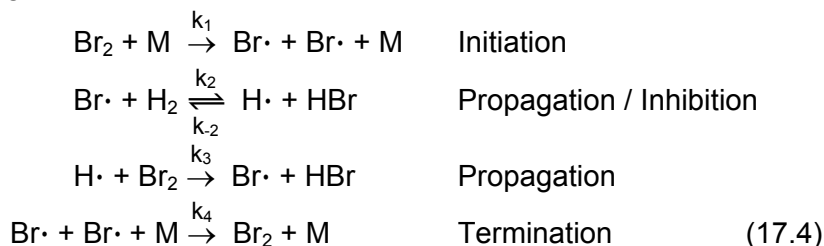
The measured order of $\frac{1}{2}$ with respect to Br_2 indicated that the reaction proceeded via a complex reaction mechanism rather than a simple bimolecular collision. Further investigation showed that this rate law in fact only holds for the early stages of the reaction, and that the true rate law takes the form:

$$\frac{d[\text{HBr}]}{dt} = \frac{k [\text{H}_2][\text{Br}_2]^{1/2}}{1 + k' [\text{HBr}]/[\text{Br}_2]} \quad (17.3)$$

Any proposed mechanism for the reaction must agree with both of these observations. The reaction can be initiated by either thermally-induced or photon-induced dissociation of Br_2 .



We will concentrate on the thermal mechanism for the purposes of deriving a rate law for the overall reaction, but the steps following the initiation step are the same for both cases. The currently accepted mechanism is:



The reaction chain contains two radical chain carriers, $\text{H}\cdot$ and $\text{Br}\cdot$. In the second step, because the H-H bond is stronger than the H-Br bond, once an appreciable amount of HBr has built up the

reverse (inhibition) reaction becomes possible. In order to arrive at an overall rate law for the reaction, we apply the steady state approximation to the two chain carriers.

$$\frac{d[\text{H}]}{dt} = 0 = k_2[\text{Br}][\text{H}_2] - k_2[\text{H}][\text{Br}] - k_3[\text{H}][\text{Br}_2] \quad (17.5)$$

$$\frac{d[\text{Br}]}{dt} = 0 = 2k_1[\text{Br}_2][\text{M}] - k_2[\text{Br}][\text{H}_2] + k_2[\text{H}][\text{HBr}] + k_3[\text{H}][\text{Br}_2] - 2k_4[\text{Br}]^2[\text{M}] \quad (17.6)$$

We can solve these two equations to obtain expressions for the concentrations of H and Br in terms of the reactant and product concentrations and the various rate constants. The two equations each depend on both carrier concentrations, and also share terms. We can simplify the equations by adding them together to give:

$$0 = 2k_1[\text{Br}_2][\text{M}] - 2k_4[\text{Br}]^2[\text{M}] \quad (17.7)$$

which can be rearranged to give the steady state concentration of Br atoms.

$$[\text{Br}] = \left(\frac{k_1[\text{Br}_2]}{k_4} \right)^{1/2} \quad (17.8)$$

Note that (17.7) implies that the rate of initiation is the same as the rate of termination, as expected under steady state conditions (this is a good check that we have made no mistakes up to this point). This result also leads to a considerable simplification in Equation (17.6), which now becomes

$$0 = -k_2[\text{Br}][\text{H}_2] + k_2[\text{H}][\text{HBr}] + k_3[\text{H}][\text{Br}_2] \quad (17.9)$$

and may be rearranged to give an expression for the steady state H atom concentration.

$$[\text{H}] = \frac{k_2[\text{Br}][\text{H}_2]}{k_2[\text{HBr}] + k_3[\text{Br}_2]} = \frac{k_2[\text{H}_2]}{k_2[\text{HBr}] + k_3[\text{Br}_2]} \left(\frac{k_1[\text{Br}_2]}{k_4} \right)^{1/2} \quad (17.10)$$

We are now ready to determine the overall reaction rate.

$$\frac{d[\text{HBr}]}{dt} = k_2[\text{Br}][\text{H}_2] - k_2[\text{H}][\text{HBr}] + k_3[\text{H}][\text{Br}_2] \quad (17.11)$$

Substituting in our expressions for [H] and [Br] gives

$$\frac{d[\text{HBr}]}{dt} = \frac{2k_2(k_1/k_4)^{1/2}[\text{Br}_2]^{1/2}[\text{H}_2]}{1 + (k_2/k_3)[\text{HBr}]/[\text{Br}_2]} \quad (17.12)$$

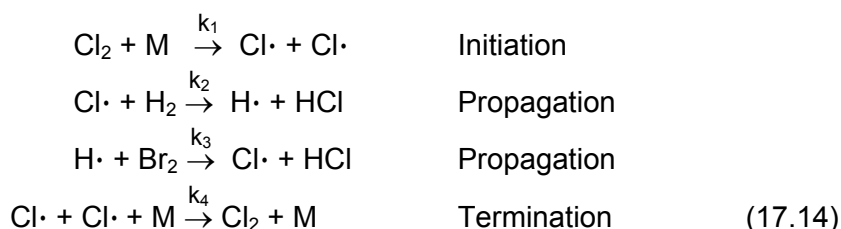
We see that this agrees with the measured rate law, Equation (17.3). In the early stages of the reaction, the concentration of the HBr product is much lower than that of the reactant Br_2 , and the second term in the denominator becomes negligible. The rate law then reduces to

$$\frac{d[\text{HBr}]}{dt} = 2k_2(k_1/k_4)^{1/2}[\text{Br}_2]^{1/2}[\text{H}_2] \quad (17.13)$$

again reproducing the experimental observations. The proposed mechanism therefore fits well with the experimental measurements.

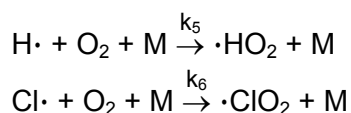
The hydrogen – chlorine reaction

The mechanism for the hydrogen-chlorine reaction is essentially identical to that for the hydrogen-bromine reaction



The reaction may also be initiated photochemically. Unlike the $\text{H}_2 + \text{Br}_2$ reaction, both propagation steps are very efficient, and the inhibition step is very slow (and has therefore been omitted from the above mechanism), so the overall reaction rate is much faster. Chain lengths up to 10^6 are possible, and coupled with the exothermicity of the reaction, this can lead to a thermal explosion.

This reaction provides a good example of a case where the steady state approximation breaks down. Since both propagation steps are very efficient, when the radical concentrations $[\text{H}]$ and $[\text{Cl}]$ are much lower than the reactant concentrations $[\text{H}_2]$ and $[\text{Cl}_2]$, reactive collision of a Cl atom with H_2 (propagation) is much more likely than a terminating collision with another Cl atom. This means that the reaction may be very advanced before the steady state condition – that the rates of initiation and termination are equal – is reached. In practice, the situation is usually simplified somewhat due to the extreme sensitivity of the reaction to inhibition by contaminants such as O_2 . Oxygen reacts with H and Cl radicals to form inert radicals, providing an alternative termination pathway and increasing the overall rate of termination. If O_2 is present at a concentration of around 1% or greater, the following termination steps dominate to the point where the steady-state approximation becomes valid.



If we replace the termination step 4 of our above mechanism with the termination steps above, we can apply the SSA to obtain expressions for the steady state $[\text{H}]$ and $[\text{Cl}]$ concentrations and (after some algebra – left as an exercise for the keen reader!) for the overall rate.

$$\frac{d[\text{HCl}]}{dt} = \frac{2k_a[\text{H}_2][\text{Cl}_2]^2}{[\text{O}_2]([\text{H}_2] + k_b[\text{Cl}_2])} \quad \text{with} \quad k_a = \frac{k_1 k_2}{k_5} \quad \text{and} \quad k_b = \frac{k_3 k_6}{k_2 k_5}$$

The hydrogen-iodine reaction

We might expect the hydrogen-iodine to have a similar mechanism to the bromine and chlorine analogues. However, the second step in the mechanism ($\text{I} + \text{H}_2 \rightarrow \text{H} + \text{HI}$) occurs much too slowly at normal temperatures for this mechanism to be viable. Various kinetic mechanisms operate at different temperatures, for example



Unlike the complicated rate laws followed by the chlorine and bromine reactions, the hydrogen-iodine reaction follows a simple ‘bimolecular’ rate law (you could prove this as an exercise).

Comparison of the hydrogen-halogen reactions

The key difference between the reactions of Cl_2 , Br_2 and I_2 with hydrogen lies in the exothermicity of the atomic halogen reactions with H_2 (step 2 in the chain reaction sequences).

Cl	$\Delta H = 4.4 \text{ kJ mol}^{-1}$
Br	$\Delta H = 69.6 \text{ kJ mol}^{-1}$
I	$\Delta H = 137.7 \text{ kJ mol}^{-1}$

The iodine reaction is so slow that it does not occur at accessible temperatures, ruling out the chain mechanism observed for the other two halogens. The chlorine reaction is fast, and the bromine reaction slow. While the reverse (inhibition) step $\text{H} + \text{HX} \rightarrow \text{X} + \text{H}_2$ is thermodynamically favourable for both Cl and Br, it is unimportant for Cl due to the very low steady state concentration of H atoms. In contrast, the inhibition step has a considerable effect on the overall kinetics of the bromine reaction.

18. Explosions and branched chain reactions

An explosion occurs when a reaction rate accelerates out of control. As the reaction speeds up, gaseous products are formed in larger and larger amounts, and more and more heat is generated. The rapid liberation of heat causes the gases to expand, generating extremely high pressures, and it is this sudden formation of a huge volume of expanded gas that constitutes the explosion. The pressure wave travels at very high speeds, often much faster than the speed of sound, and the 'bang' associated with an explosion is the result of a supersonic shock wave.

There are two different mechanisms that may lead to an explosion. These are related to the fact that the overall reaction rate depends on both the magnitude of the rate constant and the amounts of reactants present in the reaction mixture.

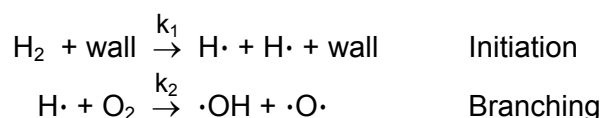
If the heat generated in a reaction due to the reaction exothermicity cannot be dissipated sufficiently rapidly, the temperature of the reaction mixture increases. This increases the rate constant, and therefore the reaction rate, producing more heat and accelerating the reaction rate still further, and so on until an explosion results. Such explosions are known as *thermal explosions*, and in principle may occur whenever the rate of heat production by a reaction mixture exceeds the rate of heat loss to the surroundings (often the walls of the reaction vessel).

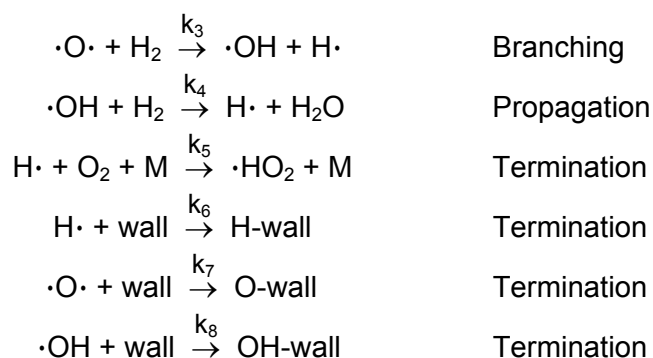
The second category of explosions arise from chain branching within a chain reaction, and are known as *chain branching explosions* (or sometimes, somewhat misleadingly, isothermal explosions). In this case, one or more steps in the reaction mechanism produce two or more chain carriers from one chain carrier, increasing the number of chain carriers, and therefore the overall reaction rate.

In practice, both mechanisms often occur simultaneously, since any acceleration in the rate of an exothermic reaction will eventually lead to an increase in temperature. However, chain branching is not a requirement for an explosion. As an example, detonation of TNT (2,4,6-trinitrotoluene) is simply the result of an extremely fast chemical decomposition that generates huge quantities of gas. The reaction $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$ provides an example of a reaction in which both mechanisms are important.

The hydrogen – oxygen reaction: $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$

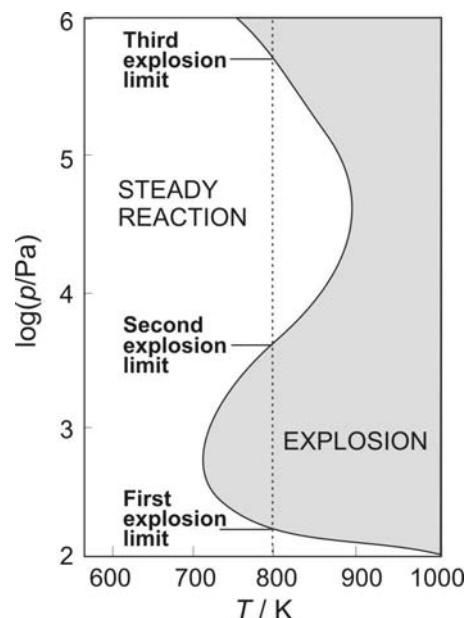
Though this may at first sight appear to be a very simple reaction, the mechanism is in fact extremely complex, and is still not fully understood. It is known to be a branched chain reaction, involving carriers such as $\text{H}\cdot$, $\cdot\text{O}\cdot$ and $\cdot\text{OH}$. A simplified version of the thermal mechanism is given below.





Each of reactions 2 and 3 produce two radical chain carriers for each chain carrier consumed. The two steps combine to give an overall branching coefficient of 3, corresponding to the hypothetical reaction $\text{H}\cdot + \text{O}_2 + \text{H}_2 \rightarrow \text{H}\cdot + \cdot\text{OH} + \cdot\text{OH}$. Even so, the mixture is not explosive under all conditions, mainly because steps 1, 2 and 3 are endothermic ($\Delta H_1 = 427 \text{ kJ mol}^{-1}$, $\Delta H_2 = 71 \text{ kJ mol}^{-1}$, $\Delta H_3 = 17 \text{ kJ mol}^{-1}$) and therefore slow at low temperatures. The efficiency of the branching steps increases with increasing temperature, and as a result, the reaction displays a complex dependence on temperature and pressure, as shown below.

1. At very low pressures the mean free path in the gas is large, and chain carriers can reach the walls and combine. Collisions with walls are more likely than collisions with other gas phase molecules, so that overall $(\nu_5 + \nu_6 + \nu_7 + \nu_8) = (\nu_1 + \nu_2 + \nu_3)$ i.e. termination balances initiation, and steady reaction occurs.
2. At higher pressures, the chain carriers react before reaching the walls and the gas phase branching ratios become too high for wall termination to control (this is largely due to the fact that the rate of gas phase reaction is proportional to p^2 , while the rate of wall reactions increases in proportion to p). Now we have $(\nu_1 + \nu_2 + \nu_3) > (\nu_5 + \nu_6 + \nu_7 + \nu_8)$, and the mixture becomes explosive. This is known as the *first explosion limit*.
3. At higher pressures, three body collisions start to become important. Termination step 5 can now match steps 1 to 3 in efficiency, and we again have $(\nu_5 + \nu_6 + \nu_7 + \nu_8) = (\nu_1 + \nu_2 + \nu_3)$ and steady reaction. This is the *second explosion limit*.
4. If the pressure is increased still further, the reaction rate increases so much and such a large amount of heat is generated that a thermal explosion results. This is the *third explosion limit*.



The factors that affect the explosion limits are fairly straightforward to understand in terms of their effects on the relative rates of initiation, propagation/branching, and termination steps. For example:

- (i) Temperature – increasing the temperature increases the efficiency of both endothermic reaction steps and steps for which there is activation barrier (steps 1-4 in the above mechanism). The termination steps are less sensitive to temperature, and may even be slowed down since they tend to be exothermic. As a result, the first explosion limit is lowered as the rates of steps 2 and 3 outpaces those of steps 6-8 more readily. The second explosion limit is increased because a higher pressure is needed for the termolecular step 5 to become important. The third limit is decreased, since at higher temperature more heat is produced, and also the heat that is produced is harder to lose from the system.

- (ii) Surface/Volume ratio – the shape and size of the reaction vessel can have a considerable effect on the explosion limits. Increasing the surface to volume ratio favours processes that involve collisions with the vessel walls over gas phase processes, which in this case means the initiation step 1 and termination steps 6, 7 and 8. The high efficiency of the branching steps means that 1 is unimportant in determining the overall rate, and the increased efficiency of the termination steps increases the pressure at which the first explosion limit is reached. The second limit has no dependence on the vessel walls and is unchanged. The third limit increases because it becomes easier to lose heat from the system due to the greater number of collisions with the walls.
- (iii) Overall pressure – adding an inert gas to the mixture decreases the mean free path of the gas molecules, and disfavours collisions with the walls. This lowers the first explosion limit since the termination steps 6, 7, and 8 become less efficient. The second limit is also decreased because the inert gas can act as the third body M, increasing the rate of step 5, a termination process. The third limit is lowered due to the reduced heat transfer from the gas to the vessel walls.

19. Temperature dependence of reaction rates

The Arrhenius equation and activation energies

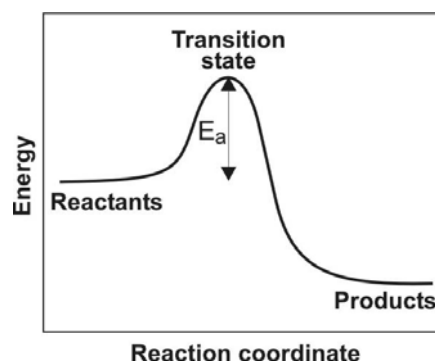
It is found experimentally that the rate constants for many chemical reactions follow the Arrhenius equation.

$$k = A \exp(-E_a/RT) \quad \text{or equivalently} \quad \ln k = \ln A - \frac{E_a}{RT} \quad (19.1)$$

where A is the pre-exponential factor and E_a is the activation energy. These parameters may be determined from experimental rate data by plotting $\ln k$ against $1/T$. This is known as an Arrhenius plot, and has an intercept of $\ln A$ and a slope of $-E_a/R$. For most reactions, the Arrhenius equation works fairly well over at least a limited temperature range. However, there are often deviations. These are generally due to the temperature dependence of the pre-exponential factor² (which you will cover in detail in statistical mechanics next year), but may also be due to more exotic effects, such as the influence of quantum mechanical tunnelling mechanisms on the reaction rate at low temperatures.

For an elementary reaction, both E_a and A have definite physical meanings; in particular, the activation energy may be interpreted as the energy difference between the reactants and the transition state involved in the collision and associated chemical rearrangement (see figure on right). The origins of the Arrhenius equation for a simple bimolecular elementary reaction will be explored in more detail in Section 20, when we develop simple collision theory.

When the Arrhenius equation is applied to the overall kinetics of a multi-step reaction, E_a simply becomes an experimental parameter describing the temperature dependence of the overall reaction rate. E_a may vary with temperature, and may take positive or negative values. In this context, we may define the activation energy as:



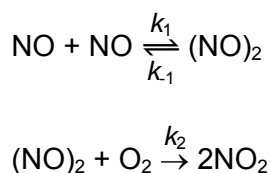
² The detailed temperature dependence of A is beyond the scope of this course, and will be covered in detail next year in the statistical mechanics course. A very approximate temperature-dependent model for A will be seen in Section 20, on simple collision theory. However, the true origin of the temperature dependence relates to the way in which temperature affects the distribution of occupied quantum states in the reacting molecules.

$$E_a = RT^2 \frac{d \ln k}{dT} \quad (19.2)$$

This is a more general definition of the activation energy than the Arrhenius equation, and the two definitions become equivalent in the case when E_a is independent of temperature (all you need to do to prove this is to integrate the above equation, treating E_a as a constant). With the above definition, we can determine E_a at a given temperature from the slope (at the temperature of interest) of a plot of $\ln k$ against T , even if the Arrhenius plot is not a straight line.

There are a few observations that follow from Equation (19.2).

1. The higher the activation energy, the stronger the temperature dependence of the rate constant.
2. A reaction with no temperature dependence has an activation energy of zero (this is common in ion-molecule reactions and radical-radical recombinations)
3. A negative activation energy implies that the rate decreases as the temperature increases, and always indicates a complex reaction mechanism. An example of a reaction with a negative activation energy was the oxidation of NO to form NO_2 , which has the mechanism.



At higher temperatures, the intermediate complex $(\text{NO})_2$ becomes more unstable and has a shorter lifetime. There is therefore less time for the O_2 to react with it to form the NO_2 products, and the reaction rate therefore decreases. Another way of thinking about this is that formation of the complex is exothermic, and increasing the temperature will therefore shift the pre-equilibrium to the left (by Le Chatelier's principle), again reducing the overall rate of reaction.

Overall activation energies for complex reactions

When dealing with complex reactions, the Arrhenius equation can often be used to estimate the overall activation energy from a knowledge of the activation energies of individual steps. For example, in the above reaction, the overall rate law is

$$v = \frac{k_1 k_2}{k_1} [\text{NO}]^2 [\text{O}_2] = k [\text{NO}]^2 [\text{O}_2] \quad (19.3)$$

where k is the observed third order rate constant. The temperature dependence of k is

$$k = \frac{k_1 k_2}{k_1} = \frac{A_1 \exp\left(\frac{-E_a^{(1)}}{RT}\right) A_2 \exp\left(\frac{-E_a^{(2)}}{RT}\right)}{A_1 \exp\left(\frac{-E_a^{(-1)}}{RT}\right)} = \frac{A_1 A_2}{A_1} \exp\left(\frac{-E_a^{(1)} - E_a^{(2)} + E_a^{(-1)}}{RT}\right) \quad (19.4)$$

We can therefore identify that for the overall reaction,

$$A = \frac{A_1 A_2}{A_1} \quad \text{and} \quad E_a = E_a^{(1)} + E_a^{(2)} - E_a^{(-1)} \quad (19.5)$$

Catalysis

As well as quantifying the temperature dependence of a rate constant, the Arrhenius equation also provides a 'mathematical' explanation for the effect of a catalyst. A catalyst works by reducing the activation energy for a reaction. From the appearance of $-E_a$ in the exponent of the Arrhenius equation, it is clear that this will have the effect of increasing the rate constant.

20. Simple collision theory

As the name suggests, simple collision theory represents one of the most basic attempts to develop a theory capable of predicting the rate constant for an elementary bimolecular reaction of the form $A + B \rightarrow P$. We begin by considering the factors we might expect a reaction rate to depend upon. Obviously, the rate of reaction must depend upon the rate of collisions between the reactants. However, not every collision leads to reaction. Some colliding pairs do not have enough energy to overcome the activation barrier, and any theory of reaction rates must take this energy requirement into account. Also, it is highly likely that reaction will not even take place on every collision for which the energy requirement is met, since the reactants may need to collide in a particular orientation (e.g. S_N2 reactions) or some of the energy may need to be present in a particular form (e.g. vibration in a bond coupled to the reaction coordinate). In summary, there are three aspects to a successful reactive collision, and we might expect an expression for the rate of a bimolecular reaction to take the following form.

$$v = (\text{encounter rate}) (\text{energy requirement}) (\text{steric requirement}) \quad (20.1)$$

We will now consider each of these factors in more detail.

1. Encounter rate

We showed in the 'Properties of gases' lecture course that the rate of collisions between molecules A and B present at number densities n_A and n_B is

$$Z_{AB} = \sigma_C \left(\frac{8kT}{\pi\mu} \right)^{1/2} n_A n_B = \sigma_C \left(\frac{8kT}{\pi\mu} \right)^{1/2} N_A^2 [A][B] \quad (20.2)$$

2. Energy requirement

For a Maxwell-Boltzmann distribution of molecular speeds, the fraction of collisions for which the energy is high enough to overcome the activation barrier is $\exp(-E_a/RT)$.

3. Steric requirement

Experimentally, measured rates are often found to be up to an order of magnitude smaller than those calculated from simple collision theory, suggesting that features such as the relative orientation of the colliding species is important in determining the reaction rate. We account for the disagreement between experiment and theory by introducing a steric factor, P , into our expression for the reaction rate. Alternatively, we can replace the collision cross section, σ_C , with a reaction cross section σ_R , where $\sigma_R = P\sigma_C$. Usually, P is considerably less than unity, but values greater than one are also possible. An example is the 'harpoon reaction' between Rb and Cl_2 . The reaction mechanism involves an electron transfer at large separations to form $Rb^+ + Cl_2^-$, after which the electrostatic attraction between the two ions guarantees reaction. P is large because the reaction cross section is determined by the electron transfer distance, which is much larger than the collision diameter.

Combining these three terms, the simple collision theory expression for the reaction rate is:

$$v = P \sigma_C \left(\frac{8kT}{\pi\mu} \right)^{1/2} \exp\left(\frac{-E_a}{RT}\right) n_A n_B \quad (20.3)$$

and we can identify the second order rate constant as

$$v = P \sigma_C \left(\frac{8kT}{\pi\mu} \right)^{1/2} \exp\left(\frac{-E_a}{RT}\right) \quad (20.4)$$

Simple collision theory provides a good first attempt at rationalising the Arrhenius temperature dependence seen for many reaction rate constants. However, at a quantitative level the predictions of the theory are far from accurate. There are a number of ways in which the model breaks down;

- (i) It does not account for the fact that, unless the collision is head on, not all of the kinetic energy of the two reactants is available for reaction. Conservation of angular momentum means that only the kinetic energy corresponding to the velocity component along the relative velocity vector of the reactants actually contributes to the collision energy.
- (ii) The energy stored in internal degrees of freedom in the reactants (vibrations, rotations etc) has been ignored. For reactions involving large molecules, this often leads to a large discrepancy between simple collision theory and experiment, though this is partly corrected for by the inclusion of the steric factor, P . This problem is largely solved in another theory known as transition state theory, which you will learn about next year.