Thermodynamics of Equilibrium

All about entropy, free energy and why chemical reactions take place

A Chem1 Reference Text

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Part 5:

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The greater part of what we call chemistry is concerned with the different kinds of reactions that substances can undergo. The statement that “hydrogen fluoride is a stable molecule” is really a way of saying that the reaction HF → 1/2 H_2 + 1/2 F_2 has a negligible tendency to occur in the forward direction and an overwhelming tendency to occur in the reverse direction. More generally, we can predict how the composition of an arbitrary mixture of H_2, F_2, and HF will tend to change by comparing the values of the **equilibrium constant** K and the **equilibrium quotient** Q; in your study of equilibrium, you will recall that if $Q/K > 1$, the reaction will proceed to the left, whereas if $Q/K < 1$ it will proceed to the right. In either case, the system will undergo a change in composition until it reaches the *equilibrium state* where $Q = K$.

Clearly, the value of K is the crucial quantity that characterizes a chemical reaction, but what factors govern the value of K? In particular, is there any way that we can predict the value of the equilibrium constant of a reaction solely from information about the products and reactants themselves, without any knowledge at all about the mechanism or other details of the reaction? The answer is yes, and this turns out to be the central purpose of chemical thermodynamics:

The purpose of thermodynamics is to predict the equilibrium composition of a system from the properties of its components.

Don’t let the significance of this pass you by; it means that we can say with complete certainty whether or not a given change is possible, and if it is possible, to what extent it will occur— without the need to study the particular reaction in question. To a large extent, this is what makes chemistry a science, as opposed to a mere cataloging of facts.

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This document covers entropy, the Second Law, and its applications to chemical equilibrium at a level appropriate for first-year college chemistry. It was last modified on 23 December 2003 .

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1 • The direction of spontaneous change

A non-natural process: Saul Steinberg's famous *New Yorker* cartoon.

Drop a tea bag into a pot of hot water, and you will see the tea diffuse into the water until it is uniformly distributed throughout the water. What you will never see is the reverse of this process, in which the tea would be sucked up and reabsorbed by the tea bag. The making of tea, like all changes that take place in the world, possesses a "natural" direction. Processes that occur in this way— that is, when left to themselves and in the absence of any attempt to drive them in reverse— are known as *spontaneous* changes. In many cases our everyday life experiences teach us the direction in which spontaneous change can occur, and anything that runs counter to these expectations is immediately sensed as weird. In other cases, including that of most *chemical change*, we often have no obvious guidelines, and must learn how to apply the laws of thermodynamics which ultimately govern all spontaneous change.

Here are a few examples of *natural processes* that are worth thinking about:

1. A stack of one hundred coins is thrown into the air. After they have come to rest on the floor, the numbers that land "heads up" and "tails up" are noted.

   Net change: ordered coins → randomized coins (roughly equal numbers of heads and tails.)

   Energetics: no relevant net change in energy.

   Why can this process not operate in reverse? simple statistics shows that the probability of creating more order (reducing disorder) through a random process such as tossing the coins again is vanishingly small.

2. Two identical blocks of copper, one at 200°C and the other at 100°C, are brought into contact in a thermally-insulated environment. Eventually the temperatures of both blocks reach 150°C.

   Net change: block (200°) + block (100°) → 2 blocks (150°)

   Energetics: Heat (randomized molecular kinetic energy) flows from the warmer block to the cooler one until their temperatures are identical. No net change in the energy of the system (the two blocks).

   Why can this process not operate in reverse? Dispersal of kinetic energy amongst the copper atoms is a random process; the chances that such a process would lead to a non-uniform sharing of the energy are even smaller than in the case of the 100 coins because of the much greater number (around 10^{22}) of particles involved.

3. A book or some other solid object is held above a table top, and is then allowed to fall.

   Net change: book in air → book on table top;
   potential energy → organized kinetic energy → thermal energy.

   Energetics: At the instant just before the end of its fall, the potential energy the object acquired when it was raised will exist entirely as kinetic energy $mv^2/2$ in which m is the mass of the object and v is its velocity. Each atom of which the object is composed will of course possess a proportionate fraction of this energy, again with its principal velocity component pointing down. Superimposed on this, however, will be minute thermal displacements that vary randomly in magnitude and direction from one instant to the next. The sum total of these constitutes the *thermal energy* contained in the object.

   When the object strikes the table top, its motion ceases and we say its kinetic energy is zero. Energy is supposed to be conserved, so where did it disappear to? The shock of impact has resulted in its dispersal into greatly augmented thermal motions of the atoms, both of the object itself and of the area of the table top where the impact occurred. In other words, the kinetic energy of *organized motion* the object had just before its motion stopped has been transformed into kinetic energy of random or *disorganized motion* (thermal energy) which spreads rapidly away from the point of impact.

Why can this process not operate in reverse? Once the kinetic energy of the book has been dispersed amongst the molecules of the book and the table top, the probability of these randomized motions reappearing at the surface where the two objects are in contact and then acting in concert to propel the object back into the air) is negligible.

4. One mole of gas, initially at 300 and 2 atm pressure, is allowed to expand to double its volume, keeping the temperature constant.

   Net change: increase in volume of gas.

   Energetics: no change in energy if the gas behaves ideally.

   Why can this process not operate in reverse? Simple statistics: the probability that N randomly moving objects (flies in a bottle, for example,) will at any time all be located in one half of the container is $(1/2)^N$. For chemically-significant values of N (10^{20}, say) this probability is indistinguishable from zero.

1.1 Energy and the direction of spontaneous change

All of the changes described above take place *spontaneously*, meaning that

1. Once they are allowed to commence, they will proceed to the finish without any outside intervention.
2. It would be inconceivable that any of these changes could occur in the reverse direction (that is, be undone) without changing the conditions or actively disturbing the system in some way.

What determines the *direction* in which spontaneous change will occur? It is clearly not a fall in the energy, since in most of the examples cited above the energy of the system did not change. Even in the case of the falling book, it which the potential energy of the system (the book) falls, energy is conserved overall; if there is no net loss of energy when these processes operate in the forward or natural direction, it would not require any expenditure of energy for them to operate in reverse. In other words, ***energy conservation, as embodied in the First Law of thermodynamics, does not govern the direction of natural processes***.

1.2 Direction through disorder

In our examination of the processes described above, we saw that although the total energy of the system and the surroundings (and thus, of the *world*) is unchanged, there is something about the world that *has* changed, and this is its degree of randomness.

After coins have been tossed or cards shuffled, the final state is invariably one of greater disorder. Similarly, the molecules of a gas can occupy a larger number of possible positions in space if the volume is larger, so the expansion of a gas is similarly accompanied by an increase in randomness.

A closer look at disorder

How can we express disorder quantitatively? From the example of the coins, you can probably see that simple statistics plays a role: the probability of obtaining three heads and seven tails after tossing ten coins is just the ratio of the number of ways that ten different coins can be arranged in this way, to the number of all possible arrangements of ten coins.

Using the language of molecular statistics, we say that a collection of coins in which a given fraction of its members are heads-up constitutes a *macroscopic state* of the system. Since we don’t care which coins are heads-up, there are clearly numerous configurations of the individual coins which can result in this “macrostate”. Each of these configurations specifies a *microscopic state* of the system.

The greater the number of microstates that correspond to a given macrostate, the greater the probability of that macrostate. To see what this means, study consider the possible outcomes of a toss of four coins.

macrostate	ways	probability	microscopic states
0 heads	1	1/16	TTTT
1 head	4	4/16 = 1/4	HTTT THTT TTHT TTTH
2 heads	6	6/16 = 3/8	HHTT HTHT HTTH THHT TTHH THTH
3 heads	4	4/16 = 1/4	HHHT HTHH HHTH THHH
4 heads	1	1/16	HHHH

Table 1: Macroscopic and microscopic states of a set of four coins.

A toss of four coins will yield one of the five outcomes (macrostates) listed in the leftmost column of the table. The second column gives the number of "ways"— that is, the number of head/tail configurations of the set of coins (the number of microstates)— that can result in the macrostate. The probability of a toss resulting in a particular macrostate is proportional to the number of microstates corresponding to the macrostate, and is equal to this number, divided by the total number of possible microstates (in this example, $2^4 = 16$). An important assumption here is that *all microstates are equally probable*; that is, the toss is a "fair" one in which the many factors that determine the trajectory of each coin operate in an entirely random way.

1.3 From coins to molecules: the spreading of energy

Disorder is more probable than order because there are so many more ways of achieving it. Thus coins and cards tend to assume random configurations when tossed or shuffled, and socks and books tend to become more scattered about a teenager's room during the course of daily living. But there are some important differences between these large-scale mechanical, or *macro* systems, and the collections of sub-microscopic particles that constitute the stuff of chemistry. In systems of chemical interest

1. **We are dealing with *huge numbers* of particles.**
   This is important because statistical predictions are always more accurate for larger samples. Thus although for the four tosses there is a good chance (62%) that the H/T ratio will fall outside the range of 0.45 - 0.55, this probability becomes almost zero for 1000 tosses. To express this in a different way, the chances that 1000 gas molecules moving about randomly in a container would at any instant be distributed in a sufficiently uniform manner to produce a detectable pressure difference between the two halves of a container will be extremely small. If we increase the number of molecules to a chemically significant number (around 10^{20}, say), then the same probability becomes indistinguishable from zero.
2. **Once the change begins, it proceeds spontaneously.**
   That is, no external agent (a tosser, shuffler, or teen-ager) is needed to keep the process going. As long as the temperature is high enough for sufficiently energetic collisions to occur between the reacting molecules in a gas, the reaction will proceed to completion on its own once the reactants have been brought together.
3. **Thermal energy is continually being exchanged between the particles of the system, and between the system and the surroundings.**
   Collisions between molecules result in exchanges of momentum (and thus of kinetic energy) amongst the particles of the system, and (through collisions with the walls of a container, for

example) with the surroundings.

4. **Thermal energy spreads rapidly and randomly throughout the various energetically accessible microstates of the system.**

The importance of these last two points is far greater than you might at first think, but to fully appreciate this, you must recall the various ways in which thermal energy is stored in molecules— hence the following brief review.

How thermal energy is stored in molecules

Thermal energy is kinetic energy, and thus relates to *motion* at the molecular scale. What kinds of molecular motions are possible? For monatomic molecules, there is only one: actual movement from one location to another, which we call *translation*.Since there are three directions in space, all molecules possess three modes of translational motion.

For polyatomic molecules, two additional kinds of motions are possible. One of these is *rotation*; a linear molecule such as CO_2 in which the atoms are all laid out along the x-axis can rotate along the y- and z-axes, while molecules having less symmetry can rotate about all three axes. Thus linear molecules possess two modes of rotational motion, while non-linear ones have three rotational modes.

Finally, molecules consisting of two or more atoms can undergo internal *vibrations*. For freely moving molecules in a gas, the number of vibrational modes or patterns depends on both the number of atoms and the shape of the molecule, and it increases rapidly as the molecule becomes more complicated.

Quantum states, microstates, and energy spreading

At the atomic and molecular level, all energy is *quantized*; each particle possesses discrete states of kinetic energy and is able to accept thermal energy only in packets whose values correspond to the energies of one or more of these states. Polyatomic molecules can store energy in rotational and vibrational motions, and all molecules (even monatomic ones) will possess tranlational kinetic energy (thermal energy) at all temperatures above absolute zero. The energy difference between adjacent translational states is so minute (roughly 10^{-30} J) that translational kinetic energy can be regarded as *continuous* (non-quantized) for most practical purposes.

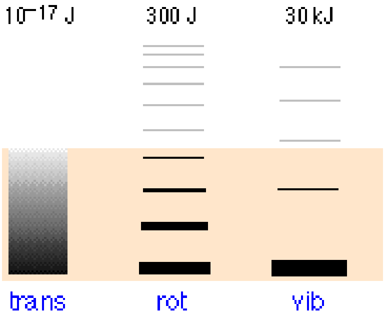
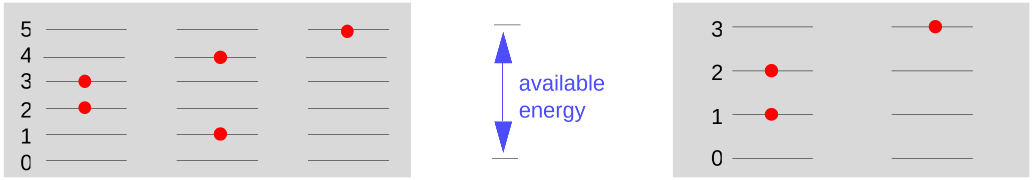


Fig. 1: Modes of thermal energy storage
The relative populations of the translational, rotational and vibrational microstates of a typical diatomic molecule are depicted by the thickness of the lines in this schematic (not-to-scale!) diagram. The colored shading indicates the total thermal energy available at a given temperature. The numbers at the top show order-of-magnitude spacings between adjacent levels. It is readily apparent that virtually all the thermal energy resides in translational states.

In any quantized system, there are various alternative ways in which energy can be distributed amongst the allowed states. Suppose, for example, that we have a system consisting of three molecules and enough kinetic energy to excite three energy states (see below). We can give all the kinetic energy to one molecule, leaving the others with none, we can give two units to one molecule and one unit to another, or we can share out the energy equally and give one unit to each molecule. All told, there are ten possible ways of distributing three units of energy among three identical molecules.



a) The quantity of energy indicated by the vertical arrow can be distributed in three ways in a collection of molecules whose allowed energy levels are spaced as shown here.

b) In molecules with more widely-spaced energy levels, there are fewer ways to store (and thus to "dilute") the same amount of energy.

Fig. 2: Microscopic energy states

The more closely spaced the quantized translational energy states of a molecule, the greater will be the number of ways (microstates) in which a given quantity of thermal energy can be distributed amongst them.

However, if the allowed energy levels of the molecule are closer together so that the same amount of energy can be accepted in smaller packets, then the number of possible distributions is greatly increased, and so is the number of energetically accessible microstates of the system. The spacing of these energy states becomes closer as the mass and number of bonds in the molecule increases, so we can generally say that the more complex the molecule, the greater the density of its energy states.

1.4 Energy-spreading changes the world

Energy is conserved; if you lift a book off the table, and let it fall, the total amount of energy in the world remains unchanged. All you have done is transferred it from the form in which it was stored within the glucose in your body to your muscles, and then to the book (that is, you did *work* on the book by moving it up against the earth's gravitational field). After the book has fallen, this same quantity of energy exists as thermal energy (heat) in the book and table top.

What *has* changed, however, is the *availability* of this energy. Once the energy has spread into the huge number of thermal microstates in the warmed objects, the probability of its spontaneously (that is, by chance) becoming un-dispersed is essentially zero. Thus although the energy is still "there", it is forever beyond utilization or recovery.

The profundity of this conclusion was recognized around 1900, when it was first described at the "heat death" of the world. This refers to the fact that every spontaneous process (essentially every change that occurs) is accompanied by the "dilution" of energy. The obvious implication is that all of the molecular-level kinetic energy will be spread out completely, and nothing more will ever change. Not a happy thought!

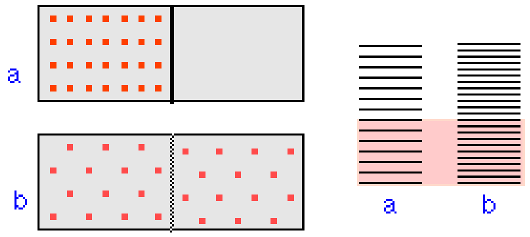
Why do gases tend to expand but never contract?

Everybody knows that a gas, if left to itself, will tend to expand so as to fill the volume within which it is confined completely and uniformly. What "drives" this expansion? At the simplest level it is clear that with more space available, random motions of the individual molecules will inevitably disperse them throughout the space. But as we mentioned on page 6, the allowed energy states that molecules can occupy are spaced more closely in a larger volume than in a smaller one[1]. The larger the volume available to the gas, the greater the number of microstates its thermal energy can occupy. Since all such states within the thermally accessible range of energies are equally probable, the expansion of the gas can viewed as a consequence of the tendency of *energy* to be spread and shared as widely as possible. Once this has happened, the probability that this sharing of energy will reverse itself (that is, that the gas will spontaneously contract) is so minute as to be unthinkable.

> The same can in fact be said for even other highly probable distributions, such as having 49.999% of the molecules in the left half of the container and 50.001% in the right half. Even though the number of possible configurations that would yield this distribution of molecules is uncountably great, it is essentially negligible compared to the number that would correspond to an exact 50-percent distribution.

Fig. 3: Expansion of a gas

The illustration at the far right represents the allowed thermal energy states of an ideal gas. The larger the volume in which the gas is enclosed, the more closely-spaced are the microstates. The tendency of thermal energy to spread over as many states as are accessible can be considered the thermodynamic “driving force” for spontaneous expansion.

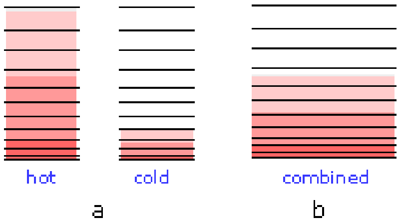


How energy spreading and sharing is related to heat and temperature

Just as gases spontaneously change their volumes from “smaller-to-larger”, the flow of heat from a warmer body to a cooler always operates in the direction “warmer-to-cooler” because this allows thermal energy to occupy a larger number of energy microstates as new ones are made available by bringing the cooler body into contact with the warmer one; in effect, the thermal energy becomes more “diluted”.

Fig. 4: Heat flow end energy spreading

(a) Schematic depiction of the thermal energy states in two separated identical bodies at different temperatures (indicated by shading.)
(b) When the bodies are brought into thermal contact, thermal energy flows from the higher occupied levels in the warmer object into the unoccupied levels of the cooler one until equal numbers are occupied in both bodies, bringing them to the same temperature.



As you might expect, the increase in the amount of energy spreading and sharing is proportional to amount of heat transferred q, but there is one other factor involved, and that is the temperature at which the transfer occurs. When a quantity of heat q passes into a system at temperature T, the degree of dilution of the thermal energy is given by

$$q / T$$

To understand why we have to divide by the temperature, consider the effect of very large and very small values of T in the denominator. If the body receiving the heat is initially at a very low temperature, relatively few thermal energy states are occupied, so the amount of energy spreading can be very great. Conversely, if the temperature is initially large, more

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[1] This is a consequence of quantum theory, which holds that all energies, including translational kinetic energy, can have only certain discrete values. If you know about the “electron-in-a-box” model, the concept should be familiar to you.

thermal energy is already spread around within it, and absorption of the same amount of energy will have a relatively small effect on the degree of thermal disorder within the body.

Energy spreading and sharing in chemical reactions

When a chemical reaction takes place, two kinds of changes relating to thermal energy are involved:

1. The ways that thermal energy can be stored within the reactants will generally be different from those for the products. For example, in the reaction $H_2 \rightarrow 2\ H$, the reactant dihydrogen possesses vibrational and rotational energy states, while the atomic hydrogen in the product has translational states only— but the total number of translational states in two moles of H is twice as great as in one mole of H_2. Because of their extremely close spacing, translational states are the only ones that really count at ordinary temperatures, so we can say that thermal energy can become twice as diluted ("spread out") in the product than in the reactant. If this were the only factor to consider, then dissociation of dihydrogen would always be spontaneous and this molecule would not exist.
2. In order for this dissociation to occur, however, a quantity of thermal energy (heat) $q = \Delta U$ must be taken up from the surroundings in order to break the H–H bond. In other words, the *ground state* (the energy at which the manifold of energy states begins) is higher in H, as indicated by the vertical displacement of the right half in each of the four panels below.

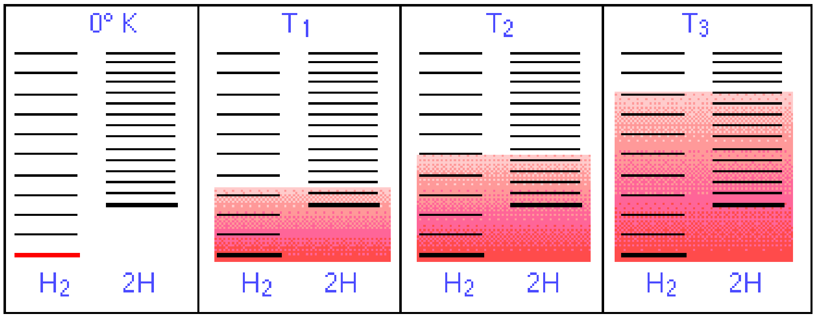

Fig. 5: Energy levels in H_2 and 2H

The number of thermally accessible microstates (indicated by the shading) increases with temperature, but because 2 moles of H possess twice as many translational states as one mole of H2, dissociation becomes increasingly favored at higher temperatures.

All molecules spontaneously absorb heat and dissociate at high temperatures.

The ability of energy to spread into the product molecules is constrained by the availability of sufficient thermal energy to produce these molecules. This is where the temperature comes in. At absolute zero the situation is very simple; no thermal energy is available to bring about dissociation, so the only component present will be dihydrogen.

- As the temperature increases, the number of populated energy states rises, as indicated by the shading in the diagram. At temperature T_1, the number of populated states of H_2 is greater than that of 2H, so some of the latter will be present in the equilibrium mixture, but only as the minority component.
- At some temperature T_2 the numbers of populated states in the two components of the reaction system will be identical, so the equilibrium mixture will contain H_2 and "2H" in equal amounts; that is, the mole ratio of H_2/H will be 1:2.
- As the temperature rises to T_3 and above, we see that the number of energy states that are thermally accessible in the product begins to exceed that for the reactant.

The result is exactly what the LeChâtelier Principle predicts: the equilibrium state for an endothermic reaction is shifted to the right at higher temperatures.

This is all very well for helping you understand the direct connection between energy spreading when a chemical reaction occurs, but it is of little help in achieving our goal of predicting the direction and extent of chemical change. For this, we need to incorporate the concept of energy spreading into thermodynamics.

2 • The entropy

The previous section explained how the tendency of thermal energy to disperse as widely as possible is what drives all spontaneous processes, including, of course chemical reactions. We now need to understand how the direction and extent of the spreading and sharing of energy can be related to measurable thermodynamic properties of substances— that is, of reactants and products. You will recall that when a quantity of heat q flows from a warmer body to a cooler one, permitting the available thermal energy to spread into and populate more microstates, that the ratio q/T measures the extent of this energy spreading. It turns out that we can generalize this to other processes as well, but there is a difficulty with using q because it is not a state function; that is, its value is dependent on the pathway or manner in which a process is carried out. This means, of course, that the quotient q/T cannot be a state function either, so we are unable to use it to get differences between reactants and products as we do with the other state functions. The way around this is to restrict our consideration to a special class of pathways that are designated *reversible*.

Reversible and irreversible changes.

A change is said to occur reversibly when it can be carried out in a series of infinitessimal steps, each one of which can be undone by making a similarly minute change to the conditions that bring the change about. For example, the reversible expansion of a gas can be achieved by reducing the external pressure in a series of infinitessimal steps; reversing any step will restore the system and the surroundings to their previous state. Similarly, heat can be transferred reversibly between two bodies by changing the temperature difference between them in infinitessimal steps each of which can be undone by reversing the temperature difference.

The most widely cited example of an *irreversible* change is the free expansion of a gas into a vacuum. Although the system can always be restored to its original state by recompressing the gas, doing so would require that the surroundings perform work on the gas. Since the gas does no work on the surroundings in a free expansion (the external pressure is zero, so $P\Delta V = 0$,) there will be a permanent change in the surroundings. Another example of irreversible change is the conversion of mechanical work into frictional heat; there is no way, by reversing the motion of a weight along a surface, that the heat released due to friction can be restored to the system

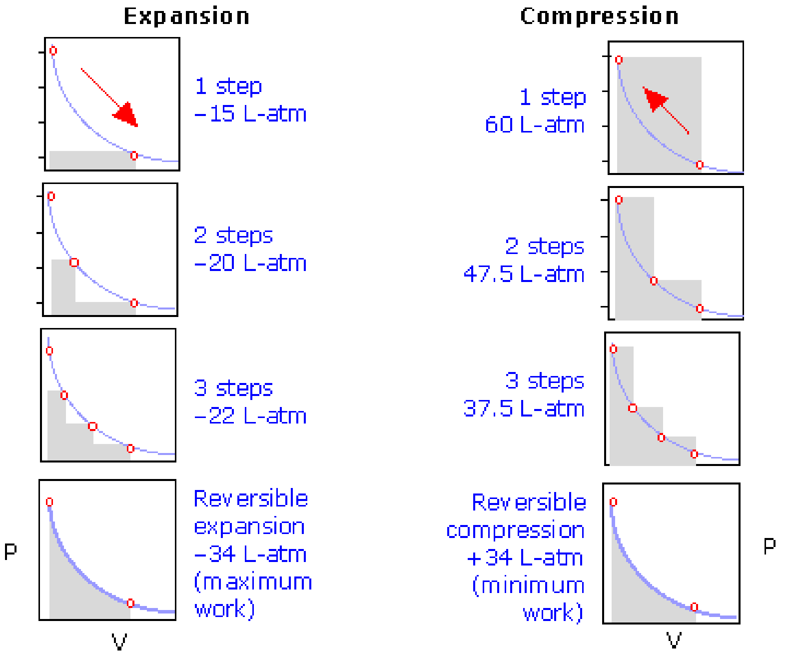

Fig. 6: Reversible and irreversible gas expansion and compression
As the number of steps increases, the processes become less irreversible; that is, the difference between the work done in expansion and that required to re-compress the gas diminishes. In the limit of an "infinite" number of steps (bottom), these work terms are identical, and both the system and surroundings (the "world") are unchanged by the expansion-compression cycle. In all other cases the system (the gas) is restored to its initial state, but the surroundings are forever changed.

In summary, then, a reversible change is one that is carried out in such as way that, when undone, both the system *and* surroundings (that is, the *world*) remain unchanged.

Reversible = impossible: so why bother? It should go without saying, of course, that any process that proceeds in infinitessimal steps would take infinitely long to occur, so thermodynamic reversibility is an idealization that is never achieved in real processes, except when the system is already at equilibrium, in which case no change will occur anyway! So why is the concept of a reversible process so important?

The answer can be seen by recalling that the change in the internal energy that characterizes any process can be distributed in an infinity of ways between heat flow across the boundaries of the system and work done on or by the system, as expressed by the First Law $\Delta U = q + w$. Each combination of q and w represents a different *pathway* between the initial and final states. It can be shown that as a process such as the expansion of a gas is carried out in successively longer series of smaller steps, the absolute value of q approaches a minimum, and that of w approaches a maximum that is characteristic of the particular process. **Thus when a process is carried out reversibly, the w -term in the First Law expression has its greatest possible value, and the q -term is at its smallest. These special quantities w_{max} and q_{min} (which we denote as q_{rev} and pronounce "q reversible") have unique values for any given process and are therefore state functions.**

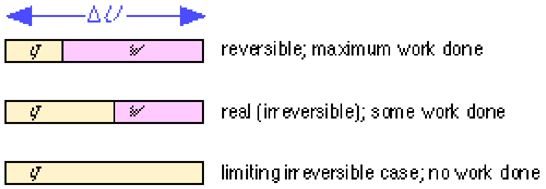

Fig. 7: work and reversibility
Note that the reversible condition implies w_{max} and q_{min}. The impossibility of extracting *all* of the internal energy as work is essentially a statement of the Second Law.

Since q_{rev} is a state function, so is q_{rev}/T. This quotient is one of the most important quantities in thermodynamics, because it expresses the change in energy spreading and sharing that accompanies a process. Note carefully that this change is always related to the limiting (reversible) value even when the process is carried out irreversibly and the actual value of q/T is different. Being a state function, q_{rev}/T. deserves a name and symbol of its own; it is called the *entropy*, designated by S. Since q_{rev}/T describes a *change* in state, we write the definition

$$\Delta S = q_{rev}/T \tag{6}$$

…but if no real process can take place reversibly, what use is an expression involving qrev?

This is a rather fine point that you should understand: although transfer of heat between the system and surroundings is impossible to achieve in a truly reversible manner, this idealized pathway is only crucial for the *definition* of ΔS; by virtue of its being a state function, the same value of ΔS will apply when the system undergoes the same net change via *any* pathway. For example, the entropy change a gas undergoes when its volume is doubled at constant temperature will be the same regardless of whether the expansion is carried out in 1000 tiny steps (as reversible as patience is likely to allow) or by a single-step (as irreversible a pathway as you can get!) expansion into a vacuum.

2.1 The physical meaning of entropy

Entropy is a measure of the degree of spreading and sharing of thermal energy within a system.

This “spreading and sharing” can be spreading of the thermal energy in *space* or its sharing amongst *previously inaccessible microstates* of the system. The following table shows how this concept applies to a number of common processes.

system and process	source of entropy increase of system
A deck of cards is shuffled, or 100 coins, initially heads up, are randomly tossed.	**This has nothing to do with entropy** because macro objects are unable to exchange thermal energy with the surroundings within the time scale of the process.
Two identical blocks of copper, one at 20°C and the other at 40°C, are placed in contact.	The cooler block contains more unoccupied microstates, so heat flows from the warmer block until equal numbers of microstates are populated in the two blocks.
A gas expands isothermally to twice its initial volume.	The existing thermal energy in the gas spreads into a larger volume of space, creating huge numbers of new isoenergetic microstates.
1 mole of water is heated by 1C°.	The increased thermal energy makes additional microstates accessible. (The increase is by a factor of about $10^{20,000,000,000,000,\ 000,000,000}$.)
Equal volumes of two gases are allowed to mix.	The effect is the same as allowing each gas to expand to twice its volume; the thermal energy in each is now spread over a larger volume.
One mole of dihydrogen, H_2, is placed in a container and heated to 3000K.	Some of the H_2 dissociates to H because at this temperature there are more thermally accessible microstates in the 2 moles of H. (See the column labeled T_4 in Table 5 on page 9.)

system and process	source of entropy increase of system
The above reaction mixture is cooled to 300K.	The composition shifts back to virtually all H_2 because this molecule contains more thermally accessible microstates at low temperatures. (Column T_1 in Table 5.)

Entropy is an *extensive* quantity; that is, it is proportional to the quantity of matter in a system; thus 100 g of metallic copper has twice the entropy of 50 g at the same temperature. This makes sense because the larger piece of copper contains twice as many quantized states able to contain the thermal energy.

Entropy and disorder

Entropy is still described, particularly in older textbooks, as a measure of *disorder*. In a narrow technical sense this is correct, since the spreading and sharing of thermal energy does have the effect of randomizing the disposition of thermal energy within a system. But to simply equate entropy with "disorder" without further qualification is extremely misleading because these qualifications— that it relates only to the ordering of thermal energy and only at the molecular scale— are too easily forgotten. And once this happens, one is easily led to any number of false predictions. It is far better to avoid the term "disorder" altogether in discussing entropy.[1]

As was explained on page 6, the distribution of thermal energy in a system depends on the number of quantized microstates that are accessible at a particular temperature; the more of these there are, the greater the entropy of the system. This is the basis of an alternative definition of entropy

$$S = k \ln \Omega \qquad (8)$$

in which k is the Boltzmann constant (the gas constant per molecule, 1.38×10^{-23} J K^{-1}) and Ω (omega) is the number of microstates the correspond to a given macrostate of the system. The quantity Ω is an unimaginably large number, typically around

$$10^{10^{24}}$$

for one mole. By comparison, the number of atoms in the earth is about 10^{50}.

> The reason S depends on the *logarithm* of Ω is easy to understand. Suppose we have two systems (containers of gas, say) with S_1, Ω_1 and S_2, Ω_2. If we now redefine this as a single system (without actually mixing the two gases), then the entropy of the new system will be $S = S_1 + S_2$ but the number of microstates will be the product $\Omega_1\Omega_2$ because for each state of system 1, system 2 can be in any of Ω_2 states. Because $\ln(\Omega_1\Omega_2) = \ln \Omega_1 + \ln \Omega_2$, the additivity of the entropy is preserved.

2.2 Absolute entropies

Energy values, as you know, are all relative, and must be defined on a scale that is completely arbitrary; there is no such thing as the absolute energy of a substance, so we can arbitrarily define the enthalpy or internal energy of an element in its most stable form at 298 and 1 atm pressure as zero.

The same is not true of the entropy; since entropy is a measure of the "dilution" of thermal energy, it follows that the less thermal energy available to spread through a system (that is, the lower the temperature), the smaller will be its entropy. In other words, as the absolute

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[1] See *Entropy is simple, qualitatively.* Frank Lambert, *J. Chem. Education* 79(10) 2002: 1241-46.

temperature of a substance approaches zero, so does its entropy.

This principle is the basis of the *Third law of thermodynamics*, which states that the entropy of a perfectly-ordered solid at 0° K is zero.

The absolute entropy of a substance at any temperature above 0° K must be determined by calculating the increments of heat q required to bring the substance from 0° K to the temperature of interest, and then summing the ratios q/T. Two kinds of experimental measurements are needed:

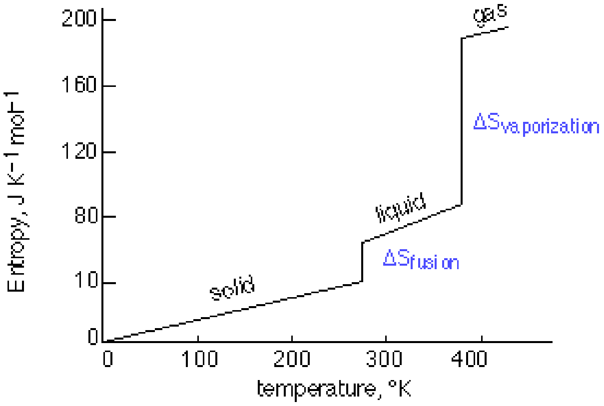
1. The enthalpies associated with any *phase changes* the substance may undergo within the temperature range of interest. Melting of a solid and vaporization of a liquid correspond to sizeable increases in the number of microstates available to accept thermal energy, so as these processes occur, energy will flow into a system, filling these new microstates to the extent required to maintain a constant temperature (the freezing or boiling point); these inflows of thermal energy correspond to the heats of fusion and vaporization. The entropy increase associated with melting, for example, is just $\Delta H_{fusion}/T_m$.
2. The *heat capacity* C_p of a phase expresses the quantity of heat required to change the temperature by a small amount ΔT, or more precisely, by an infinitessimal amount dT. Thus the entropy increase brought about by warming a substance over a range of temperatures that does not encompass a phase transition is given by the sum of the quantities $C_p dT/T$ for each increment of temperature dT. This is of course just the integral

$$S_{0°K \to T°K} = \int_{0°K}^{T°K} \frac{C_p}{T}\, dT \tag{9}$$

Because the heat capacity is itself slightly temperature dependent, the most precise determinations of absolute entropies require that the functional dependence of C_p on T be used in the above integral in place of a constant C_p. For rough determinations, one can simply plot the enthalpy increment $C_p \Delta T$ as a function of temperature and measure the area under the curve.

Fig. 8: How the entropy of water changes with temperature

As the temperature rises, more microstates become accessible, allowing thermal energy to be more widely dispersed. The vertical steps correspond to phase changes in which the number and spacing of microstates changes massively and discontinuously.



2.3 Standard entropies of substances

The standard entropy of a substance is its entropy at 1 atm pressure. The values found in tables are normally those for 298K, and are expressed in units of J K^{-1} mol^{-1}. The tables below shows some typical values for gaseous substances. Note especially how the values given in Table 2 illustrate these important points:

- Although the standard internal energies and enthalpies of these substances would be zero, the entropies are not. This is because there is no absolute scale of energy, so we conventionally set the “energies of formation” of elements in their standard states to zero. Entropy, however, measures not energy itself, but its dispersal amongst the various quantum states available to accept it, and these exist even in pure elements.

- It is apparent that entropies generally increase with molecular weight. For the noble gases, this is of course a direct reflection of the principle that translational quantum states are more closely packed in heavier molecules, allowing of them to be occupied.
- The entropies of diatomic and polyatomic molecules show the additional effects of rotational quantum levels.

He	126	H_2	131	CH_4	186
Ne	146	N_2	192	$H_2O(g)$	187
Ar	155	CO	197	CO_2	213
Kr	164	F_2	203	C_2H_6	229
Xe	170	O_2	205	$n\text{-}C_3H_8$	270
		Cl_2	223	$n\text{-}C_4H_{10}$	310

Table 2: Standard entropies of some gases, $JK^{-1} mol^{-1}$ 298K

The entropies of the solid elements are strongly influenced by the manner in which the atoms are bound to one another. The contrast between diamond and graphite is particularly striking; graphite, which is built up of loosely-bound stacks of hexagonal sheets, appears to be more than twice as good at soaking up thermal energy as diamond, in which the carbon atoms are tightly locked into a three-dimensional lattice, thus affording them less opportunity to vibrate around their equilibrium positions. Looking at all the examples in the above table, you will note a general inverse correlation between the *hardness* of a solid and its entropy. Thus sodium, which can be cut with a knife, has almost twice the entropy of iron; the much greater entropy of lead reflects both its high atomic weight and the relative softness of this metal. These trends are consistent with the oft-expressed principle that the more "disordered" a substance, the greater its entropy.

$C_{(diamond)}$	$C_{(graphite)}$	Fe	Na	Pb	$S_{(rhombic)}$	Si	W
2.5	5.7	27.1	51.0	64.9	32.0	18.9	33.5

Table 3: Entropies of some solid elements ($J K^{-1} mol^{-1}$) at 298K

Gases, which serve as efficient vehicles for spreading thermal energy over a large volume of space, have much higher entropies than condensed phases. Similarly, liquids, in which the molecular units can interact with each other in a multiplicity of ways (that is, more microstates) have higher entropies than solids. An especially interesting comparison can be made by extrapolating the entropy of ice as measured at 0°C to 25°C so that it can be compared to the values for liquid and gaseous water at the same temperature.

solid	liquid	gas
41	70	186

Table 4: Entropy of water at 298 K.

2.4 Effect of temperature, volume, and concentration on the entropy

As discussed previously, the entropy of a substance always increases with temperature. This is due mainly to the increased number of ways that the thermal energy can be distributed amongst the allowed energy levels as the latter become accessible. The rate of increase dS/dT is just the ratio of the heat capacity to the temperature C/T. When integrated over a range of temperatures, this yields (for an ideal gas confined to a fixed volume)

$$\Delta S = C_v \ln\left(\frac{T_2}{T_1}\right) \tag{10}$$

In general, a larger volume also leads to increased entropy. For an ideal gas that expands at a constant temperature (meaning that it absorbs heat from the surroundings to compensate for the work it does during the expansion), the increase in entropy is given by

$$\Delta S = R \ln\left(\frac{V_2}{V_1}\right) \tag{11}$$

Because the pressure of a gas is inversely proportional to its volume, we can easily alter the above relation to express the entropy change associated with a change in the pressure of a perfect gas:

$$\Delta S = R \ln\left(\frac{P_1}{P_2}\right) \tag{12}$$

The pressure of a gas is directly proportional to its concentration in moles per liter, so we can re-cast this equation in terms of concentrations:

$$\Delta S = R \ln\left(\frac{C_1}{C_2}\right) \tag{13}$$

Although Eqs. 10 - 12 apply only to perfect gases and cannot be used at all for liquids and solids, it turns out that in a dilute solution, the solute can often be treated as a gas dispersed in the volume of the solution, so Eq. 13 can actually give a fairly accurate value for the *entropy of dilution* of a solution. We will see later that this has important consequences in determining the equilibrium concentration of a homogeneous reaction mixture.

2.5 The second law of thermodynamics

You will recall that the first law of thermodynamics, expressed as $\Delta U = q + w$, is essentially a statement of the law of conservation of energy. The significance of this law is that it tells us that any proposed process that would violate this condition can be dismissed as impossible, without even inquiring further into the details of the process.

The second law of thermodynamics goes beyond this by saying, in effect, that the extent to which any natural process can occur is limited by the dilution of thermal energy (increase in entropy) that accompanies it, and once the change has occurred, it can never be un-done without spreading even more energy around. For example, a piece of ice placed in a warm room will quickly melt, spreading the heat of fusion it absorbs from the surroundings into the much larger number of energy microstates available in liquid water. At some later time we can always re-freeze the water by placing it in a refrigerator, but decreasing the entropy of the water by this means will increase the entropy of the surroundings by a greater amount as the heat removed by the refrigerator is dissipated into the surroundings.

There are several formal ways of stating the Second Law, but these will not mean much until we get to the section on heat engines. For the time being, it is best to just express the most important consequence of this law: *just because the energy is "there" does not mean it will be available to do anything useful.* For example, one might propose a scheme to propel a ship by means of a machine that takes in water, extracts part of its thermal energy which is used to rotate the propeller, and then tosses the resulting ice cubes overboard. Such a device would be formally called a *perpetual motion machine of the second kind* and would violate the Second Law. (A perpetual motion machine of the *first* kind is one that would violate the First Law.)

> The U.S. Patent Office frequently receives applications to patent devices whose operation would not be in accord with the Second Law; in the majority of cases the inventor appears to be unaware of this fact or, for that matter, of the Second Law. For some time, it has been the practice of the Patent Office to require that a working model of the device be made available to verify its operation.

2.6 The direction of spontaneous change

The entropy of the world only increases All natural processes that allow the free exchange of thermal energy amongst chemically-significant numbers of particles are accompanied by a spreading or "dilution" of energy that leaves the world forever changed. In other words, *all spontaneous change leads to an increase in the entropy of the world.* At first sight, this might seem to be inconsistent with our observations of very common instances in which there is a clear decrease in entropy, such as the freezing of a liquid, the formation of a precipitate, or the growth of an organism.

... but it's the entropy of the system *plus* surroundings that counts! It is important to understand that the criterion for spontaneous change is the entropy change of the system *and* the surroundings- that is, of the *"world"*:

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

The only way the entropy of the *surroundings* can be affected is by exchange of heat with the system; if the system absorbs a quantity of heat q, then $\Delta S_{surroundings} = (-q)/T$.

> Note that it does not matter whether the change in the system occurs reversibly or irreversibly; as mentioned previously, it is always possible to define an alternative (irreversible) pathway in which the amount of heat exchanged with the surroundings is the same as q_{rev}; because ΔS is a state function, the entropy change of the surroundings will have the same value as for the unrealizable reversible pathway.

If there is no flow of heat into or out of the surroundings, the entropy change of the system and that of the world are identical. Examples of such processes, which are always spontaneous, are the free expansion of an ideal gas into a vacuum, and the mixing of two ideal gases. In practice, almost all processes involving mixing and diffusion can be regarded as driven exclusively by the entropy increase of the system.

Most processes involving chemical and phase changes involve the exchange of heat with the surroundings, so their tendency to occur cannot always be predicted by focussing attention on the system alone. Further, owing to the $-q/T$ term in ΔS_{surr}, the spontaneity of all such processes will depend on the temperature, as we illustrated for the dissociation of H_2 in Fig. 5 on page 9

> As a quantitative example, let us consider the **freezing of water**. We know that liquid water will spontaneously change into ice when the temperature drops below 0°C at 1 atm pressure. Since the entropy of the solid is less than that of the liquid, we know the entropy of the water (the *system* here) will decrease on freezing. The amount of decrease is found by dividing the heat of fusion of ice by the temperature for the reversible pathway, which occurs at the normal freezing point:

$$\Delta S_{system} = \frac{-6000 \text{ J/mol}}{273 \text{ K}} = -21.978 \text{ J/K}-\text{mol}$$

> If the process is actually carried at 0°C, then the heat of fusion is transferred to the sur-

roundings at the same temperature, and the entropy of the surroundings increases by

$$\Delta S_{surroundings} = \frac{6000\text{J /mol}}{273\text{ K}} = 21.978\text{J / K}-\text{mol}$$

so that $\Delta S_{total} = 0$. Under these conditions the process can proceed in either direction (freezing or melting) without affecting the entropy of the world; this means that both ice and liquid water can be present simultaneously without any change occurring; the system is said to be *in equilibrium*.

Suppose now that the water is supercooled to –1°C before it freezes. The entropy change of the water still corresponds to the reversible value $q_{rev}/T = –6000\text{J}/273\text{K}$. The entropy change of the surroundings, however, is now given by

$$\Delta S_{surroundings} = \frac{6000\text{J /mol}}{272\text{ K}} = 22.059\text{J / K}-\text{mol}$$

The total entropy change is now

$\Delta S_{total} = (–21.978 + 22.059)\text{ J K}^{-1}\text{ mol}^{-1} = +0.081\text{ J K}^{-1}\text{ mol}^{-1}$

indicating that the process can now occur (“is spontaneous”) only in the one direction.

Why did we use 273 K when evaluating ΔS_{system} and 272 K for calculating $\Delta S_{surroundings}$? In the latter case it is possible to formulate a reversible pathway by which heat can be transferred to the surroundings at any temperature. ΔS_{system}, however, is a state function of water, and will vary with temperature only slightly.

$$\Delta S_{surroundings} = \frac{6000\text{J /mol}}{272\text{ K}} = 22.059\text{J / K}-\text{mol}$$

Note that in order to actually freeze water, it must be cooled to very slightly below its normal freezing point, a condition known as *supercooling*. Freezing of supercooled water is of course an irreversible process (once it starts, it cannot be stopped except by raising the temperature by a finite amount), and the positive value of ΔS_{total} tells us that this process will occur spontaneously at temperatures below 273K. Under these conditions, the process is driven by the entropy increase of the surroundings resulting from flow of the heat of fusion of water into the surroundings.

In any spontaneous macroscopic change, the entropy of the world increases. If a process is endothermic or exothermic, heat is exchanged with the surroundings, and we have to consider the entropy change of the surroundings as well as that of the system in order to predict what the direction of change will be. Failure to take the surroundings into account is what leads to the apparent paradox that freezing of a liquid, compression of a gas, and growth of an organism are all processes in which entropy decreases. It is only the entropy of the system that undergoes a decrease when these processes occur.

Does the entropy of the world ever *decrease*?

The principle that thermal energy (and the molecules containing it) tends to spread out is based on simple statistics. It must be remembered, however, that the laws of probability have meaningful application only to systems made up of large numbers of independent actors. If you trap a hundred flies in a bottle, they will generally distribute themselves more or less uniformly throughout the container; if there are only four flies, however, it is quite likely that all of them will occasionally be located in one particular half of the bottle.

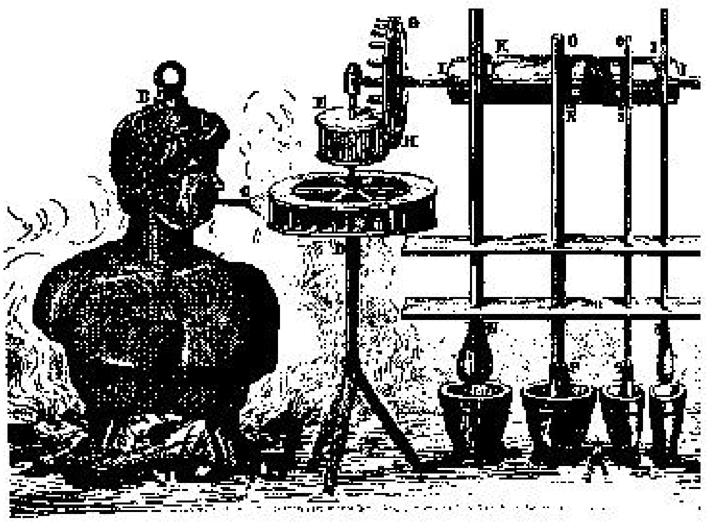
Why the sky is blue. Similarly, you can trust with complete certainty that the spontaneous movement of half the molecules of the air to one side of the room you now occupy will not occur, even though the molecules are moving randomly and independently. On the other hand, if we consider a box whose dimensions are only a few molecular diameters, then we would expect that the random and short-term displacement of the small number of particles it contains to one side of the box would occur quite frequently. This is, in fact, the cause of the blueness of the sky: random fluctuations in the air density over tiny volumes of space whose dimensions are comparable with the wavelength of light results in selective scattering of the shorter wavelengths, so that blue light is scattered out, leaving the red light for the enjoyment of sunset-watchers to the east.

Brownian motion. This refers to the irregular zig-zag-like movement of extremely small particles such as plant pollen when they are suspended in a drop of liquid. Any such particle is continually being buffeted by the thermal motions of the surrounding liquid molecules. If size of the particle is very large compared to that the liquid molecules, the forces that result from collisions of these molecules with the particle will cancel out and the particle remains undisturbed. If the particle is very small, however (perhaps only a thousand times larger than a molecule of the liquid), then the chances that it will undergo sufficiently more hits from one direction than from another during a brief interval of time become significant.

In these two examples, the entropy of the system decreases without any compensating flow of heat into the surroundings, leading to a net (but only temporary) decrease in the entropy of the world. This does not represent a failure of the Second Law, however, because no one has ever devised a way to extract useful work from these processes.

2.7 What is a heat engine, and why should you care?

Strictly speaking, the content of this section has to do more with mechanical engineering than with chemistry. Nevertheless, the principles developed below have such far-reaching consequences that they form an important part of the common intellectual background than everyone with training in the physical sciences is expected to possess. Further, the whole concept of entropy and the Second Law, which is central to chemistry, had its origin in the development and theoretical study of heat engines.



The Industrial Revolution of the 19th century was largely driven by the invention of the steam engine. The first major use of such engines was to pump water out of mines, whose flooding from natural seepage seriously limited the depths to which they could be driven, and thus the availability of the metal ores that were essential to the expansion of industrial activities. The steam engine is a type of *heat engine*, a device that converts heat, provided by burning a *fuel*, into mechanical *work*, typically delivered through the motion of a piston in opposition to an opposing force. An engine is therefore an energy conversion device in which, ideally, every joule of heat released by combustion of the fuel could be extracted as work at the output shaft; such an engine would operate at 100 percent efficiency. However, engineers of the time were perplexed to find that the efficiencies of steam engines were rather low (usually around 20%), with most of the heat being exhausted uselessly to the environment. Everyone understood that an efficiency exceeding 100% would be impossible (that would violate conservation of energy, and thus the First Law), but it was not clear why efficiencies could not rise significantly beyond the small values observed even as mechanical designs improved.

The answer was found by a young French engineer, Sadi Carnot, who in 1824 published an analysis of an idealized heat engine that is generally considered to be the foundation of the science of thermodynamics— notwithstanding the fact that Carnot still accepted the belief that heat is a fluid-like substance called “caloric”. We will not replicate his analysis here (this is normally done in more advanced courses in physical chemistry), but will simply state his conclusion in his own [translated] words:

> The production of motive power is then due in steam-engines not to an actual consumption of caloric, but to its transportation from a warm body to a cold body... the production of heat alone is not sufficient to give birth to the impelling power: it is necessary that there should also be cold; without it, the heat would be useless. the ultimate attainable efficiency of any heat engine will depend on the *temperatures* at which heat is supplied to and removed from it.

The fall of heat

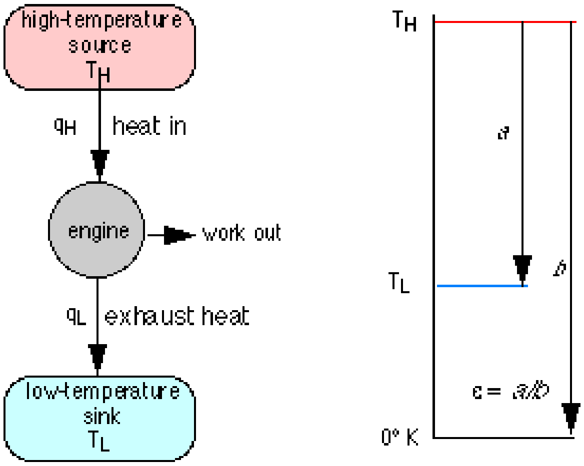


Fig. 9: Efficiency of a heat engine

Left: common schematic representation of a heat engine. *Right:* diagrammatic representation of Eq. 15; the efficiency is the ratio of the temperature intervals *a*:*b*.

The left side of the figure represents a generalized heat engine into which a quantity of heat q_H, extracted from a source or “reservoir” at temperature T_H is partly converted into work w. The remainder of the heat q_L is exhausted to a reservoir at a lower temperature T_L. In practice, T_H would be the temperature of the steam in a steam engine, or the temperature of the combustion mixture in an internal combustion or turbine engine. The low temperature reservoir is ordinarily that of the local environment. The efficiency ε (*epsilon*) of a heat engine is the fraction of the heat abstracted from the high temperature reservoir that can be converted into work:

$$\varepsilon = w/q_H \qquad (14)$$

Carnot’s crucial finding (for which we would certainly have deserved a Nobel prize if these had existed at the time) is that the efficiency is proportional to the ``distance" in temperature that the heat can “fall” as it passes through the engine:

$$\varepsilon = 1 - \frac{T_L}{T_H} \qquad (15)$$

This is illustrated graphically in the right half of the figure, in which the efficiency is simply the fraction of the “complete” fall (in temperature) to absolute zero (arrow *b*) that the heat undergoes in the engine (arrow *a*.) Clearly, the only way to attain 100% efficiency would be to set the temperature of the exhaust reservoir to 0°K, which would be impossible. For most terrestrial heat engines, T_L is just the temperature of the environment, normally around

300K, so the only practical way to improve the efficiency is to make T_H as high as possible. This is the reason that high pressure (superheated) steam is favored in commercial thermal power plants. The highest temperatures (and the greatest operating efficiencies) are obtained in gas turbine engines. However, as operating temperatures rise, the costs of dealing with higher steam pressures and the ability of materials such as turbine blades to withstand high temperatures become significant factors, placing an upper limit of around 600K on T_H, thus imposing a maximum of around 50 percent efficiency on thermal power generation.

> For nuclear plants, in which safety considerations require lower steam pressures, the efficiency is lower. One consequence of this is that a larger fraction of the heat is exhausted to the environment, which may result in greater harm to aquatic organisms when the cooling water is returned to a stream or estuary.

Problem Example 1:

Several proposals have been made to build a heat engine that makes use of the temperature differential between the surface waters of the ocean and cooler waters that, being more dense, reside at greater depth. If the exhaust temperature is 5°C, what is the maximum amount of work that could be extracted from 1000 L of surface water at 10°C? (The specific heat capacity of water is 4.184 J $g^{-1}K^{-1}$.)

> *Solution:* The amount of heat (q_H) that must be extracted to cool the water by 5 K is (4.184 J $g^{-1}K^{-1}$)(10^6 g)(5 K) = 2.09×10^7 J. The ideal thermodynamic efficiency is given by
>
> $$1 - \frac{278}{283} = 0.018$$
>
> The amount of work that could be done would be (.018)(2.09×10^7 J) = 3.7×10^6 J

Comment: It may be only 1.8% efficient, but it's free!

Heat pumps

If a heat engine is run "in reverse" by performing work on it (that is, changing "work out" to "work in" in Fig 9), it becomes a device for transporting heat against a thermal gradient. Refrigerators and air conditioners are she most commonly-encountered heat pumps. A heat pump can also be used to heat the interior of a building. In this application, the low temperature reservoir can be a heat exchanger buried in the earth or immersed in a well. In this application heat pumps are more efficient than furnaces or electric heating, but the capital cost is rather high.

The Second Law: what is means

It was the above observation by Carnot that eventually led to the formulation of the **Second Law of Thermodynamics** near the end of the 19th Century. One statement of this law (by Kelvin and Planck) is as follows:

> *It is impossible for a **cyclic process** connected to a reservoir **at one temperature** to produce a **positive amount of work** in the surroundings.*

To help you understand this statement and how it applies to heat engines, consider the schematic heat engine in the figure in which a *working fluid* (combustion gases or steam) expands against the restraining force of a weight that is mechanically linked to the piston. From a thermodynamic perspective, the working fluid is the system and everything else is surroundings. Expansion of the fluid occurs when it absorbs heat from the surroundings;

return of the system to its initial state requires that the surrounding do work on the system. Now re-read the above statement of the Second Law, paying special attention to the following italicized phrases:

- A **cyclic process** is one in which the system returns to its initial state. A simple steam engine undergoes an expansion step (the power stroke), followed by a compression (exhaust stroke) in which the piston, and thus the engine, returns to its initial state before the process repeats.
- "At **one temperature**" means that the expansion and compression steps operate *isothermally.* This means that $\Delta U = 0$; just enough heat is absorbed by the system to perform the work required to raise the weight, so for this step $q = -w$.
- "A **positive amount of work** in the surroundings" means that the engine does more work on the surroundings than the surroundings do on the engine. Without this condition the engine would be useless.

Note carefully that the Second Law applies only to a *cyclic* process— isothermal expansion of a gas against a non-zero pressure always does work on the surroundings, but an engine must repeat this process continually; to do so it must be returned to its initial state at the end of every cycle. When operating isothermally, the work $-w$ it does on the surroundings in the expansion step (power stroke) is nullified by the work $+w$ the surroundings must do on the system in order to complete the cycle.

The Second Law can also be stated in an alternative way:

> *It is impossible to construct a machine operating in cycles that will convert heat into work without producing any other changes.* (Max Planck)

Thus the Second Law does allow an engine to convert heat into work, but only if "other changes" (transfer of a portion of the heat directly to the surroundings) are allowed. And since heat can only flow spontaneously from a source at a higher temperature to a sink at a lower temperature, the impossibility of *isothermal* conversion of heat into work is implied.

> A device that accomplishes the isothermal conversion of heat into work (essentially Fig. 9 with the low-temperature sink missing) is known as a *perpetual motion machine of the second kind.* (A perpetual motion machine of the first kind violates the First Law.) The U.S. Patent and Trademark office is said to receive about 1500 applications for patents on such devices every year; many of the inventors have no idea that their proposals would violate the laws of thermodynamics.

3 • Free energy: the Gibbs function

In the previous section we saw that it is the *sum* of the entropy changes of the system and surroundings that determines whether a process will occur spontaneously. In chemical thermodynamics we prefer to focus our attention on the system rather than the surroundings, and would like to avoid having to calculate the entropy change of the surroundings explicitly. The key to doing this is to define a new state function known as the *Gibbs free energy*

$$G = H - TS \tag{16}$$

Since H, T and S are all state functions, G is a function of state. For a process that takes place reversibly, we can write

$$\Delta S_{total} = \frac{q_{surr}}{T} + \frac{q_{sys}}{T} \tag{17}$$

Multiplying through by $-T$, we obtain

$$T\Delta S_{total} = -q_{surr} - T\frac{q_{sys}}{T} = H_{sys} - T\Delta S_{sys}$$

which expresses the entropy change of the world in terms of thermodynamic properties of the system exclusively. If $-T\Delta S_{\text{total}}$ is denoted by ΔG, then we have

$$\Delta G = \Delta H - T\Delta S \tag{18}$$

which defines the *Gibbs free energy change* for the process.

From the foregoing, you should convince yourself that G (now often referred to as the *Gibbs function* rather than as free energy) will decrease in any process occurring at constant temperature and pressure which is accompanied by an overall increase in the entropy. (The constant temperature and pressure are a consequence of the temperature and the enthalpy appearing in the preceding equation.) Since most chemical and phase changes of interest to chemists take place under such conditions, the Gibbs function is the most useful of all the thermodynamic properties of a substance, and it is closely linked to the equilibrium constant.

Problem Example 2:

One mole of an ideal gas at 300 K is allowed to expand slowly and isothermally to twice its initial volume. Calculate q, w, $\Delta S°_{sys}$, $\Delta S°_{surr}$, and $\Delta G°$ for this process.

Solution: Assume that the process occurs slowly enough that the it can be considered to take place reversibly.

a) The work done in a reversible expansion is $w = \int_{V_1}^{V_2} P\,dV = nRT\int_{V_1}^{V_2}\frac{dV}{V} = nRT\ln\left(\frac{V_2}{V_1}\right)$
so w = (1 mol)(8.314 J mol^{-1} K^{-1})(300K)(ln 2) = 1730 J.

b) In order to maintain a constant temperature, an equivalent quantity of heat must be absorbed by the system: q = 1730 J.

c) The entropy change of the system is given by Eq. 11 on page 16:
$\Delta S°_{sys} = R \ln (V_2/V_1)$ = (8.314 J mol^{-1} K^{-1})(ln 2) = 5.8 J mol^{-1} K^{-1}

d) The entropy change of the surroundings is given by Eq. 6 on page 12:
$\Delta S°_{surr}$, = q/T = (–1730 J) / (300 K) = – 5.8 J mol^{-1} K^{-1}.

e) The free energy change is
$\Delta G° = \Delta H° - T\,\Delta S°_{sys}$ = 0 – (300 K)(5.8 J K^{-1}) = –1740 J

Comment: Recall that for the expansion of an ideal gas, $\Delta H° = 0$. Note also that the entropy changes in (*c*) and (*d*) cancel out, so that $\Delta S°_{world} = 0$. This would not be the case if the expansion were carried out irreversibly.

More about the Gibbs free energy

Its physical meaning: the maximum work. As we explained on page 11, the two quantities q_{rev} (q_{min}) and w_{max} associated with reversible processes are state functions. We gave the quotient q_{rev}/T a new name, the *entropy*. What we did not say is that w_{max} also has its own name, the *free energy.*

> The Gibbs free energy is the *maximum useful work* (excluding *PV* work associated with volume changes of the system) that a system can do on the surroundings when the process occurs reversibly at constant temperature and pressure. This work is done at the expense of the internal energy of the system, and whatever part of that is not extracted as work is exchanged with the surroundings as heat; this latter quantity will have the value $–T\Delta S$.

The Gibbs function: is it free? Is it energy? The appellation "free energy" for *G* has led to so much confusion that many scientists now refer to it simply as the *Gibbs functio*n. The "free" part of the name reflects the steam-engine origins of thermodynamics with its interest in converting heat into work: $\Delta G = w_{max}$, the maximum amount of energy which can be "freed" from the system to perform useful work. A much more serious difficulty, particularly in the context of chemistry, is that although *G* has the units of energy (joules, or in its intensive form, J mol^{-1}), it lacks one of the most important attributes of energy in that it is not conserved. Thus although the free energy always falls when a gas expands or a chemical reaction takes place, there need be no compensating increase in energy anywhere else. Referring to *G* as an energy also reinforces the false but widespread notion that a fall in energy must accompany any change. But if we accept that energy is conserved, it is apparent that the only necessary condition for change (whether the dropping of a weight, expansion of a gas, or a chemical reaction) is the *redistribution* of energy. The quantity $–\Delta G$ associated with a process represents the quantity of energy that is "shared and spread", which as we have already explained in the meaning of the increase in the entropy. The quotient $–\Delta G/T$ is in fact identical with ΔS_{total}, the entropy change of the world, whose increase is the primary criterion for any kind of change (pagepage 18.)

Who was Gibbs, anyway?

J. Willard Gibbs is considered the father of modern thermodynamics and the most brilliant American-born scientist of the 19th century. He did most of his work in obscurity, publishing his difficult-to-understand papers in the *Proceedings of the Connecticut Academy of Sciences*, a little-read journal that was unknown to most of the world.

3.1 The standard Gibbs free energy

In order to make use of free energies to predict chemical changes, we need to know the free energies of the individual components of the reaction. For this purpose we can combine the standard enthalpy of formation and the standard entropy of a substance according to Eq. 16 on page 23 to get its standard free energy of formation $\Delta G°_f$ for a given temperature. As with standard heats of formation, the standard free energy of a substance represents the free energy change associated with the formation of the substance from the elements in their most stable forms as they exist under the standard conditions of 1 atmosphere pressure and 298K.

Standard Gibbs free energies of formation are normally found directly from tables. Once the values for all the components of a reaction are known, the standard Gibbs free energy change for the reaction is found in the normal way.

The interpretation of $\Delta G°$ for a chemical change is very simple. For a reaction A → B, one of the following three situations will always apply:

$\Delta G° < 0$	process occurs to the right, producing more B
$\Delta G° > 0$	process occurs to the left, producing more A
$\Delta G° = 0$	no net change; A and B are in equilibrium

Table 5: $\Delta G°$ as a criterion for change

Some textbooks and teachers still say that the ΔG° and thus the criterion for chemical change depends on the two factors ΔH° and ΔS°, and they sometimes even refer to reactions in which one of these terms dominates as "energy driven" or "entropy driven" processes. This can be extremely misleading! As explained above, ***all*** **processes are entropy driven**; when –ΔH° exceeds the –TΔS° term, this merely means that the entropy change of the surroundings is the greater contributor to the entropy change of the system.

Why are chemical reactions affected by the temperature?

The $T\Delta S°$ term in the equation $\Delta G° = \Delta H° - T\Delta S°$ tells us that the temperature dependence of $\Delta G°$ depends almost entirely on the entropy change associated with the process. (We say *almost* because the values of $\Delta H°$ and $\Delta S°$ *are* themselves slightly temperature dependent; both gradually increase with temperature). In particular, notice that *the sign of the entropy change determines whether the reaction becomes more or less spontaneous as the temperature is raised*. Since the signs of both $\Delta H°$ and $\Delta S°$ can be positive or negative, we can identify four possibilities as outlined in the table on the next page.

Combining $\Delta H°$, T, and $\Delta S°$ according to Eq 18 in order to determine $\Delta G°$ and thus whether or not a reaction can occur is a convenient shortcut widely used in chemistry. Never forget, however, that this hides the true criterion for spontaneous change, namely the spreading and sharing of thermal energy amongst more microstates— that is, in the increase in the entropy of the world.

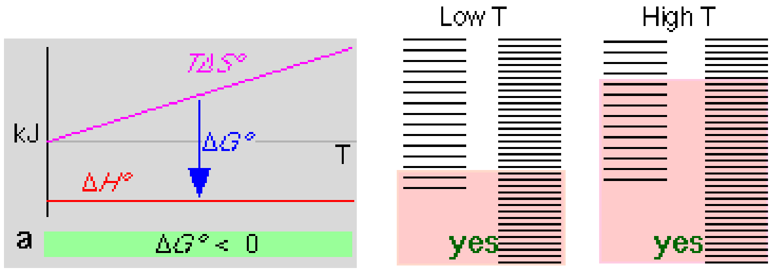
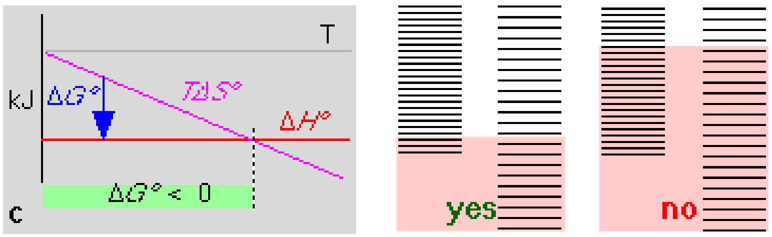
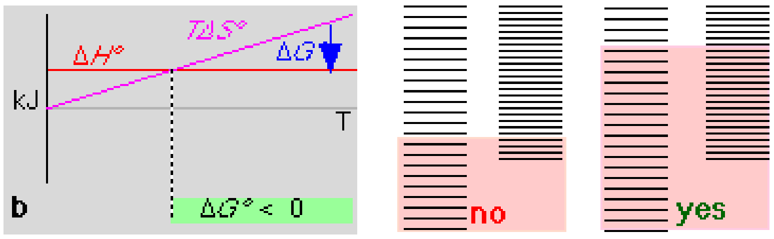
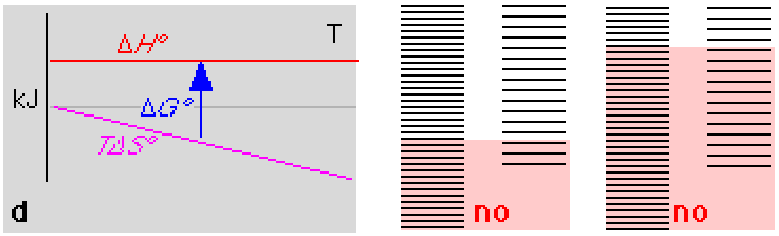
exothermic reaction, $\Delta S > 0$  	$C(graphite) + O_2(g) \rightarrow CO_2(g)$ $\Delta H° = -393$ kJ $\Delta S° = +2.9$ J K^{-1} $\Delta G° = -394$ kJ at 298 K This combustion reaction, like most such reactions, is spontaneous at all temperatures. The positive entropy change is due mainly to the greater mass of CO_2 compared to O_2.
exothermic reaction, $\Delta S < 0$  	$3\ H_2 + N_2 \rightarrow 2\ NH_3(g)$ $\Delta H° = -46.2$ kJ $\Delta S° = -389$ J K^{-1} $\Delta G° = -16.4$ kJ at 298 K The decrease in moles of gas in the Haber ammonia synthesis drives the entropy change negative. Thus higher T, which speeds up the reaction, also reduces its extent.
endothermic reaction, $\Delta S > 0$  	$N_2O_4(g) \rightarrow 2\ NO_2(g)$ $\Delta H° = -57.1$ kJ $\Delta S° = +176$ J K^{-1} $\Delta G° = +4.8$ kJ at 298 K Dissociation reactions are typically endothermic with positive entropy change. Ultimately, *all* molecules decompose to their atoms at sufficiently high temperatures.
endothermic reaction, $\Delta S < 0$  	$1/2\ N_2 + O_2 \rightarrow NO_2(g)$ $\Delta H° = 33.2$ kJ $\Delta S° = -249$ J K^{-1} $\Delta G° = +51.3$ kJ at 298 K Although NO_2 is thermodynamically unstable, the reverse of this reaction is kinetically hindered, so this oxide can exist indefinitely at ordinary temperatures.

Table 6: Effects of temperature on reaction spontaneity

The plots on the left show how $\Delta H°$ and $T\Delta S°$ combine according to Eq. 18 to determine the range of temperatures over which a reaction can take place spontaneously. Be sure you understand these graphs and can reproduce them for each of the four sign combinations of $\Delta H°$ and $\Delta S°$. These relations are of course governed by the relative entropies of the reactants and products, illustrated schematically by the spacing of the thermal energy states. The right column contains an example of each class of reaction.

Finding the equilibrium temperature

Notice that the reactions which are spontaneous only above or below a certain temperature have identical signs for $\Delta H°$ and $\Delta S°$. In these cases there will be a unique temperature at which $\Delta H° = T\Delta S°$ and thus $\Delta G° = 0$, corresponding to chemical equilibrium. This temperature is given by

$$T = \frac{\Delta H°}{\Delta S°} \qquad (20)$$

and corresponds to the point at which the lines representing $\Delta H°$ and $T\Delta S°$ cross in a plot of these two quantities as a function of the temperature.

> The values of both $\Delta H°$ and $\Delta S°$ are themselves somewhat temperature dependent, both increasing with the temperature. This means that substitution of 298 K-values of these quantities into Eq. 20 will give only an estimate of the equilibrium temperature if this differs greatly from 298 K.

Nevertheless, the general conclusions regarding the temperature dependence of reactions such as those shown in Table 6 are always correct, even if the equilibrium temperature cannot be predicted accurately.

Problem Example 1:

Estimate the normal boiling point of water from its 298-K heat and entropy of vaporization (44.03 kJ mol^{-1} and 118.9 J K^{-1} mol^{-1}, respectively.

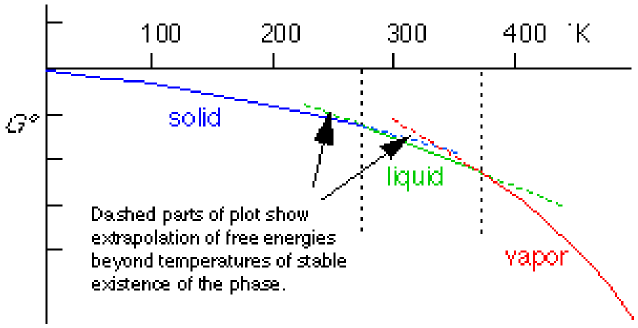
Solution: The temperature at which $\Delta G° = 0$ is given by

$$T = \frac{\Delta H°}{\Delta S°} = \frac{44030 \text{ J mol}^{-1}}{118.9 \text{ J K}^{-1}\text{ mol}^{-1}} = 370\text{K}$$

Comment: The low value (compared to the correct one of 373K) is due to failure to take into account the temperature dependence of $\Delta H°$ and $\Delta S°$.

Why do most substances have definite melting and boiling points?

As a crystalline substance is heated it eventually melts to a liquid, and finally vaporizes. The transitions between these phases occur abruptly and at definite temperatures; except at the melting and boiling temperatures, only one of these three phases will be stable— that is, its free energy will be lower than that of either of the other two phases. To understand the reason for this, recall that as the temperature rises, $T\Delta S°$ increases faster than $\Delta S°$, so the free energy (which of course depends on $-T\Delta S°$) always falls with temperature. Furthermore, the temperature dependence of G depends on the entropy (we won't try to prove this here), so G falls off fastest for the high-entropy gas phase, and for liquids faster than for solids. In Fig. 10 the free energies of each of the three phases of water are plotted as a function of temperature. At any given temperature, one of these phases will have a lower free energy than either of the others; this will of course be the stable phase at that temperature. The cross-over points where two phases have identical free energies are the temperatures at which both phases can coexist— in other words, the melting and boiling temperatures. At any other temperature, there is only a single stable phase.



Dashed parts of plot show extrapolation of free energies beyond temperatures of stable existence of the phase.

Fig. 10: Free energy of solid, liquid and gaseous water as a function of temperature.

These plots of $G°$ as a function of the temperature explain why substances have definite melting and boiling points. The stable phase is always the one that has the lowest Gibbs free energy. The temperatures at which one phase becomes more stable than the others are the melting and boiling points.

3.2 Free energy, concentrations and escaping tendency

The free energy of a pure liquid or solid at 1 atm pressure is just its molar free energy of formation $\Delta G°$ multiplied by the number of moles present. For gases and substances in solution, we have to take into account the *concentration* (which, in the case of gases, is normally expressed in terms of the pressure). We know that the lower the concentration, the greater the entropy (Eq. 13 on page 16), and thus the smaller the free energy.

The free energy of a gas: Standard states

The free energy of a gas depends on its pressure; the higher the pressure, the higher the free energy. Thus the free expansion of a gas, a spontaneous process, is accompanied by a fall in the free energy. Using Eq. 12 on page 16we can express the change in free energy when a gas undergoes a change in pressure from P_1 to P_2 as

$$\Delta G = \Delta H - T\Delta S = 0 - RT \ln\left(\frac{P_1}{P_2}\right) \qquad (21)$$

How can we evaluate the free energy of a specific sample of a gas at some arbitrary pressure? First, recall that the *standard* molar free energy $G°$ that you would look up in a table refers to a pressure of 1 atm. The free energy per mole of our sample is just the sum of this value and any change in free energy that would occur if the pressure were changed from 1 atm to the pressure of interest

$$G = G° + RT \ln\left(\frac{P_1}{1\ \text{atm}}\right) \qquad (22)$$

which we normally write in abbreviated form

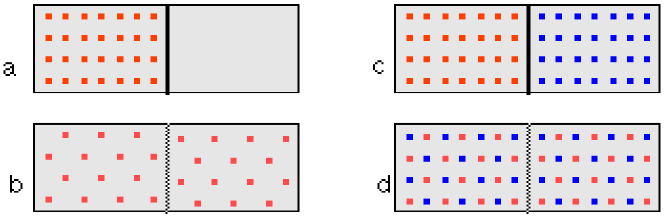
$$G = G° + RT \ln P \qquad (23)$$

Escaping tendency. The higher the pressure of a gas, the greater will be the tendency of its molecules to leave the confines of the container; we will call this the *escaping tendency.* The above equation tells us that the pressure of a gas is a directly observable measure of its free energy (G, not $G°$). Combining these two ideas, we can say that the free energy of a gas is also a measure of its escaping tendency. The latter term is not used in traditional thermodynamics because it is essentially synonymous with the free energy, but it is worth knowing because it helps us appreciate the physical significance of free energy in certain contexts.

Thermodynamics of mixing and dilution

All substances, given the opportunity to form a homogeneous mixture with other substances, will tend to become more dilute. This can be rationalized simply from elementary statistics;

there are more equally probable ways of arranging one hundred black marbles and one hundred white marbles, than two hundred marbles of a single color. For massive objects like marbles this has nothing to do with entropy, of course. But when we are dealing with huge numbers of molecules capable of storing, exchanging and spreading thermal energy, mixing and expansion are definitely entropy-driven processes. It can be argued, in fact, that mixing and expansion are really very similar; after all, when we mix two gases, each is expanding into the space formerly occupied exclusively by the other.



$\Delta S = \ln 2$; $\Delta G = -\ln 2$

$\Delta S = 2 \ln 2$; $\Delta G = -2 \ln 2$

Fig. 11: Entropy and free energy of mixing

The two ideal gases in *(c)* are separated by a barrier. When the barrier is removed *(d)*, the two gases spontaneously mix. ΔS and ΔG for this process are just twice what they would be for the expansion of a single gas *(a)* to twice its volume *(b)*.

In terms of the spreading of thermal energy the situation is particularly dramatic; the addition of even a *single molecule* of B to one mole of a gas A results in a huge increase in the number of energetically-identical (degenerate) microstates that correspond to the interchange of every molecule in the gas with the new molecule. When actual molar quantities of two gases mix, the number of new microstates created is beyond comprehension.

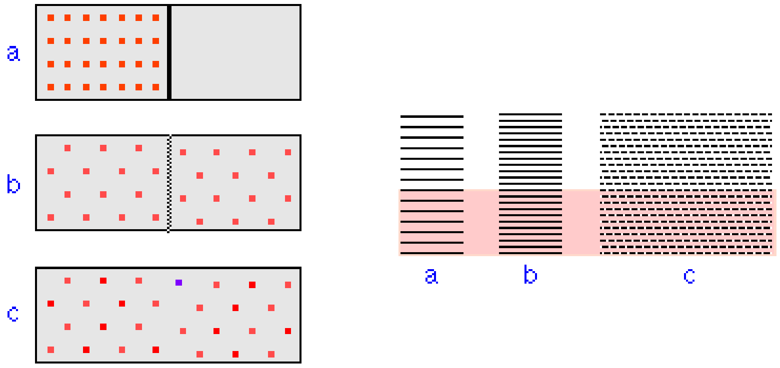


Fig. 12: Energy spreading in expansion and mixing

The tendency of a gas to expand is due to the more closely-spaced thermal microstates in the larger volume *(b)*. When one molecule of a different kind is introduced into the gas *(c)*, each microstate in *(b)* splits into a huge number of energetically-identical new states, denoted (inadequately) by the dashed lines in *(c)*.

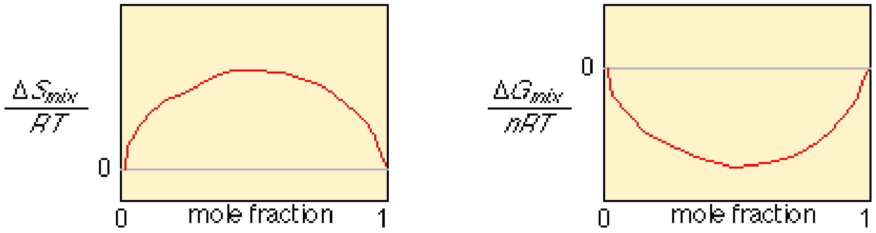


Fig. 13: The equilibrium state for mixing

If identical numbers of molecules of two gases are allowed to mix as in c-d in the Figure above, the equilibrium mole fraction of each gas will be 0.5.

The entropy increase that occurs when the concentration of a substance is reduced through dilution or mixing is given by Eq. 13 on page 16.

We can similarly define the Gibbs free energy of dilution or mixing by substituting this equation into the definition of $\Delta G°$:

$$\Delta G_{dil} = \Delta H_{dil} - RT \ln\left(\frac{C_1}{C_2}\right) \tag{24}$$

If the substance in question forms an *ideal solution* with the other components, then ΔH_{dil} is by definition zero, and we can write[1]

$$\Delta G_{dil} = RT \ln\left(\frac{C_2}{C_1}\right) \tag{25}$$

These relations tell us that the dilution of a substance from an initial concentration C_1 to a more dilute concentration C_2 is accompanied by a decrease in the free energy, and thus will occur spontaneously.

By the same token, the spontaneous “un-dilution” of a solution will not occur (we do not expect the tea to diffuse back into the tea bag!) However, un-dilution can be forced to occur if some means can be found to supply to the system an amount of energy (in the form of work) equal to ΔG_{dil}. An important practical example of this is the metabolic work performed by the kidney in concentrating substances from the blood for excretion in the urine.

To find the free energy of a solute at some arbitrary concentration, we proceed in very much the same way as we did for a gas: we take the sum of the standard free energy, and any change in the free energy that would accompany a change in concentration from the standard state to the actual state of the solution. Using Eq. 25 it is easy to derive an expression analogous to Eq. 23

$$G = G° + RT \ln C \tag{26}$$

which gives the free energy of a solute at some arbitrary concentration C in terms of its value $G°$ in its standard state.

> Although this expression has the same simple form as Eq. 23, its practical application is fraught with difficulties, the major one being that it doesn’t usually give values of G that are consistent with experiment, especially for solutes that are ionic or are slightly soluble. In such solutions, intermolecular interactions between solute molecules and between solute and solvent bring back the enthalpy term that we left out in deriving Eq. 23 (and thus Eq. 26). In addition, the structural organization of the solution becomes concentration dependent, so that the entropy depends on concentration in a more complicated way than is implied by Eq. 13 on page 16.

Activity and standard state of the solute

Instead of complicating $G°$ by trying to correct for all of these effects, chemists have chosen to retain its simple form by making a single small change in the form of 26:

$$G = G° + RT \ln a \tag{27}$$

This equation is guaranteed to work, because a, the *activity* of the solute, is its *thermodynamically effective concentration.* The relation between the activity and the concentration is given by

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[1] A more rigorous treatment of the thermodynamics of mixing requires that we take into account the dilution of the solvent as well as that of the solute, and yields a slightly more complicated formula containing mole fractions rather than concentrations.

$$a = \gamma C \qquad (28)$$

where γ (*gamma is* the *activity coefficient*. As the solution becomes more dilute, the activity coefficient approaches unity:

$$\lim_{C \to 0} \gamma = 1 \qquad (29)$$

The price we pay for the simplicity of 27 is that the relation between the concentration and the activity at higher concentrations can be quite complicated, and must be determined experimentally for every different solution.

> The question of what standard state we choose for the solute (that is, at what concentration is G° defined, and in what units is it expressed?) is one that you will wish you had never asked. We might be tempted to use a concentration of 1 molar, but a solution this concentrated would be subject to all kinds of intermolecular interaction effects, and would not make a very practical standard state. These effects could be eliminated by going to the opposite extreme of an "infinitely dilute" solution, but by Eq 26 this would imply a free energy of minus infinity for the solute, which would be awkward. Chemists have therefore agreed to define the standard state of a solute as one in which the concentration is 1 molar, but all solute-solute interactions are magically switched off, so that γ is effectively unity. Since this is impossible, no solution corresponding to this standard state can actually exist, but this turns out to be only a small drawback, and seems to be the best compromise between convenience, utility, and reality.

3.3 Free energy and equilibrium

Approaching equilibrium: the free energy can only fall

All natural processes tend to proceed in a direction that leads to the maximum possible spreading and sharing of thermal energy.

> This principle, which we developed in Section 1.4 (page 7), led to the definition of entropy in 2.1 (page 12) as a measure of the degree of energy dispersal. We saw that every process and change that happens in the world is accompanied by an increase in the entropy of the system-plus-surroundings. And in Section 3 (page 23) we introduced the concept of the Gibbs free energy (the Gibbs function) that expresses the tendency for change in terms of the properties of the system alone under conditions of constant temperature and pressure: ***chemical change will tend to occur in whatever direction leads to a decrease in the value of the Gibbs function.***

This means, of course, that if the total free energy G of a mixture of reactants and products goes through a minimum value as the composition changes, then all net change will cease—the reaction system will be in a state of *chemical equilibrium*.

To keep things as simple as possible, we will consider a homogeneous chemical reaction of the form

$$A + B \rightarrow C + D$$

in which all components are gases at the temperature of interest. If the standard free energies of the products is less than that of the reactants, $\Delta G°$ for the reaction will be negative and the reaction will proceed to the right. But how far? If the reactants are completely transformed into products, the equilibrium constant would be infinity. The equilibrium constants we actually observe all have finite values, implying that even if the products have a lower free energy than the reactants, some of the latter will always remain when the process comes to equilibrium.

In order to understand how equilibrium constants relate to $\Delta G°$ values, assume that all of the reactants are gases, so that the free energy of gas A, for example, is given at all times by

$$G_A = G_A^\circ + RT \ln P_A \qquad (30)$$

(This relation was developed on page 28.) The free energy change for the reaction is sum of the free energies of the products, minus that of the reactants:

$$\Delta G = G_\mathrm{C} + G_\mathrm{D} - G_\mathrm{A} - G_\mathrm{B} \qquad (31)$$

Using Eq 30 to expand each term on the right, we have

$$\Delta G = (G^\circ_\mathrm{C} + RT \ln P_\mathrm{C}) + (G^\circ_\mathrm{D} + RT \ln P_\mathrm{D}) - (G^\circ_\mathrm{B} + RT \ln P_B) - (G^\circ_\mathrm{A} + RT \ln P_\mathrm{A}) \qquad (32)$$

We can now express the $G°$ terms collectively as $\Delta G°$, and combine the logarithmic terms into a single fraction

$$\Delta G \;=\; \Delta G^\circ + RT \ln \frac{P_C P_D}{P_A P_B} \qquad (33)$$

which is more conveniently expressed in terms of the *reaction quotient* Q_P

$$\Delta G = \Delta G^\circ + RT \ln Q_P \qquad (34)$$

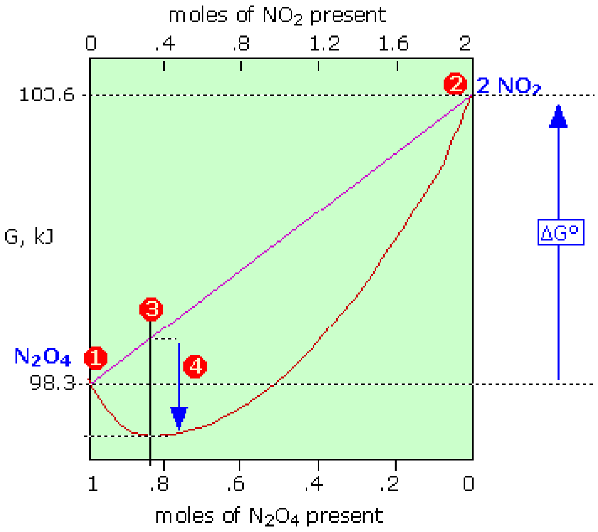
What this all means: when G is as small as it can get, the reaction is in equilibrium

Let's pause at this point to make sure you understand the significance of this equation.

First, recall that the free energy G is a quantity that becomes more negative during the course of any natural process. Thus as a chemical reaction takes place, G only falls and will never become more positive. Eventually a point is reached where any further transformation of reactants into products would cause G to increase. At this point G is at a minimum (see the plot below), and *no further change can take place; the reaction is at equilibrium.*

Fig. 14: Free energy changes in the dissociation of N_2O_4

The gas-phase reaction $N_2O_4 \rightarrow 2\,NO_2$ furnishes a simple example of the free energy relationships in a homogeneous reaction. The free energy of 1 mole of N_2O_4 **(1)** is smaller than that of 2 moles of NO_2 **(2)** by 5.3 kJ; thus $\Delta G° = +5.3$ kJ for the complete transformation of reactants into products. The staight diagonal line shows the free energy of all possible compositions if the two gases were prevented from mixing. The red curved line show the free energy of the actual reaction mixture. This passes through a minimum at **(3)** where 0.814 mol of N_2O_4 are in equilibrium with 0.372 mol of NO_2. The difference **(4)** corresponds to the free energy of mixing of reactants and products which always results in an equilibrium mixture whose free energy is lower than that of either pure reactants or pure products. Thus some amount of reaction will occur even if $\Delta G°$ for the process is positive.



What's the difference between ΔG and ΔG? It's very important to be aware of this distinction; that little ° symbol makes a world of difference! First, the standard free energy change $\Delta G°$ has a single value for a particular reaction at a given temperature and pressure; this is the difference ($\Sigma G°_{f,\ products} - \Sigma G°_{f,\ reactants}$) that you get from tables. It corresponds to the free energy change for *a process that never really happens*, the *complete* transformation of pure N_2O_4 into pure NO_2 at a constant pressure of 1 atm.

The other quantity ΔG, defined by Eq. 34, represents the total free energies of all substances in the reaction mixture at any particular system composition. As was explained on the previous page, total is smaller than the sum of the free energies of the same numbers of moles of the pure components by the free energy of mixing (remember that free energy always descreases as a substance becomes more dilute.)

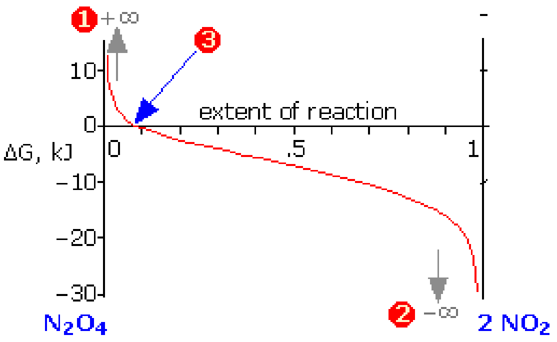


Fig. 15: How ΔG varies with composition
ΔG is the "distance" (in free energy) from the equilibrium state of a given reaction. Thus for a sample of pure N_2O_4 or NO_2 (as far from the equilibrium state as the system can be!), $Q = [NO_2]^2/[N_2O_4]$ is +∞ or 0, respectively, making the logarithm in Eq 34, and thus the value of ΔG, +∞ **(1)** or –∞ **(2)**. As the reaction proceeds in the appropriate direction ΔG approaches zero; once there **(3)**, the system is at its equilibrium composition and no further net change will occur.

Thus in contrast to $\Delta G°$ which is a constant for a given reaction, ΔG varies continuously as the composition changes, finally reaching zero at equilibrium.

> **The importance of mixing of reactants and products.** We are now in a position to answer the question posed earlier: if $\Delta G°$ for a reaction is negative, meaning that the free energies of the products are more negative than those of the reactants, why will some of the latter remain after equilibrium is reached? The answer is that no matter how low the free energy of the products, the free energy of the system can be reduced even more by allowing some of the products to be contaminated (i.e., diluted) by some reactants. Owing to the entropy associated with mixing of reactants and products, *no homogeneous reaction will be 100% complete.* An interesting corollary of this is that *any* reaction for which a balanced chemical equation can be written can in principle take place to some extent.

3.4 The equilibrium constant

Now let us return to Eq. 34 which we reproduce here:

$$\Delta G = \Delta G° + RT \ln Q_P$$

As the reaction approaches equilibrium, ΔG becomes less negative and finally reaches zero. At equilibrium $\Delta G = 0$ and $Q = K$, so we can write

$$\Delta G° + RT \ln K_P \qquad \textbf{(35)}$$

in which K_P the equilibrium constant expressed in pressure units, is the special value of Q that corresponds to the equilibrium composition.

This relation is one of the most important in chemistry because it relates the equilibrium composition of a chemical reaction system to measurable physical properties of the reactants and products. If you know the entropies and the enthalpies of formation of a set of substances, you can predict the equilibrium constant of any reaction involving these substances without the need to know anything about the mechanism of the reaction.

> Instead of writing Eq. 35 in terms of K_P, we can use any of the other forms of the equilibrium constant such as K_P, K_x(mole fractions), K_n (numbers of moles), etc. Remember, however, that for ionic solutions especially, only the K_a, in which activities are used, will be strictly valid.

It is often useful to solve Eq. 35 for the equilibrium constant, yielding

$$K = \exp\left(\frac{-\Delta G°}{RT}\right) \qquad \textbf{(36)}$$

Notice that an equilibrium constant of unity implies a standard free energy change of zero, and that positive values of $\Delta G°$ lead to values of K less than unity.

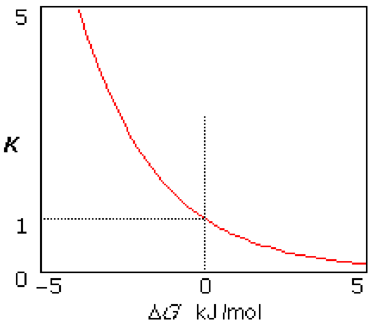
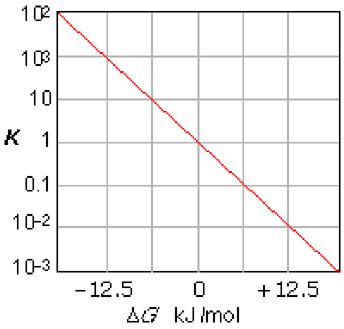


Fig. 16: The equilibrium constant and $\Delta G°$
These two plots show this relation linearly (left) and logarithmically (right). Notice that an equilibrium constant of unity implies a standard free energy change of zero, and that positive values of $\Delta G°$ lead to values of K less than unity.



3.5 Equilibrium and temperature

We have already discussed how changing the temperature will increase or decrease the tendency for a process to take place, depending on the sign of $\Delta S°$. This relation can be developed formally by differentiating the relation

$$\Delta G° = \Delta H° - T\Delta S° \qquad (37)$$

with respect to the temperature:

$$\frac{d(\Delta G°)}{dT} = -\Delta S° \qquad (38)$$

... so *the sign of the entropy change determines whether the reaction becomes more or less allowed as the temperature increases.*

We often want to know how a change in the temperature will affect the value of an equilibrium constant whose value is known at some fixed temperature. Suppose that the equilibrium constant has the value K_1 at temperature T_1 and we wish to estimate K_2 at temperature T_2. Expanding Eq. 35 in terms of $\Delta H°$ and $\Delta S°$, we obtain

$$-RT_1 \ln K_1 = \Delta H° - T_1 \Delta S°$$

and

$$-RT_2 \ln K_2 = \Delta H° - T_2 \Delta S°$$

Dividing both sides by RT and subtracting, we obtain

$$\ln K_1 - \ln K_2 = -\left(\frac{\Delta H^\circ}{RT_1} + \frac{\Delta H^\circ}{RT_2}\right) \tag{39}$$

Which is most conveniently expressed as the ratio

$$\ln \frac{K_1}{K_2} = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{40}$$

Do you remember the **Le Châtelier Principle**? Here is its theoretical foundation with respect to the effect of the temperature on equilibrium: if the reaction is exothermic ($\Delta H^\circ < 0$), then increasing temperature will make the second exponential term smaller and K will decrease- that is, the equilibrium will “shift to the left”. If $\Delta H^\circ > 0$ then increasing T will make the exponent less negative and K will increase.

(41)

This is an extremely important relationship, but not just because of its use in calculating the temperature dependence of an equilibrium constant. Even more important is its application in the “reverse” direction to experimentally determine ΔH° from two values of the equilibrium constant measured at different temperatures. Direct calorimetric determinations of heats of reaction are not easy to make; relatively few chemists have the equipment and experience required for this rather exacting task. Measurement of an equilibrium constant is generally much easier, and often well within the capabilities of anyone who has had an introductory Chemistry course. Once the value of ΔH° is determined it can be combined with the Gibbs free energy change (from a single observation of K, through Eq. 35) to allow ΔS° to be calculated through Eq. 37.

Problem Example 3:

The vapor pressure of solid ammonium perchlorate was found to be 0.026 torr at 520 and 2.32 torr at 620 K. Addition of NH_3 gas was observed to repress the vaporization, suggesting that the equilibrium under study is

$$NH_4ClO_4(s) \rightarrow NH_3(g) + HClO_4(g)$$

Use this information to calculate ΔH° and ΔS° for this process.

Solution. In problems of this kind the first step is usually to express the equilibrium constant in terms of the observed pressures. From the stoichiometry of this reaction it is apparent that $Kp = P(NH_3)P(HClO_4)$ and that each of these partial pressures is just half the vapor pressure of the solid P, so that Kp = (.026)/(760 × 2). This gives $K_1 = 2.92E{-}10$ and $K_2 = 2.33E{-}6$. Substituting these into Eq. 40 and solving for the enthalpy change $\Delta H^\circ = 241\ \text{kJ mol}^{-1}$. Next, we substitute the two equilibrium constants into Eq. 35 and obtain $\Delta G_1^\circ = 94.9\ \text{kJ mol}^{-1}$ and $\Delta G_2^\circ = 56.1\ \text{kJ mol}^{-1}$. The entropy change is estimated from Eq. 38, using the non-calculus form $\Delta(\Delta G^\circ)/\Delta T$ since the functional relation between ΔH° and the temperature is not known. This gives $\Delta S^\circ = +338\ \text{J mol}^{-1}\text{K}^{-1}$. Notice that the sign of this entropy change could have been anticipated by inspection of the reaction equation, since the volume increase due to the gaseous products will dominate other entropy differences.

Equilibrium without mixing: it's all or nothing

You should now understand that for *homogeneous reactions*— those that take place entirely in the gas phase or in solution, the equilibrium composition will never be 100% products, no matter how much lower their free energy relative to the reactants. As was summarized in Fig.14 (page 32), this is due to dilution of the products by the reactants. In *heterogeneous reactions* (those in which the components are not all in the same phase) this dilution, and the effects that flow from it, may not be possible.

A particularly simple but important type of a heterogeneous process is *phase change*. Consider, for example, an equilibrium mixture of ice and liquid water. The concentration of H_2O in each phase is dependent only on the density of the phase; there is no way that ice can be "diluted" with water, or vice versa. This means that at all temperatures other than the freezing point, the lowest free energy state will be that corresponding to pure ice or pure liquid. Only at the freezing point, where the free energies of water and ice are identical, can both phases coexist, and they may do so in any proportion.

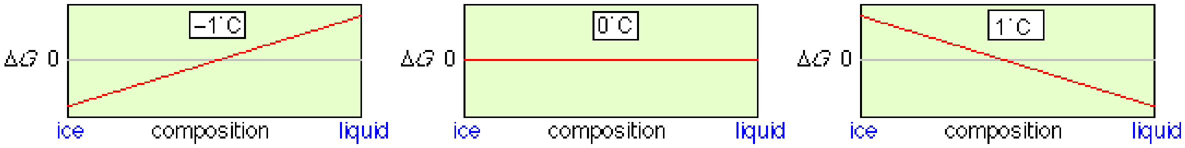


Fig. 17: Free energy of ice-water system

Only at 0°C can ice and liquid water coexist in any proportion. Note that in contrast to Fig. 14 (page 32), there is no free energy minimum at intermediate compositions.

3.6 Coupled reactions

Two reactions are said to be *coupled* when the product of one of them is the reactant in the other:

$$A \rightarrow B \qquad\qquad B \rightarrow C$$

If the standard free energy of the first reaction is positive but that of the second reaction is sufficiently negative, then $\Delta G°$ for the overall process will be negative and we say that the first reaction is “driven” by the second one. This, of course, is just another way of describing an effect that you already know as the *Le Châtelier principle*: the removal of substance B by the second reaction causes the equilibrium of the first to “shift to the right”. Similarly, the equilibrium constant of the overall reaction is the product of the equilibrium constants of the two steps.

(1) $Cu_2S(s) \rightarrow 2\ Cu(s) + S(s)$ $\Delta G° = +\ 86.2$ kJ $\Delta H° = +\ 76.3$ kJ
(2) $S(s) + O_2(g) \rightarrow SO_2(g)$ $\Delta G° = –300.1$ kJ $\Delta H° = +\ 296.8$ kJ

(3) $Cu_2S(s) \rightarrow 2\ Cu(s) + SO_2(g)$ $\Delta G° = –213.9$ kJ $\Delta H° = –\ 217.3$ kJ

In the above example, the thermal decomposition reaction **1** is needed to obtain metallic copper from one of its principal ores. However, it is both endothermic and has a positive free energy change, and thus will not proceed spontaneously at any temperature. By carrying it out in the presence of air, the sulfur produced in the first step is removed as rapidly as it is formed by oxidation in the highly spontaneous reaction **2**, which supplies the free energy required to drive the first step. The combined process (reaction **3**, the sum of **1** and **2**), known as “roasting”, is of considerable industrial importance and is one of a large class of reduction processes employed for winning metals from their ores described in more detail on page 39.

4 • Some other applications of entropy and free energy

4.1 Colligative properties of solutions

Vapor pressure lowering, boiling point elevation, freezing point depression and osmosis are well-known phenomena that occur when a non-volatile solute such as sugar or a salt is dissolved in a volatile solvent such as water. All these effects result from "dilution" of the *solvent* by the added solute, and because of this commonality they are referred to as *colligative properties* (Lat. *co ligare*, connected to.) The key role of the *solvent* concentration is obscured by the expressions used to calculate the magnitude of these effects, in which only the solute concentration appears[1]. The details of how to carry out these calculations and the many important applications of colligative properties are covered in the unit on solutions. Our purpose here is to offer a more complete explanation of why these phenomena occur.

> Basically, these all result from the effect of dilution (of the solvent) on its entropy, and thus in the increase in the density of microstates of the system in the solution compared to that in the pure liquid. These microstates are depicted schematically in the upper part of Fig. 18. Equilibrium between two phases (liquid-gas for boiling and solid-liquid for freezing) occurs when equal numbers of microstates are occupied in each phase. The temperatures at which this occurs are depicted by the shading. (See Section 1.4 on page 7 for a more complete explanation of this type of diagram.)

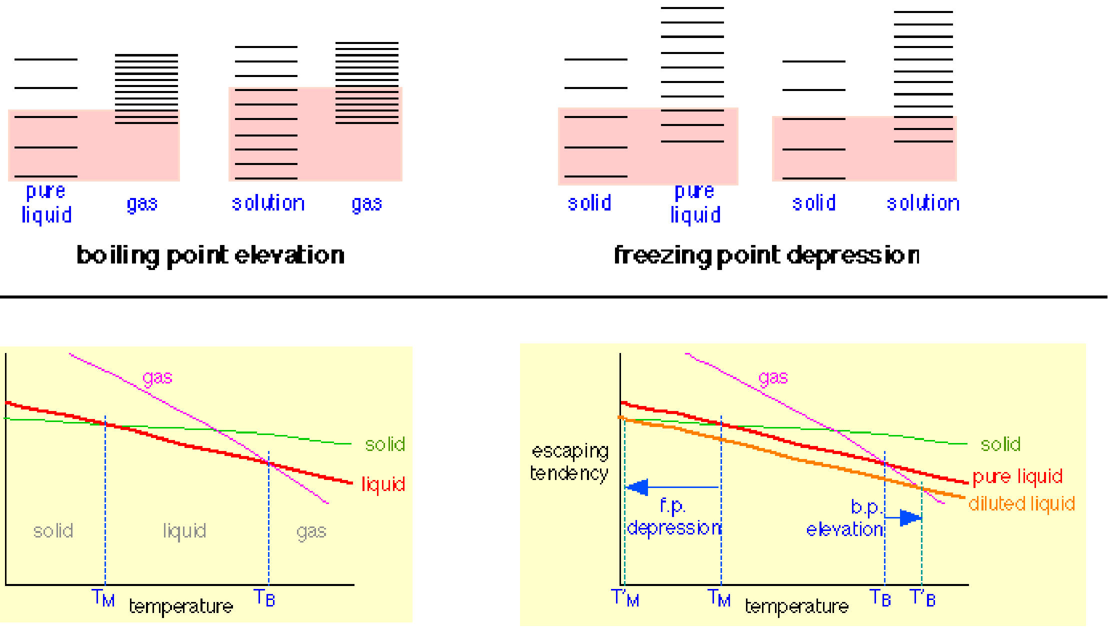


Fig. 18: Boiling point elevation and freezing point depression

Top: Explanation in terms of microstates. The vertical offset between the energy levels for the two phases corresponds to the heat of fusion or vaporization. Recall that the higher the entropy of a phase, the more closely spaced are its energy states.

Below: normal graphical explanation in terms of free energies. See also Fig. 10 on page 28.)

The bottom part of the Figure shows the same effects, this time in terms of plots of $-T\Delta S°$ for each phase in terms of the temperature.

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[1] The formulas normally used to calculate boiling point elevation, freezing point depressions and particularly osmotic pressure are "approximations to approximations" and yield reliable results only at very low solute concentrations.

Effects of pressure on the entropy

When a liquid is subjected to hydrostatic pressure— for example, by an inert, non-dissolving gas that occupies the vapor space above the surface, the vapor pressure of the liquid is raised. The pressure acts to compress the liquid very slightly, effectively narrowing the potential energy well in which the individual molecules reside and thus increasing their tendency to escape from the liquid phase. (Because liquids are not very compressible, the effect is quite small; a 100-atm applied pressure will raise the vapor pressure of water at 25°C by only about 2 torr.) In terms of the entropy, we can say that the applied pressure reduces the dimensions of the "box" within which the principal translational motions of the molecules are confined within the liquid, thus reducing the density of microstates in the liquid phase.

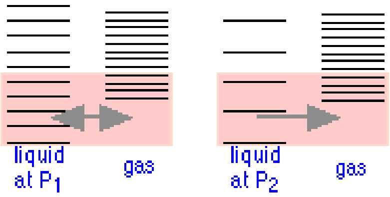
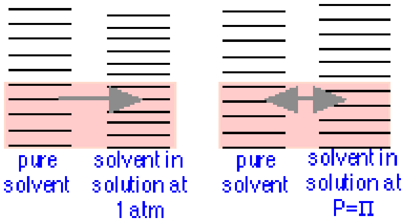


Fig. 19: Effect of pressure on vapor pressure of a liquid
If the hydrostatic pressure on a liquid is raised (from P1 to P2 in this example), the spacing between translational microstates is reduced, thus increasing the proportion of accessible microstates in the vapor phase.

This phenomenon can explain **osmotic pressure**. Osmotic pressure, students must be reminded, is *not* what drives osmosis, but is rather the hydrostatic pressure that must be applied to the more concentrated solution (more dilute solvent) in order to *stop* osmotic flow of solvent into the solution. The effect of this pressure Π is to slightly increase the spacing of solvent microstates on the high-pressure (dilute-solvent) side of the membrane to match that of the pure solvent, restoring osmotic equilibrium.

Fig. 20: Entropy and osmotic equilibrium
Osmotic flow occurs as long as there are more energetically accessible microstates in the solution than in the pure solvent. Increasing the hydrostatic pressure of the solution reduces this number; when the pressure reaches the osmotic pressure Π, the number of accessible microstates on each side is the same, and osmotic flow ceases.



4.2 Extraction of metals from their oxides

Since ancient times, the recovery of metals from their ores has been one of the most important applications of chemistry to civilization and culture. The oldest, and still the most common smelting process for oxide ores involves heating them in the presence of carbon. Originally, charcoal was used, but industrial-scale smelting uses coke, a crude form of carbon prepared by pyrolysis (heating) of coal.

The basic reactions are:

$$MO + C \rightarrow M + CO \qquad (i)$$
$$MO + 1/2\ O_2 \rightarrow M + 1/2\ CO_2 \qquad (ii)$$
$$MO + CO \rightarrow M + CO_2 \qquad (iii)$$

Each of these can be regarded as a pair of coupled reactions in which the metal M and the carbon are effectively competing for the oxygen atom. Using *(i)* as an example, we can write

$$MO \rightarrow M + 1/2\ O_2 \qquad (iv)$$

$C + 1/2\ O_2 \rightarrow CO$ *(v)*

At ordinary environmental temperatures, reaction *(iv)* is always spontaneous in the reverse direction (that is why ores form in the first place!), so $\Delta G°$ *(iv))* will be positive. $\Delta G°$*(v)* is always negative, but at low temperatures it will not be sufficiently negative to drive *(iv)*.

The smelting process depends on the different ways in which the free energies of reactions like *(iv)* and *(v)* vary with the temperature. This temperature dependence is almost entirely dominated by the $T\Delta S°$ term in the Gibbs function, and thus by the entropy change. The latter depends mainly on Δn_g, the change in the number of moles of gas in the reaction. Removal of oxygen from the ore is always accompanied by a large increase in volume, so ΔS for this step is always positive and the reaction becomes more spontaneous at higher temperatures. The temperature dependences of the reactions that take up oxygen vary, however:

reaction	Δn_g	$d(\Delta G°)/dT$
$C + 1/2\ O_2 \rightarrow CO$	0.5	< 0
$C + O_2 \rightarrow CO_2$	0	0
$CO + 1/2\ O_2 \rightarrow CO_2$	–0.5	> 0

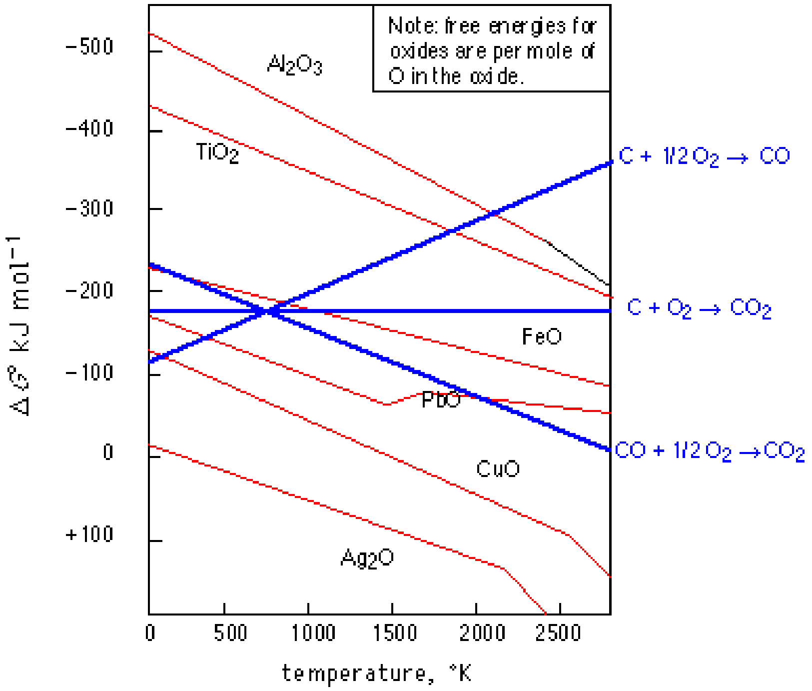


Fig. 21: Ellingham diagram

An ore can be reduced by carbon only if its Gibbs free energy of formation falls below that of one of the carbon reduction reactions. Practical refining temperatures are generally limited to about 1500°K.

A plot of the temperature dependences of the free energies of these reactions, superimposed on similar plots for the oxygen removal reactions *(iv)* is called an *Ellingham diagram*. In order for a given oxide MO to be smeltable, the temperature must be high enough that *(iv)* falls below that of at least one of the oxygen-consuming reactions. The slopes of the lines on this diagram are given by

$$\frac{d(\Delta G^\circ)}{dT} = -\Delta S^\circ$$

Examination of the Ellingham diagram shown above illustrates why the metals known to the ancients were mainly those such as copper and lead, which can be obtained by smelting at the relatively low temperatures that were obtainable by the methods available at the time in which a charcoal fire supplied both the heat and the carbon. Thus the bronze age preceded the iron age; the latter had to await the development of technology capable of producing higher temperatures, such as the blast furnace. Smelting of aluminum oxide by carbon requires too high temperatures to be practical; commercial production of aluminum is accomplished by electrolysis of the molten ore.

4.3 Bioenergetics

Many of the reactions that take place in living organisms require a source of free energy to drive them. The immediate source of this energy in heterotrophic organisms, which include animals, fungi, and most bacteria, is the sugar *glucose*. Oxidation of glucose to carbon dioxide and water is accompanied by a large negative free energy change.

$$C_6H_{12}O_6 + O_2 \rightarrow 6CO_2 + 6\,H_2O \qquad \Delta G^\circ = -\,2880 \text{ kJ mol}^{-1} \qquad (42)$$

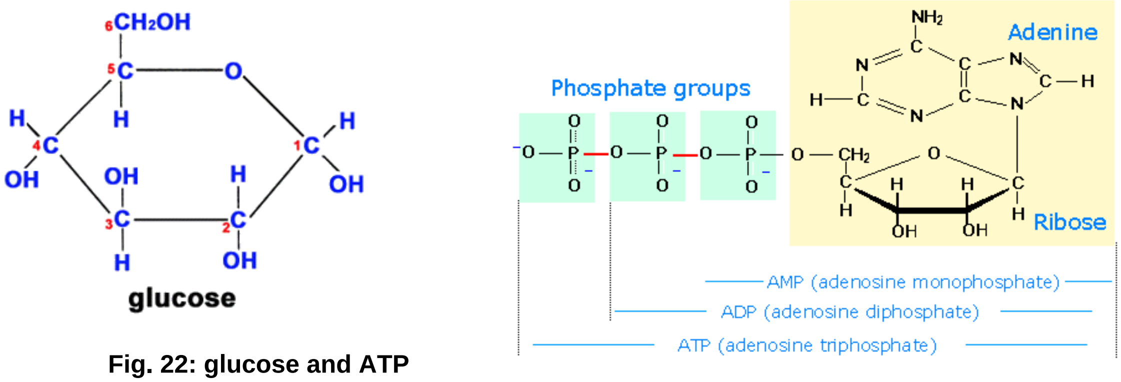


Fig. 22: glucose and ATP

Of course it would not do to simply “burn” the glucose in the normal way; the energy change would be wasted as heat, and rather too quickly for the well-being of the organism. Effective utilization of this free energy requires a means of capturing it from the glucose and then releasing it in small amounts when and where it is needed. This is accomplished by breaking down the glucose in a series of a dozen or more steps in which the energy liberated in each step is captured by an “energy carrier” molecule, of which the most important is adenosine diphosphate, known as ADP. At each step in the breakdown of glucose, an ADP molecule reacts with inorganic phosphate (denoted by P_i) and changes into ATP:

$$\text{ADP} + P_i \rightarrow \text{ATP} \qquad \Delta G^\circ = +30 \text{ kJ mol}^{-1}$$

The 30 kJ mol^{-1} of free energy stored in each ATP molecule is released when the molecule travels to a site where it is needed and loses one of its phosphate groups, yielding inorganic phosphate and ADP, which eventually finds its way back the site of glucose metabolism for recycling back into ATP. The complete breakdown of one molecule of glucose is coupled with the production of 38 molecules of ATP, according to the overall reaction

$$C_6H_{12}O_6 + 6\,O_2 + 38\,P_i + 38\,\text{ADP} \rightarrow 38\,\text{ATP} + 6CO_2 + 44\,H_2O$$

For each mole of glucose metabolized, 38 × (30 kJ) = 1140 kJ of free energy is captured as ATP, representing an energy efficiency of 1140/2880 = 0.4. That is, 40% of the free energy available from the oxidation of glucose is made available to drive other metabolic processes. The rest is liberated as heat.

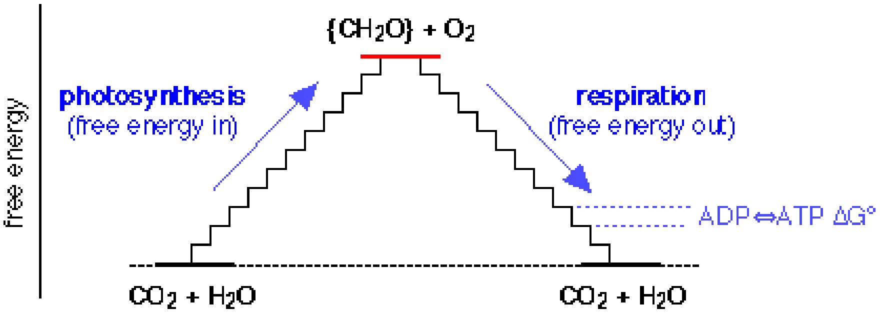


Fig. 23: The photosynthesis-respiration free energy cycle
(The zigzags represent the individual steps of energy capture by ADP and its delivery to metabolic processes by ATP.)

Where does the glucose come from? Animals obtain their glucose from their food, especially cellulose and starches that, like glucose, have the empirical formula $\{CH_2O\}$. Animals obtain this food by eating plants or other animals. Ultimately, all food comes from plants, most of which are able to make their own glucose from CO_2 and H_2O through the process of photosynthesis. This is just the reverse of Eq. 42 in which the free energy is supplied by the quanta of light absorbed by chlorophyll and other photosynthetic pigments.

This describes *aerobic respiration*, which evolved after the development of photosynthetic life on Earth began to raise the concentration of atmospheric oxygen. Oxygen is a poison to most life processes at the cellular level, and it is believed that aerobic respiration developed as a means to protect organisms from this peril. Those that did not adapt to this new environment have literally "gone underground" and constitute the more primitive anaerobic bacteria.

The function of oxygen in respiration is to serve as an acceptor of the electrons that glucose loses when it undergoes oxidation. Other electron acceptors can fulfill the same function when oxygen is not available, but none yields nearly as much free energy. For example, if oxygen cannot be supplied to mammalian muscle cells as rapidly as it is needed, they switch over to an anaerobic process yielding lactic acid instead of CO_2:

$$C_6H_{12}O_6 + 2\,ADP \rightarrow 2CH3CH(OH)COOH \qquad \Delta G° = -218 \text{ kJ mol}^{-1}$$

In this process, only (2 × 30 kJ) = 60 kJ of free energy is captured, so the efficiency is only 28% on the basis of this reaction, and it is even lower in relation to glucose. In "aerobic" exercising, one tries to maintain sufficient lung capacity and cardiac output to supply oxygen to muscle cells at a rate that promotes the aerobic pathway.

4.4 The fall of the electron.

Oxidation-reduction reactions proceed in a direction that allows the electron to “fall” (in free energy) from a “source” to a “sink”. Later on when you study electrochemistry you will see how this free energy can manifest itself as an electrical voltage and be extracted from the system as electrical work. In organisms, the free energy is captured in a series of coupled reactions as described above, and eventually made available for the various free energy-consuming processes associated with life processes.

The figure on the next page shows the various electron sources (foodstuffs) and sinks (oxidizing agents) on a vertical scale that illustrates the relative free energy of an electron in each sink. Notice that carbohydrate is at the top of this scale and dioxygen is at the bottom, indicating that O_2 is the best possible electron acceptor in terms of free energy yield.

Organisms that live in environments where oxygen is lacking, such as marshes, muddy soils, and the intestinal tracts of animals, must utilize other electron acceptors to extract free energy from carbohydrate. A wide variety of inorganic ions such as sulfate and nitrate, as well as other carbon compounds can serve as electron acceptors, yielding the gaseous products like H_2S, NH_3 and CH_4 which are commonly noticed in such locations. From the location of these acceptors on the scale, it is apparent that the amount of energy they can extract from a given quantity of carbohydrate is much less than for O_2. One reason that aerobic organisms have dominated the earth is believed to be the much greater energy-efficiency of oxygen as an electron acceptor.

What did organisms use for food before there was a widespread supply of carbohydrate in the world? Any of the electron sources near the upper left of the table can in theory serve this function, although at reduced energy efficiency. As a matter of fact, there are still a number of these autotrophic bacteria around whose “food” is CH_4, CH_3OH, $FeCO_3$, and even H_2!

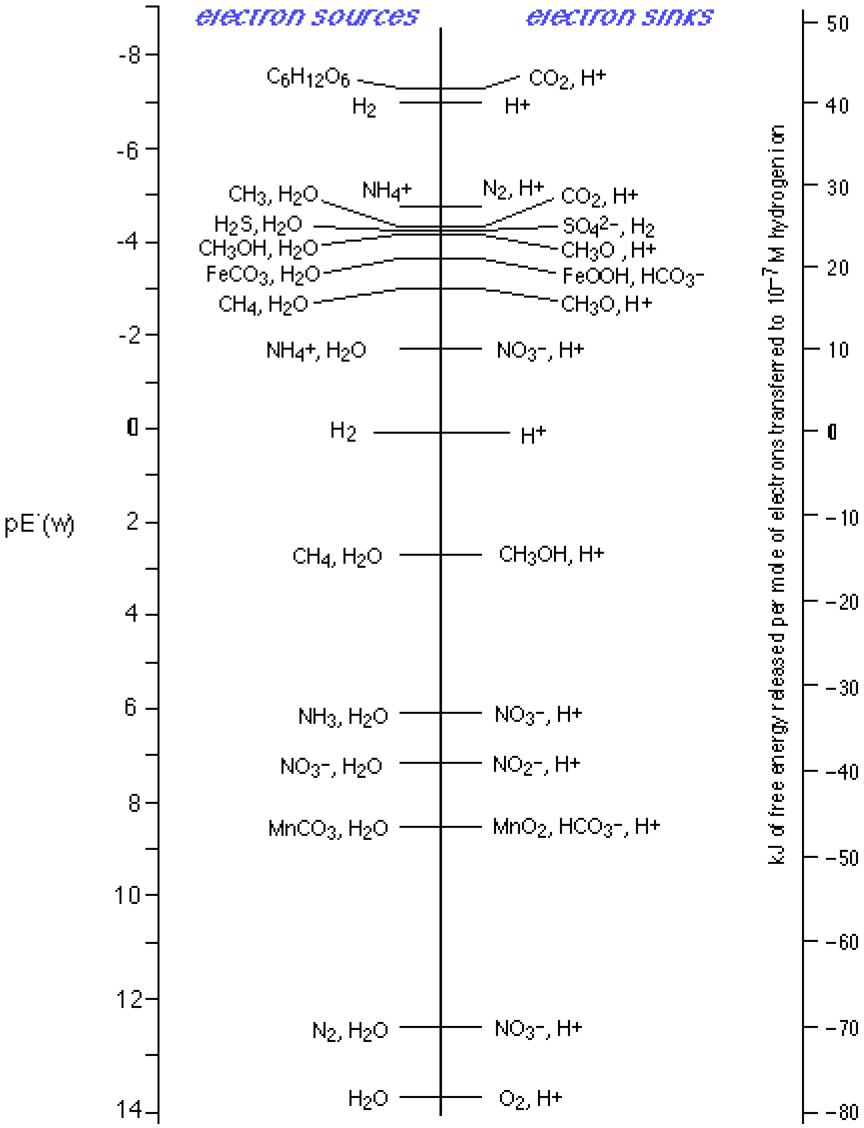


Fig. 24: Electron free energy levels in bioenergetics

4.5 The fall of the proton

According to the widely useful Brønsted-Lowry concept, an acid is a proton donor and a base is a proton acceptor. In 1953, Gurney showed how this idea could be made even more useful by placing acid-base conjugate pairs on a *proton-free energy scale.*

In this view, acids are proton sources and bases are proton sinks. Protons fall spontaneously from acids to fill sinks in which the proton free energy levels are lower. The pH is a measure of the average proton free energy in the solution; when this quantity is the same as the proton free energy level of a conjugate pair, the two species are present in equal concentrations (this corresponds, of course to the equality of pH and pKa in the conventional theory.)

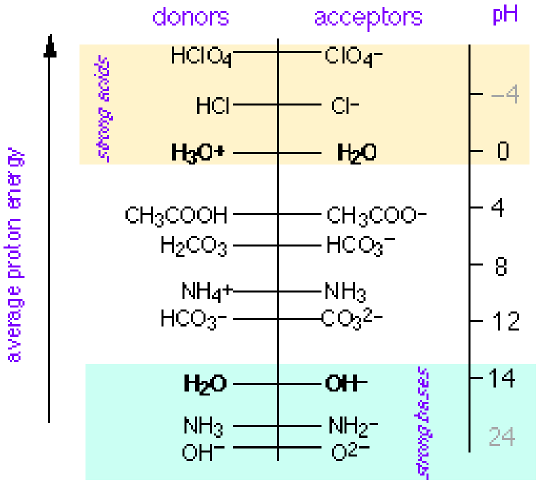


Fig. 25: Proton-free energy scale

The positions of the acids on this scale represent ΔG° for the transfer of the proton from the acid to water. The pH is a measure of the average proton free energy in the solution; when this quantity is equal to the proton free energy level of the acid, then pH = pK_a and half the acid is in its conjugate base form.

Note that H_3O^+ is the strongest acid, and OH^- the strongest base that can exist in water; this is the basis of the *leveling effect.*

"Hydrolysis" of a base such as HCO3– occurs when it acquires a proton from H_2O (the one at the bottom) by thermal excitation, leaving OH^-.

For a more detailed exposition, see http://www.chem1.com/acad/webtut/aquatic/FallProt.html .

The proton-free energy concept is commonly employed in aquatic environmental chemistry in which multiple acid-base systems must be dealt with on a semi-quantitative bases. It is, however, admirably adapted to any presentation of acid-base chemistry, even at the first-year college level, and it seems a shame that it never seems to have made its way into the ordinary curriculum.