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The Second Law

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The purpose of this chapter is to explain the origin of the spontaneity of physical and chemical change. We examine two simple processes and show how to define, measure, and use a property, the entropy, to discuss spontaneous changes quantitatively. The chapter also introduces a major subsidiary thermodynamic property, the Gibbs energy, which lets us express the spontaneity of a process in terms of the properties of a system. The Gibbs energy also enables us to predict the maximum non-expansion work that a process can do. As we began to see in Chapter 2, one application of thermodynamics is to find relations between properties that might not be thought to be related. Several relations of this kind can be established by making use of the fact that the Gibbs energy is a state function. We also see how to derive expressions for the variation of the Gibbs energy with temperature and pressure and how to formulate expressions that are valid for real gases. These expressions will prove useful later when we discuss the effect of temperature and pressure on equilibrium constants.

Some things happen naturally; some things don't. A gas expands to fill the available volume, a hot body cools to the temperature of its surroundings, and a chemical reaction runs in one direction rather than another. Some aspect of the world determines the **spontaneous** direction of change, the direction of change that does not require work to be done to bring it about. A gas can be confined to a smaller volume, an object can be cooled by using a refrigerator, and some reactions can be driven in reverse (as in the electrolysis of water). However, none of these processes is spontaneous; each one must be brought about by doing work. An important point, though, is that throughout this text 'spontaneous' must be interpreted as a natural *tendency* that may or may not be realized in practice. Thermodynamics is silent on the rate at which a spontaneous change in fact occurs, and some spontaneous processes (such as the conversion of diamond to graphite) may be so slow that the tendency is never realized in practice whereas others (such as the expansion of a gas into a vacuum) are almost instantaneous.

The recognition of two classes of process, spontaneous and non-spontaneous, is summarized by the **Second Law of thermodynamics**. This law may be expressed in a variety of equivalent ways. One statement was formulated by Kelvin:

No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work.

For example, it has proved impossible to construct an engine like that shown in Fig. 3.1, in which heat is drawn from a hot reservoir and completely converted into work. All real heat engines have both a hot source and a cold sink; some energy is always discarded into the cold sink as heat and not converted into work. The Kelvin

statement is a generalization of another everyday observation, that a ball at rest on a surface has never been observed to leap spontaneously upwards. An upward leap of the ball would be equivalent to the conversion of heat from the surface into work.

The direction of spontaneous change

What determines the direction of spontaneous change? It is not the total energy of the isolated system. The First Law of thermodynamics states that energy is conserved in any process, and we cannot disregard that law now and say that everything tends towards a state of lower energy: the total energy of an isolated system is constant.

Is it perhaps the energy of the *system* that tends towards a minimum? Two arguments show that this cannot be so. First, a perfect gas expands spontaneously into a vacuum, yet its internal energy remains constant as it does so. Secondly, if the energy of a system does happen to decrease during a spontaneous change, the energy of its surroundings must increase by the same amount (by the First Law). The increase in energy of the surroundings is just as spontaneous a process as the decrease in energy of the system.

When a change occurs, the total energy of an isolated system remains constant but it is parcelled out in different ways. Can it be, therefore, that the direction of change is related to the *distribution* of energy? We shall see that this idea is the key, and that spontaneous changes are always accompanied by a dispersal of energy.

3.1 The dispersal of energy

We can begin to understand the role of the distribution of energy by thinking about a ball (the system) bouncing on a floor (the surroundings). The ball does not rise as high after each bounce because there are inelastic losses in the materials of the ball and floor. The kinetic energy of the ball's overall motion is spread out into the energy of thermal motion of its particles and those of the floor that it hits. The direction of spontaneous change is towards a state in which the ball is at rest with all its energy dispersed into random thermal motion of molecules in the air and of the atoms of the virtually infinite floor (Fig. 3.2).

A ball resting on a warm floor has never been observed to start bouncing. For bouncing to begin, something rather special would need to happen. In the first place, some of the thermal motion of the atoms in the floor would have to accumulate in a single, small object, the ball. This accumulation requires a spontaneous localization of energy from the myriad vibrations of the atoms of the floor into the much smaller number of atoms that constitute the ball (Fig. 3.3). Furthermore, whereas the thermal motion is random, for the ball to move upwards its atoms must all move in the same direction. The localization of random, disorderly motion as concerted, ordered motion is so unlikely that we can dismiss it as virtually impossible.¹

We appear to have found the signpost of spontaneous change: *we look for the direction of change that leads to dispersal of the total energy of the isolated system.* This principle accounts for the direction of change of the bouncing ball, because its energy is spread out as thermal motion of the atoms of the floor. The reverse process is not spontaneous because it is highly improbable that energy will become localized, leading to uniform motion of the ball's atoms. A gas does not contract spontaneously because

¹ Concerted motion, but on a much smaller scale, is observed as *Brownian motion*, the jittering motion of small particles suspended in water.

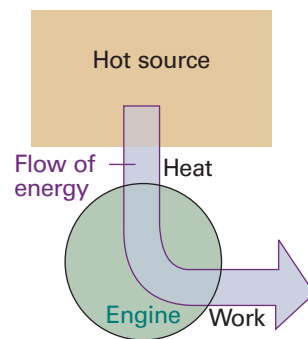


Fig. 3.1 The Kelvin statement of the Second Law denies the possibility of the process illustrated here, in which heat is changed completely into work, there being no other change. The process is not in conflict with the First Law because energy is conserved.

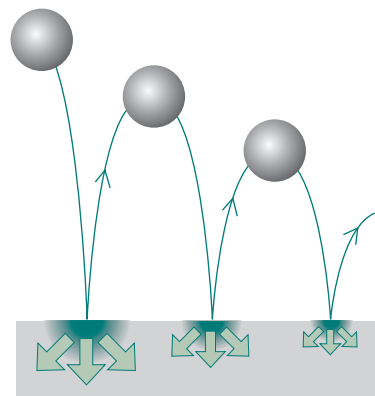


Fig. 3.2 The direction of spontaneous change for a ball bouncing on a floor. On each bounce some of its energy is degraded into the thermal motion of the atoms of the floor, and that energy disperses. The reverse has never been observed to take place on a macroscopic scale.

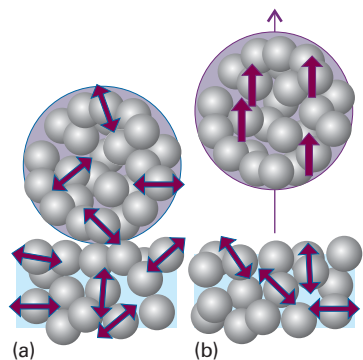


Fig. 3.3 The molecular interpretation of the irreversibility expressed by the Second Law. (a) A ball resting on a warm surface; the atoms are undergoing thermal motion (vibration, in this instance), as indicated by the arrows. (b) For the ball to fly upwards, some of the random vibrational motion would have to change into coordinated, directed motion. Such a conversion is highly improbable.

to do so the random motion of its molecules, which spreads out the distribution of kinetic energy throughout the container, would have to take them all into the same region of the container, thereby localizing the energy. The opposite change, spontaneous expansion, is a natural consequence of energy becoming more dispersed as the gas molecules occupy a larger volume. An object does not spontaneously become warmer than its surroundings because it is highly improbable that the jostling of randomly vibrating atoms in the surroundings will lead to the localization of thermal motion in the object. The opposite change, the spreading of the object's energy into the surroundings as thermal motion, is natural.

It may seem very puzzling that the spreading out of energy and matter, the collapse into disorder, can lead to the formation of such ordered structures as crystals or proteins. Nevertheless, in due course, we shall see that dispersal of energy and matter accounts for change in all its forms.

3.2 Entropy

The First Law of thermodynamics led to the introduction of the internal energy, U . The internal energy is a state function that lets us assess whether a change is permissible: only those changes may occur for which the internal energy of an isolated system remains constant. The law that is used to identify the signpost of spontaneous change, the Second Law of thermodynamics, may also be expressed in terms of another state function, the **entropy**, S . We shall see that the entropy (which we shall define shortly, but is a measure of the energy dispersed in a process) lets us assess whether one state is accessible from another by a spontaneous change. The First Law uses the internal energy to identify *permissible* changes; the Second Law uses the entropy to identify the *spontaneous changes* among those permissible changes.

The Second Law of thermodynamics can be expressed in terms of the entropy:

The entropy of an isolated system increases in the course of a spontaneous change:

$$\Delta S_{\text{tot}} > 0$$

where S_{tot} is the total entropy of the system and its surroundings. Thermodynamically irreversible processes (like cooling to the temperature of the surroundings and the free expansion of gases) are spontaneous processes, and hence must be accompanied by an increase in total entropy.

(a) The thermodynamic definition of entropy

The thermodynamic definition of entropy concentrates on the change in entropy, dS , that occurs as a result of a physical or chemical change (in general, as a result of a 'process'). The definition is motivated by the idea that a change in the extent to which energy is dispersed depends on how much energy is transferred as heat. As we have remarked, heat stimulates random motion in the surroundings. On the other hand, work stimulates uniform motion of atoms in the surroundings and so does not change their entropy.

The thermodynamic definition of entropy is based on the expression

$$dS = \frac{dq_{\text{rev}}}{T} \quad [3.1]$$

For a measurable change between two states i and f this expression integrates to

$$\Delta S = \int_i^f \frac{dq_{\text{rev}}}{T} \quad (3.2)$$

That is, to calculate the difference in entropy between any two states of a system, we find a *reversible* path between them, and integrate the energy supplied as heat at each stage of the path divided by the temperature at which heating occurs.

Example 3.1 Calculating the entropy change for the isothermal expansion of a perfect gas

Calculate the entropy change of a sample of perfect gas when it expands isothermally from a volume V_i to a volume V_f .

Method The definition of entropy instructs us to find the energy supplied as heat for a reversible path between the stated initial and final states regardless of the actual manner in which the process takes place. A simplification is that the expansion is isothermal, so the temperature is a constant and may be taken outside the integral in eqn 3.2. The energy absorbed as heat during a reversible isothermal expansion of a perfect gas can be calculated from $\Delta U = q + w$ and $\Delta U = 0$, which implies that $q = -w$ in general and therefore that $q_{\text{rev}} = -w_{\text{rev}}$ for a reversible change. The work of reversible isothermal expansion was calculated in Section 2.3.

Answer Because the temperature is constant, eqn 3.2 becomes

$$\Delta S = \frac{1}{T} \int_i^f dq_{\text{rev}} = \frac{q_{\text{rev}}}{T}$$

From eqn 2.11, we know that

$$q_{\text{rev}} = -w_{\text{rev}} = nRT \ln \frac{V_f}{V_i}$$

It follows that

$$\Delta S = nR \ln \frac{V_f}{V_i}$$

As an illustration of this formula, when the volume occupied by 1.00 mol of any perfect gas molecules is doubled at any constant temperature, $V_f/V_i = 2$ and

$$\Delta S = (1.00 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln 2 = +5.76 \text{ J K}^{-1}$$

A note on good practice According to eqn 3.2, when the energy transferred as heat is expressed in joules and the temperature is in kelvins, the units of entropy are joules per kelvin (J K^{-1}). Entropy is an extensive property. Molar entropy, the entropy divided by the amount of substance, is expressed in joules per kelvin per mole ($\text{J K}^{-1} \text{ mol}^{-1}$).² The molar entropy is an intensive property.

Self-test 3.1 Calculate the change in entropy when the pressure of a perfect gas is changed isothermally from p_i to p_f . $[\Delta S = nR \ln(p_i/p_f)]$

We can use the definition in eqn 3.1 to formulate an expression for the change in entropy of the surroundings, ΔS_{sur} . Consider an infinitesimal transfer of heat dq_{sur} to the surroundings. The surroundings consist of a reservoir of constant volume, so the energy supplied to them by heating can be identified with the change in their

² The units of entropy are the same as those of the gas constant, R , and molar heat capacities.

internal energy, dU_{sur} .³ The internal energy is a state function, and dU_{sur} is an exact differential. As we have seen, these properties imply that dU_{sur} is independent of how the change is brought about and in particular is independent of whether the process is reversible or irreversible. The same remarks therefore apply to dq_{sur} , to which dU_{sur} is equal. Therefore, we can adapt the definition in eqn 3.1 to write

$$dS_{\text{sur}} = \frac{dq_{\text{sur,rev}}}{T_{\text{sur}}} = \frac{dq_{\text{sur}}}{T_{\text{sur}}} \quad (3.3a)$$

Furthermore, because the temperature of the surroundings is constant whatever the change, for a measurable change

$$\Delta S_{\text{sur}} = \frac{q_{\text{sur}}}{T_{\text{sur}}} \quad (3.3b)$$

That is, regardless of how the change is brought about in the system, reversibly or irreversibly, we can calculate the change of entropy of the surroundings by dividing the heat transferred by the temperature at which the transfer takes place.

Equation 3.3 makes it very simple to calculate the changes in entropy of the surroundings that accompany any process. For instance, for any adiabatic change, $q_{\text{sur}} = 0$, so

$$\text{For an adiabatic change:} \quad \Delta S_{\text{sur}} = 0 \quad (3.4)$$

This expression is true however the change takes place, reversibly or irreversibly, provided no local hot spots are formed in the surroundings. That is, it is true so long as the surroundings remain in internal equilibrium. If hot spots do form, then the localized energy may subsequently disperse spontaneously and hence generate more entropy.

Illustration 3.1 Calculating the entropy change in the surroundings

To calculate the entropy change in the surroundings when 1.00 mol $\text{H}_2\text{O}(\text{l})$ is formed from its elements under standard conditions at 298 K, we use $\Delta H^\circ = -286 \text{ kJ}$ from Table 2.7. The energy released as heat is supplied to the surroundings, now regarded as being at constant pressure, so $q_{\text{sur}} = +286 \text{ kJ}$. Therefore,

$$\Delta S_{\text{sur}} = \frac{2.86 \times 10^5 \text{ J}}{298 \text{ K}} = +960 \text{ J K}^{-1}$$

This strongly exothermic reaction results in an increase in the entropy of the surroundings as energy is released as heat into them.

Self-test 3.2 Calculate the entropy change in the surroundings when 1.00 mol $\text{N}_2\text{O}_4(\text{g})$ is formed from 2.00 mol $\text{NO}_2(\text{g})$ under standard conditions at 298 K.
[−192 J K^{−1}]

Molecular interpretation 3.1 The statistical view of entropy

The entry point into the molecular interpretation of the Second Law of thermodynamics is the realization that an atom or molecule can possess only certain energies, called its ‘energy levels’. The continuous thermal agitation that molecules

³ Alternatively, the surroundings can be regarded as being at constant pressure, in which case we could equate dq_{sur} to dH_{sur} .

experience in a sample at $T > 0$ ensures that they are distributed over the available energy levels. One particular molecule may be in one low energy state at one instant, and then be excited into a high energy state a moment later. Although we cannot keep track of the energy state of a single molecule, we can speak of the **population** of the state, the average number of molecules in each state; these populations are constant in time provided the temperature remains the same.

Only the lowest energy state is occupied at $T = 0$. Raising the temperature excites some molecules into higher energy states, and more and more states become accessible as the temperature is raised further (Fig. 3.4). Nevertheless, whatever the temperature, there is always a higher population in a state of low energy than one of high energy. The only exception occurs when the temperature is infinite: then all states of the system are equally populated. These remarks were summarized quantitatively by the Austrian physicist Ludwig Boltzmann in the *Boltzmann distribution*:

$$N_i = \frac{N e^{-E_i/kT}}{\sum_i e^{-E_i/kT}}$$

where $k = 1.381 \times 10^{-23} \text{ J K}^{-1}$ and N_i is the number of molecules in a sample of N molecules that will be found in a state with an energy E_i when it is part of a system in thermal equilibrium at a temperature T . Care must be taken with the exact interpretation, though, because more than one state may correspond to the same energy: that is, an energy level may consist of several states.

Boltzmann also made the link between the distribution of molecules over energy levels and the entropy. He proposed that the entropy of a system is given by

$$S = k \ln W \quad (3.5)$$

where W is the number of *microstates*, the ways in which the molecules of a system can be arranged while keeping the total energy constant. Each microstate lasts only for an instant and has a distinct distribution of molecules over the available energy levels. When we measure the properties of a system, we are measuring an average taken over the many microstates the system can occupy under the conditions of the experiment. The concept of the number of microstates makes quantitative the ill-defined qualitative concepts of ‘disorder’ and ‘the dispersal of matter and energy’ that are used widely to introduce the concept of entropy: a more ‘disorderly’ distribution of energy and matter corresponds to a greater number of microstates associated with the same total energy.

Equation 3.5 is known as the **Boltzmann formula** and the entropy calculated from it is sometimes called the **statistical entropy**. We see that if $W = 1$, which corresponds to one microstate (only one way of achieving a given energy, all molecules in exactly the same state), then $S = 0$ because $\ln 1 = 0$. However, if the system can exist in more than one microstate, then $W > 1$ and $S > 0$. But, if more molecules can participate in the distribution of energy, then there are more microstates for a given total energy and the entropy is greater than when the energy is confined so a smaller number of molecules. Therefore, the statistical view of entropy summarized by the Boltzmann formula is consistent with our previous statement that the entropy is related to the dispersal of energy.

The molecular interpretation of entropy advanced by Boltzmann also suggests the thermodynamic definition given by eqn 3.1. To appreciate this point, consider that molecules in a system at high temperature can occupy a large number of the available energy levels, so a small additional transfer of energy as heat will lead to a relatively small change in the number of accessible energy levels. Consequently, the

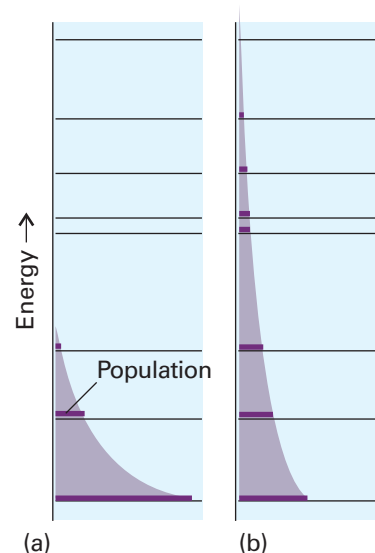


Fig. 3.4 The Boltzmann distribution predicts that the population of a state decreases exponentially with the energy of the state. (a) At low temperatures, only the lowest states are significantly populated; (b) at high temperatures, there is significant population in high-energy states as well as in low-energy states. At infinite temperature (not shown), all states are equally populated.

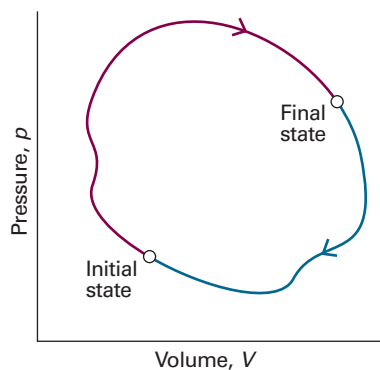


Fig. 3.5 In a thermodynamic cycle, the overall change in a state function (from the initial state to the final state and then back to the initial state again) is zero.

number of microstates does not increase appreciably and neither does the entropy of the system. In contrast, the molecules in a system at low temperature have access to far fewer energy levels (at $T = 0$, only the lowest level is accessible), and the transfer of the same quantity of energy by heating will increase the number of accessible energy levels and the number of microstates rather significantly. Hence, the change in entropy upon heating will be greater when the energy is transferred to a cold body than when it is transferred to a hot body. This argument suggests that the change in entropy should be inversely proportional to the temperature at which the transfer takes place, as in eqn 3.1.

(b) The entropy as a state function

Entropy is a state function. To prove this assertion, we need to show that the integral of dS is independent of path. To do so, it is sufficient to prove that the integral of eqn 3.1 around an arbitrary cycle is zero, for that guarantees that the entropy is the same at the initial and final states of the system regardless of the path taken between them (Fig. 3.5). That is, we need to show that

$$\oint \frac{dq_{\text{rev}}}{T} = 0 \quad (3.6)$$

where the symbol \oint denotes integration around a closed path. There are three steps in the argument:

1. First, to show that eqn 3.6 is true for a special cycle (a 'Carnot cycle') involving a perfect gas.
2. Then to show that the result is true whatever the working substance.
3. Finally, to show that the result is true for any cycle.

A **Carnot cycle**, which is named after the French engineer Sadi Carnot, consists of four reversible stages (Fig. 3.6):

1. Reversible isothermal expansion from A to B at T_h ; the entropy change is q_h/T_h , where q_h is the energy supplied to the system as heat from the hot source.
2. Reversible adiabatic expansion from B to C. No energy leaves the system as heat, so the change in entropy is zero. In the course of this expansion, the temperature falls from T_h to T_c , the temperature of the cold sink.
3. Reversible isothermal compression from C to D at T_c . Energy is released as heat to the cold sink; the change in entropy of the system is q_c/T_c ; in this expression q_c is negative.
4. Reversible adiabatic compression from D to A. No energy enters the system as heat, so the change in entropy is zero. The temperature rises from T_c to T_h .

The total change in entropy around the cycle is

$$\oint dS = \frac{q_h}{T_h} + \frac{q_c}{T_c}$$

However, we show in *Justification 3.1* that, for a perfect gas:

$$\frac{q_h}{q_c} = -\frac{T_h}{T_c} \quad (3.7)_{\text{rev}}$$

Substitution of this relation into the preceding equation gives zero on the right, which is what we wanted to prove.

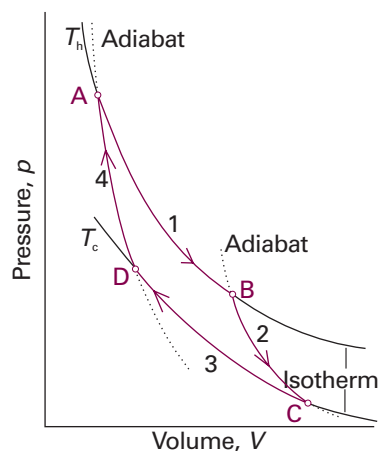


Fig. 3.6 The basic structure of a Carnot cycle. In Step 1, there is isothermal reversible expansion at the temperature T_h . Step 2 is a reversible adiabatic expansion in which the temperature falls from T_h to T_c . In Step 3 there is an isothermal reversible compression at T_c , and that isothermal step is followed by an adiabatic reversible compression, which restores the system to its initial state.

Justification 3.1 Heating accompanying reversible adiabatic expansion

This *Justification* is based on the fact that the two temperatures in eqn 3.7 lie on the same adiabat in Fig. 3.6. As explained in Example 3.1, for a perfect gas:

$$q_h = nRT_h \ln \frac{V_B}{V_A} \quad q_c = nRT_c \ln \frac{V_D}{V_C}$$

From the relations between temperature and volume for reversible adiabatic processes (eqn 2.28):

$$V_A T_h^c = V_D T_c^c \quad V_C T_c^c = V_B T_h^c$$

Multiplication of the first of these expressions by the second gives

$$V_A V_C T_h^c T_c^c = V_D V_B T_h^c T_c^c$$

which simplifies to

$$\frac{V_A}{V_B} = \frac{V_D}{V_C}$$

Consequently,

$$q_c = nRT_c \ln \frac{V_D}{V_C} = nRT_c \ln \frac{V_A}{V_B} = -nRT_c \ln \frac{V_B}{V_A}$$

and therefore

$$\frac{q_h}{q_c} = \frac{nRT_h \ln(V_B/V_A)}{-nRT_c \ln(V_B/V_A)} = -\frac{T_h}{T_c}$$

as in eqn 3.7.

In the second step we need to show that eqn 3.7 applies to any material, not just a perfect gas (which is why, in anticipation, we have not labelled it with a $^\circ$). We begin this step of the argument by introducing the **efficiency**, ε (epsilon), of a heat engine:

$$\varepsilon = \frac{\text{work performed}}{\text{heat absorbed}} = \frac{|w|}{q_h} \quad [3.8]$$

The definition implies that, the greater the work output for a given supply of heat from the hot reservoir, the greater is the efficiency of the engine. We can express the definition in terms of the heat transactions alone, because (as shown in Fig. 3.7) the energy supplied as work by the engine is the difference between the energy supplied as heat by the hot reservoir and returned to the cold reservoir:

$$\varepsilon = \frac{q_h + q_c}{q_h} = 1 + \frac{q_c}{q_h} \quad (3.9)$$

(Remember that $q_c < 0$.) It then follows from eqn 3.7 that

$$\varepsilon_{\text{rev}} = 1 - \frac{T_c}{T_h} \quad (3.10)_{\text{rev}}$$

Now we are ready to generalize this conclusion. The Second Law of thermodynamics implies that *all reversible engines have the same efficiency regardless of their construction*. To see the truth of this statement, suppose two reversible engines are coupled together and run between the same two reservoirs (Fig. 3.8). The working substances and details of construction of the two engines are entirely arbitrary. Initially, suppose that

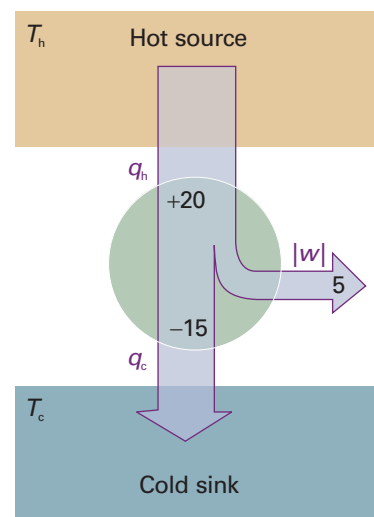


Fig. 3.7 Suppose an energy q_h (for example, 20 kJ) is supplied to the engine and q_c is lost from the engine (for example, $q_c = -15$ kJ) and discarded into the cold reservoir. The work done by the engine is equal to $q_h + q_c$ (for example, 20 kJ + (-15 kJ) = 5 kJ). The efficiency is the work done divided by the energy supplied as heat from the hot source.

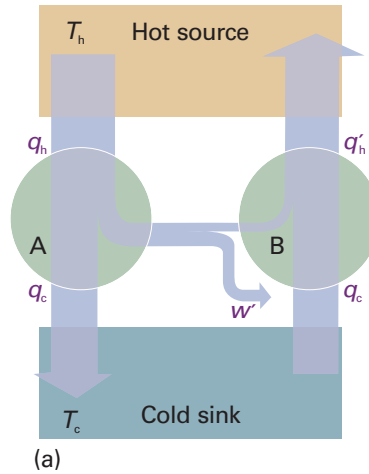


Fig. 3.8 (a) The demonstration of the equivalence of the efficiencies of all reversible engines working between the same thermal reservoirs is based on the flow of energy represented in this diagram. (b) The net effect of the processes is the conversion of heat into work without there being a need for a cold sink: this is contrary to the Kelvin statement of the Second Law.

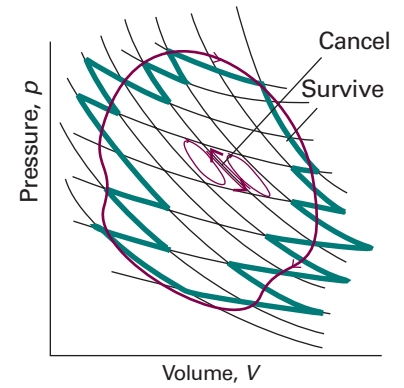
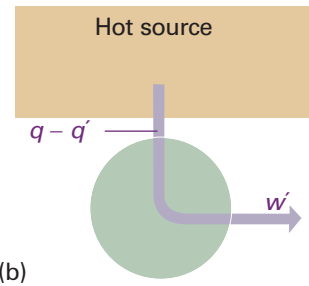


Fig. 3.9 A general cycle can be divided into small Carnot cycles. The match is exact in the limit of infinitesimally small cycles. Paths cancel in the interior of the collection, and only the perimeter, an increasingly good approximation to the true cycle as the number of cycles increases, survives. Because the entropy change around every individual cycle is zero, the integral of the entropy around the perimeter is zero too.

engine A is more efficient than engine B and that we choose a setting of the controls that causes engine B to acquire energy as heat q_c from the cold reservoir and to release a certain quantity of energy as heat into the hot reservoir. However, because engine A is more efficient than engine B, not all the work that A produces is needed for this process, and the difference can be used to do work. The net result is that the cold reservoir is unchanged, work has been done, and the hot reservoir has lost a certain amount of energy. This outcome is contrary to the Kelvin statement of the Second Law, because some heat has been converted directly into work. In molecular terms, the random thermal motion of the hot reservoir has been converted into ordered motion characteristic of work. Because the conclusion is contrary to experience, the initial assumption that engines A and B can have different efficiencies must be false. It follows that the relation between the heat transfers and the temperatures must also be independent of the working material, and therefore that eqn 3.7 is always true for any substance involved in a Carnot cycle.

For the final step in the argument, we note that any reversible cycle can be approximated as a collection of Carnot cycles and the cyclic integral around an arbitrary path is the sum of the integrals around each of the Carnot cycles (Fig. 3.9). This approximation becomes exact as the individual cycles are allowed to become infinitesimal. The entropy change around each individual cycle is zero (as demonstrated above), so the sum of entropy changes for all the cycles is zero. However, in the sum, the entropy change along any individual path is cancelled by the entropy change along the path it shares with the neighbouring cycle. Therefore, all the entropy changes cancel except for those along the perimeter of the overall cycle. That is,

$$\sum_{\text{all}} \frac{q_{\text{rev}}}{T} = \sum_{\text{perimeter}} \frac{q_{\text{rev}}}{T} = 0$$

In the limit of infinitesimal cycles, the non-cancelling edges of the Carnot cycles match the overall cycle exactly, and the sum becomes an integral. Equation 3.6 then follows immediately. This result implies that dS is an exact differential and therefore that S is a state function.

IMPACT ON ENGINEERING

13.1 Refrigeration

The discussion of the text is the basis of the thermodynamic assessment of the power needed to cool objects in refrigerators. First, we consider the work required to cool an object, and refer to Fig. 3.10.

When an energy $|q_c|$ is removed from a cool source at a temperature T_c and then deposited in a warmer sink at a temperature T_h , as in a typical refrigerator, the change in entropy is

$$\Delta S = -\frac{|q_c|}{T_c} + \frac{|q_c|}{T_h} < 0$$

The process is not spontaneous because not enough entropy is generated in the warm sink to overcome the entropy loss from the hot source. To generate more entropy, energy must be added to the stream that enters the warm sink. Our task is to find the minimum energy that needs to be supplied. The outcome is expressed as the *coefficient of performance*, c :

$$c = \frac{\text{energy transferred as heat}}{\text{energy transferred as work}} = \frac{|q_c|}{|w|}$$

The less the work that is required to achieve a given transfer, the greater the coefficient of performance and the more efficient the refrigerator.

Because $|q_c|$ is removed from the cold source, and the work $|w|$ is added to the energy stream, the energy deposited as heat in the hot sink is $|q_h| = |q_c| + |w|$. Therefore,

$$\frac{1}{c} = \frac{|q_h| - |q_c|}{|q_c|} = -\frac{|q_h|}{|q_c|} - 1$$

We can now use eqn 3.7 to express this result in terms of the temperatures alone, which is possible if the transfer is performed reversibly. This substitution leads to

$$c = \frac{T_c}{T_h - T_c}$$

for the thermodynamically optimum coefficient of performance. For a refrigerator withdrawing heat from ice-cold water ($T_c = 273 \text{ K}$) in a typical environment ($T_h = 293 \text{ K}$), $c = 14$, so, to remove 10 kJ (enough to freeze 30 g of water), requires transfer of at least 0.71 kJ as work. Practical refrigerators, of course, have a lower coefficient of performance.

The work to *maintain* a low temperature is also relevant to the design of refrigerators. No thermal insulation is perfect, so there is always a flow of energy as heat into the sample at a rate proportional to the temperature difference. If the rate at which energy leaks in is written $A(T_h - T_c)$, where A is a constant that depends on the size of the sample and the details of the insulation, then the minimum power, P , required to maintain the original temperature difference by pumping out that energy by heating the surroundings is

$$P = \frac{1}{c} \times A(T_h - T_c) = A \times \frac{(T_h - T_c)^2}{T_c}$$

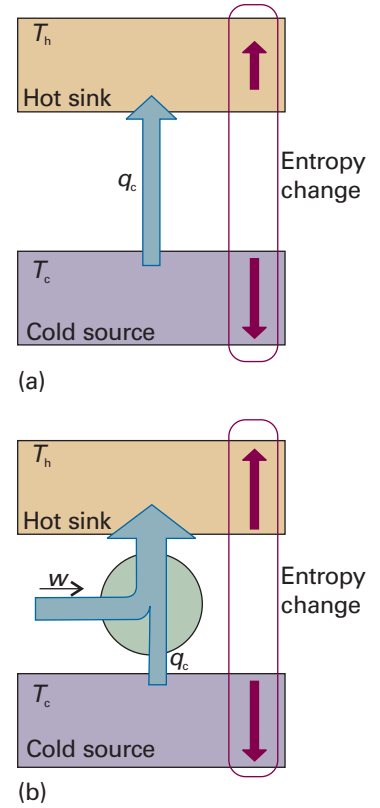


Fig. 3.10 (a) The flow of energy as heat from a cold source to a hot sink is not spontaneous. As shown here, the entropy increase of the hot sink is smaller than the entropy increase of the cold source, so there is a net decrease in entropy. (b) The process becomes feasible if work is provided to add to the energy stream. Then the increase in entropy of the hot sink can be made to cancel the entropy decrease of the hot source.

Comment 3.1

The triple point of a substance represents the set of conditions at which the three phases coexist in equilibrium. For water, the triple point occurs at 273.16 K and 611 Pa. See Section 4.2 for details.

We see that the power increases as the square of the temperature difference we are trying to maintain. For this reason, air-conditioners are much more expensive to run on hot days than on mild days.

(c) The thermodynamic temperature

Suppose we have an engine that is working reversibly between a hot source at a temperature T_h and a cold sink at a temperature T ; then we know from eqn 3.10 that

$$T = (1 - \varepsilon)T_h \quad (3.11)$$

This expression enabled Kelvin to define the **thermodynamic temperature scale** in terms of the efficiency of a heat engine. The zero of the scale occurs for a Carnot efficiency of 1. The size of the unit is entirely arbitrary, but on the Kelvin scale is defined by setting the temperature of the triple point of water as 273.16 K exactly. Then, if the heat engine has a hot source at the triple point of water, the temperature of the cold sink (the object we want to measure) is found by measuring the efficiency of the engine. This result is independent of the working substance.

(d) The Clausius inequality

We now show that the definition of entropy is consistent with the Second Law. To begin, we recall that more energy flows as work under reversible conditions than under irreversible conditions. That is, $-dw_{\text{rev}} \geq -dw$, or $dw - dw_{\text{rev}} \geq 0$. Because the internal energy is a state function, its change is the same for irreversible and reversible paths between the same two states, so we can also write:

$$dU = dq + dw = dq_{\text{rev}} + dw_{\text{rev}}$$

It follows that $dq_{\text{rev}} - dq = dw - dw_{\text{rev}} \geq 0$, or $dq_{\text{rev}} \geq dq$, and therefore that $dq_{\text{rev}}/T \geq dq/T$. Now we use the thermodynamic definition of the entropy (eqn 3.1; $dS = dq_{\text{rev}}/T$) to write

$$dS \geq \frac{dq}{T} \quad (3.12)$$

This expression is the **Clausius inequality**. It will prove to be of great importance for the discussion of the spontaneity of chemical reactions, as we shall see in Section 3.5.

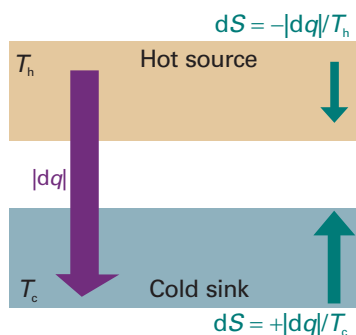


Fig. 3.11 When energy leaves a hot reservoir as heat, the entropy of the reservoir decreases. When the same quantity of energy enters a cooler reservoir, the entropy increases by a larger amount. Hence, overall there is an increase in entropy and the process is spontaneous. Relative changes in entropy are indicated by the sizes of the arrows.

Illustration 3.2 *Spontaneous cooling*

Consider the transfer of energy as heat from one system—the hot source—at a temperature T_h to another system—the cold sink—at a temperature T_c (Fig. 3.11). When $|dq|$ leaves the hot source (so $dq_h < 0$), the Clausius inequality implies that $dS \geq dq_h/T_h$. When $|dq|$ enters the cold sink the Clausius inequality implies that $dS \geq dq_c/T_c$ (with $dq_c > 0$). Overall, therefore,

$$dS \geq \frac{dq_h}{T_h} + \frac{dq_c}{T_c}$$

However, $dq_h = -dq_c$, so

$$dS \geq -\frac{dq_c}{T_h} + \frac{dq_c}{T_c} = dq_c \left(\frac{1}{T_c} - \frac{1}{T_h} \right)$$

which is positive (because $dq_c > 0$ and $T_h \geq T_c$). Hence, cooling (the transfer of heat from hot to cold) is spontaneous, as we know from experience.

We now suppose that the system is isolated from its surroundings, so that $dq = 0$. The Clausius inequality implies that

$$dS \geq 0$$

and we conclude that *in an isolated system the entropy cannot decrease when a spontaneous change occurs*. This statement captures the content of the Second Law.

3.3 Entropy changes accompanying specific processes

We now see how to calculate the entropy changes that accompany a variety of basic processes.

(a) Expansion

We established in Example 3.1 that the change in entropy of a perfect gas that expands isothermally from V_i to V_f is

$$\Delta S = nR \ln \frac{V_f}{V_i} \quad (3.13)^\circ$$

Because S is a state function, the value of ΔS of the system is independent of the path between the initial and final states, so this expression applies whether the change of state occurs reversibly or irreversibly. The logarithmic dependence of entropy on volume is illustrated in Fig. 3.12.

The *total* change in entropy, however, does depend on how the expansion takes place. For any process $dq_{\text{sur}} = -dq$, and for a reversible change we use the expression in Example 3.1; consequently, from eqn 3.3b

$$\Delta S_{\text{sur}} = \frac{q_{\text{sur}}}{T} = -\frac{q_{\text{rev}}}{T} = -nR \ln \frac{V_f}{V_i} \quad (3.14)_{\text{rev}}^\circ$$

This change is the negative of the change in the system, so we can conclude that $\Delta S_{\text{tot}} = 0$, which is what we should expect for a reversible process. If the isothermal expansion occurs freely ($w = 0$) and irreversibly, then $q = 0$ (because $\Delta U = 0$). Consequently, $\Delta S_{\text{sur}} = 0$, and the total entropy change is given by eqn 3.13 itself:

$$\Delta S_{\text{tot}} = nR \ln \frac{V_f}{V_i} \quad (3.15)^\circ$$

In this case, $\Delta S_{\text{tot}} > 0$, as we expect for an irreversible process.

(b) Phase transition

The degree of dispersal of matter and energy changes when a substance freezes or boils as a result of changes in the order with which the molecules pack together and the extent to which the energy is localized or dispersed. Therefore, we should expect the transition to be accompanied by a change in entropy. For example, when a substance vaporizes, a compact condensed phase changes into a widely dispersed gas and we can expect the entropy of the substance to increase considerably. The entropy of a solid also increases when it melts to a liquid and when that liquid turns into a gas.

Consider a system and its surroundings at the **normal transition temperature**, T_{trs} , the temperature at which two phases are in equilibrium at 1 atm. This temperature is 0°C (273 K) for ice in equilibrium with liquid water at 1 atm, and 100°C (373 K) for water in equilibrium with its vapour at 1 atm. At the transition temperature, any transfer of energy as heat between the system and its surroundings is reversible

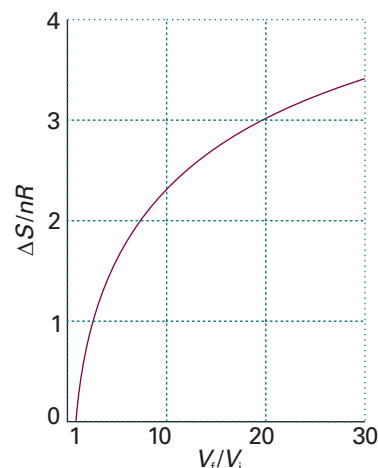


Fig. 3.12 The logarithmic increase in entropy of a perfect gas as it expands isothermally.

Exploration Evaluate the change in entropy that accompanies the expansion of 1.00 mol $\text{CO}_2(\text{g})$ from 0.001 m^3 to 0.010 m^3 at 298 K, treated as a van der Waals gas.

Synoptic Table 3.1* Standard entropies (and temperatures) of phase transitions, $\Delta_{\text{trs}}S^\ominus/(\text{J K}^{-1} \text{mol}^{-1})$

| | Fusion (at T_f) | Vaporization (at T_b) |
|---------------------------------|-------------------------|--------------------------|
| Argon, Ar | 14.17 (at 83.8 K) | 74.53 (at 87.3 K) |
| Benzene, C_6H_6 | 38.00 (at 279 K) | 87.19 (at 353 K) |
| Water, H_2O | 22.00 (at 273.15 K) | 109.0 (at 373.15 K) |
| Helium, He | 4.8 (at 8 K and 30 bar) | 19.9 (at 4.22 K) |

* More values are given in the *Data section*.**Synoptic Table 3.2*** The standard entropies of vaporization of liquids

| | $\Delta_{\text{vap}}H^\ominus/(\text{kJ mol}^{-1})$ | $\theta_b/^\circ\text{C}$ | $\Delta_{\text{vap}}S^\ominus/(\text{J K}^{-1} \text{mol}^{-1})$ |
|----------------------|---|---------------------------|--|
| Benzene | 30.8 | 80.1 | 87.2 |
| Carbon tetrachloride | 30 | 76.7 | 85.8 |
| Cyclohexane | 30.1 | 80.7 | 85.1 |
| Hydrogen sulfide | 18.7 | -60.4 | 87.9 |
| Methane | 8.18 | -161.5 | 73.2 |
| Water | 40.7 | 100.0 | 109.1 |

* More values are given in the *Data section*.

because the two phases in the system are in equilibrium. Because at constant pressure $q = \Delta_{\text{trs}}H$, the change in molar entropy of the system is⁴

$$\Delta_{\text{trs}}S = \frac{\Delta_{\text{trs}}H}{T_{\text{trs}}} \quad (3.16)$$

If the phase transition is exothermic ($\Delta_{\text{trs}}H < 0$, as in freezing or condensing), then the entropy change is negative. This decrease in entropy is consistent with localization of matter and energy that accompanies the formation of a solid from a liquid or a liquid from a gas. If the transition is endothermic ($\Delta_{\text{trs}}H > 0$, as in melting and vaporization), then the entropy change is positive, which is consistent with dispersal of energy and matter in the system.

Table 3.1 lists some experimental entropies of transition. Table 3.2 lists in more detail the standard entropies of vaporization of several liquids at their boiling points. An interesting feature of the data is that a wide range of liquids give approximately the same standard entropy of vaporization (about $85 \text{ J K}^{-1} \text{mol}^{-1}$): this empirical observation is called **Trouton's rule**.

Molecular interpretation 3.2 *Trouton's rule*

The explanation of Trouton's rule is that a comparable change in volume occurs (with an accompanying change in the number of accessible microstates) when any liquid evaporates and becomes a gas. Hence, all liquids can be expected to have similar standard entropies of vaporization.

⁴ Recall from Section 2.7 that $\Delta_{\text{trs}}H$ is an enthalpy change per mole of substance; so $\Delta_{\text{trs}}S$ is also a molar quantity.

Liquids that show significant deviations from Trouton's rule do so on account of strong molecular interactions that restrict molecular motion. As a result, there is a greater dispersal of energy and matter when the liquid turns into a vapour than would occur for a liquid in which molecular motion is less restricted. An example is water, where the large entropy of vaporization reflects the presence of structure arising from hydrogen-bonding in the liquid. Hydrogen bonds tend to organize the molecules in the liquid so that they are less random than, for example, the molecules in liquid hydrogen sulfide (in which there is no hydrogen bonding).

Methane has an unusually low entropy of vaporization. A part of the reason is that the entropy of the gas itself is slightly low ($186 \text{ J K}^{-1} \text{ mol}^{-1}$ at 298 K); the entropy of N_2 under the same conditions is $192 \text{ J K}^{-1} \text{ mol}^{-1}$. As we shall see in Chapter 13, small molecules are difficult to excite into rotation; as a result, only a few rotational states are accessible at room temperature and, consequently, the number of rotational energy levels among which energy can be dispersed is low.

Illustration 3.3 Using Trouton's rule

There is no hydrogen bonding in liquid bromine and Br_2 is a heavy molecule that is unlikely to display unusual behaviour in the gas phase, so it is probably safe to use Trouton's rule. To predict the standard molar enthalpy of vaporization of bromine given that it boils at 59.2°C , we use the rule in the form

$$\Delta_{\text{vap}}H^\ominus = T_b \times (85 \text{ J K}^{-1} \text{ mol}^{-1})$$

Substitution of the data then gives

$$\Delta_{\text{vap}}H^\ominus = (332.4 \text{ K}) \times (85 \text{ J K}^{-1} \text{ mol}^{-1}) = +2.8 \times 10^3 \text{ J mol}^{-1} = +28 \text{ kJ mol}^{-1}$$

The experimental value is $+29.45 \text{ kJ mol}^{-1}$.

Self-test 3.3 Predict the enthalpy of vaporization of ethane from its boiling point, -88.6°C .
[16 kJ mol^{-1}]

(c) Heating

We can use eqn 3.2 to calculate the entropy of a system at a temperature T_f from a knowledge of its entropy at a temperature T_i and the heat supplied to change its temperature from one value to the other:

$$S(T_f) = S(T_i) + \int_{T_i}^{T_f} \frac{dq_{\text{rev}}}{T} \quad (3.17)$$

We shall be particularly interested in the entropy change when the system is subjected to constant pressure (such as from the atmosphere) during the heating. Then, from the definition of constant-pressure heat capacity (eqn 2.22), $dq_{\text{rev}} = C_p dT$ provided the system is doing no non-expansion work. Consequently, at constant pressure:

$$S(T_f) = S(T_i) + \int_{T_i}^{T_f} \frac{C_p dT}{T} \quad (3.18)$$

The same expression applies at constant volume, but with C_p replaced by C_V . When C_p is independent of temperature in the temperature range of interest, it can be taken outside the integral and we obtain

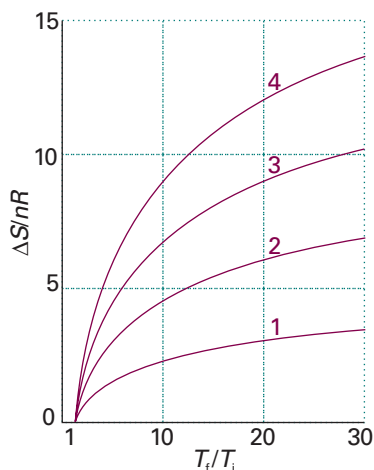


Fig. 3.13 The logarithmic increase in entropy of a substance as it is heated at constant volume. Different curves correspond to different values of the constant-volume heat capacity (which is assumed constant over the temperature range) expressed as $C_{V,m}/R$.

Exploration Plot the change in entropy of a perfect gas of (a) atoms, (b) linear rotors, (c) nonlinear rotors as the sample is heated over the same range under conditions of (i) constant volume, (ii) constant pressure.

$$S(T_f) = S(T_i) + C_p \int_{T_i}^{T_f} \frac{dT}{T} = S(T_i) + C_p \ln \frac{T_f}{T_i} \quad (3.19)$$

with a similar expression for heating at constant volume. The logarithmic dependence of entropy on temperature is illustrated in Fig. 3.13.

Example 3.2 Calculating the entropy change

Calculate the entropy change when argon at 25°C and 1.00 bar in a container of volume 0.500 dm³ is allowed to expand to 1.000 dm³ and is simultaneously heated to 100°C.

Method Because S is a state function, we are free to choose the most convenient path from the initial state. One such path is reversible isothermal expansion to the final volume, followed by reversible heating at constant volume to the final temperature. The entropy change in the first step is given by eqn 3.13 and that of the second step, provided C_V is independent of temperature, by eqn 3.19 (with C_V in place of C_p). In each case we need to know n , the amount of gas molecules, and can calculate it from the perfect gas equation and the data for the initial state from $n = p_i V_i / RT_i$. The heat capacity at constant volume is given by the equipartition theorem as $\frac{3}{2}R$. (The equipartition theorem is reliable for monatomic gases: for others and in general use experimental data like that in Table 2.7, converting to the value at constant volume by using the relation $C_{p,m} - C_{v,m} = R$.)

Answer Because $n = p_i V_i / RT_i$, from eqn 3.13

$$\Delta S(\text{Step 1}) = \left(\frac{p_i V_i}{RT_i} \right) \times R \ln \frac{V_f}{V_i} = \frac{p_i V_i}{T_i} \ln \frac{V_f}{V_i}$$

The entropy change in the second step, from 298 K to 373 K at constant volume, is

$$\Delta S(\text{Step 2}) = \left(\frac{p_i V_i}{RT_i} \right) \times \frac{3}{2} R \ln \frac{T_f}{T_i} = \frac{p_i V_i}{T_i} \ln \left(\frac{T_f}{T_i} \right)^{3/2}$$

The overall entropy change, the sum of these two changes, is

$$\Delta S = \frac{p_i V_i}{T_i} \ln \frac{V_f}{V_i} + \frac{p_i V_i}{T_i} \ln \left(\frac{T_f}{T_i} \right)^{3/2} = \frac{p_i V_i}{T_i} \ln \left\{ \frac{V_f}{V_i} \left(\frac{T_f}{T_i} \right)^{3/2} \right\}$$

At this point we substitute the data and obtain (by using 1 Pa m³ = 1 J)

$$\begin{aligned} \Delta S &= \frac{(1.00 \times 10^5 \text{ Pa}) \times (0.500 \times 10^{-3} \text{ m}^3)}{298 \text{ K}} \ln \left\{ \frac{1.000}{0.500} \left(\frac{373}{298} \right)^{3/2} \right\} \\ &= +0.173 \text{ J K}^{-1} \end{aligned}$$

A note on good practice It is sensible to proceed as generally as possible before inserting numerical data so that, if required, the formula can be used for other data and to avoid rounding errors.

Self-test 3.4 Calculate the entropy change when the same initial sample is compressed to 0.0500 dm³ and cooled to −25°C. [−0.44 J K^{−1}]

(d) The measurement of entropy

The entropy of a system at a temperature T is related to its entropy at $T = 0$ by measuring its heat capacity C_p at different temperatures and evaluating the integral in eqn 3.18, taking care to add the entropy of transition ($\Delta_{\text{trs}}H/T_{\text{trs}}$) for each phase transition between $T = 0$ and the temperature of interest. For example, if a substance melts at T_f and boils at T_b , then its entropy above its boiling temperature is given by

$$S(T) = S(0) + \int_0^{T_f} \frac{C_p(s)dT}{T} + \frac{\Delta_{\text{fus}}H}{T_f} + \int_{T_f}^{T_b} \frac{C_p(l)dT}{T} + \frac{\Delta_{\text{vap}}H}{T_b} + \int_{T_b}^T \frac{C_p(g)dT}{T} \quad (3.20)$$

All the properties required, except $S(0)$, can be measured calorimetrically, and the integrals can be evaluated either graphically or, as is now more usual, by fitting a polynomial to the data and integrating the polynomial analytically. The former procedure is illustrated in Fig. 3.14: the area under the curve of C_p/T against T is the integral required. Because $dT/T = d \ln T$, an alternative procedure is to evaluate the area under a plot of C_p against $\ln T$.

One problem with the determination of entropy is the difficulty of measuring heat capacities near $T = 0$. There are good theoretical grounds for assuming that the heat capacity is proportional to T^3 when T is low (see Section 8.1), and this dependence is the basis of the **Debye extrapolation**. In this method, C_p is measured down to as low a temperature as possible, and a curve of the form aT^3 is fitted to the data. That fit determines the value of a , and the expression $C_p = aT^3$ is assumed valid down to $T = 0$.

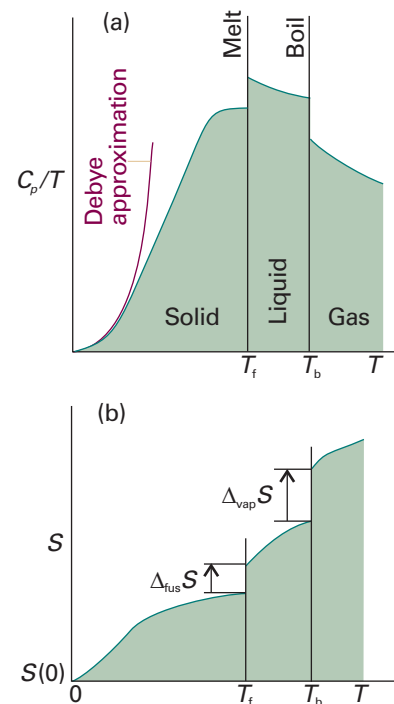


Fig. 3.14 The calculation of entropy from heat capacity data. (a) The variation of C_p/T with the temperature for a sample. (b) The entropy, which is equal to the area beneath the upper curve up to the corresponding temperature, plus the entropy of each phase transition passed.

Exploration Allow for the temperature dependence of the heat capacity by writing $C = a + bT + c/T^2$, and plot the change in entropy for different values of the three coefficients (including negative values of c).

Illustration 3.4 Calculating a standard molar entropy

The standard molar entropy of nitrogen gas at 25°C has been calculated from the following data:

| | $S_m^\circ/(\text{J K}^{-1} \text{ mol}^{-1})$ |
|---------------------------------------|--|
| Debye extrapolation | 1.92 |
| Integration, from 10 K to 35.61 K | 25.25 |
| Phase transition at 35.61 K | 6.43 |
| Integration, from 35.61 K to 63.14 K | 23.38 |
| Fusion at 63.14 K | 11.42 |
| Integration, from 63.14 K to 77.32 K | 11.41 |
| Vaporization at 77.32 K | 72.13 |
| Integration, from 77.32 K to 298.15 K | 39.20 |
| Correction for gas imperfection | 0.92 |
| Total | 192.06 |

Therefore,

$$S_m(298.15 \text{ K}) = S_m(0) + 192.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

Example 3.3 Calculating the entropy at low temperatures

The molar constant-pressure heat capacity of a certain solid at 4.2 K is $0.43 \text{ J K}^{-1} \text{ mol}^{-1}$. What is its molar entropy at that temperature?

Method Because the temperature is so low, we can assume that the heat capacity varies with temperature as aT^3 , in which case we can use eqn 3.18 to calculate the entropy at a temperature T in terms of the entropy at $T = 0$ and the constant a . When the integration is carried out, it turns out that the result can be expressed in terms of the heat capacity at the temperature T , so the data can be used directly to calculate the entropy.

Answer The integration required is

$$S(T) = S(0) + \int_0^T \frac{aT^3 dT}{T} = S(0) + a \int_0^T T^2 dT = S(0) + \frac{1}{3}aT^3$$

However, because aT^3 is the heat capacity at the temperature T ,

$$S(T) = S(0) + \frac{1}{3}C_p(T)$$

from which it follows that

$$S_m(10 \text{ K}) = S_m(0) + 0.14 \text{ J K}^{-1} \text{ mol}^{-1}$$

Self-test 3.5 For metals, there is also a contribution to the heat capacity from the electrons which is linearly proportional to T when the temperature is low. Find its contribution to the entropy at low temperatures. $[S(T) = S(0) + C_p(T)]$

3.4 The Third Law of thermodynamics

At $T = 0$, all energy of thermal motion has been quenched, and in a perfect crystal all the atoms or ions are in a regular, uniform array. The localization of matter and the absence of thermal motion suggest that such materials also have zero entropy. This conclusion is consistent with the molecular interpretation of entropy, because $S = 0$ if there is only one way of arranging the molecules and only one microstate is accessible (the ground state).

(a) The Nernst heat theorem

The experimental observation that turns out to be consistent with the view that the entropy of a regular array of molecules is zero at $T = 0$ is summarized by the **Nernst heat theorem**:

The entropy change accompanying any physical or chemical transformation approaches zero as the temperature approaches zero: $\Delta S \rightarrow 0$ as $T \rightarrow 0$ provided all the substances involved are perfectly crystalline.

Illustration 3.5 Using the Nernst heat theorem

Consider the entropy of the transition between orthorhombic sulfur, $S(\alpha)$, and monoclinic sulfur, $S(\beta)$, which can be calculated from the transition enthalpy (-402 J mol^{-1}) at the transition temperature (369 K):

$$\Delta_{\text{trs}}S = S_m(\alpha) - S_m(\beta) = \frac{(-402 \text{ J mol}^{-1})}{369 \text{ K}} = -1.09 \text{ J K}^{-1} \text{ mol}^{-1}$$

The two individual entropies can also be determined by measuring the heat capacities from $T = 0$ up to $T = 369 \text{ K}$. It is found that $S_m(\alpha) = S_m(\alpha, 0) + 37 \text{ J K}^{-1} \text{ mol}^{-1}$

and $S_m(\beta) = S_m(\beta, 0) + 38 \text{ J K}^{-1} \text{ mol}^{-1}$. These two values imply that at the transition temperature

$$\Delta_{\text{trs}} S = S_m(\alpha, 0) - S_m(\beta, 0) = -1 \text{ J K}^{-1} \text{ mol}^{-1}$$

On comparing this value with the one above, we conclude that $S_m(\alpha, 0) - S_m(\beta, 0) \approx 0$, in accord with the theorem.

It follows from the Nernst theorem that, if we arbitrarily ascribe the value zero to the entropies of elements in their perfect crystalline form at $T = 0$, then all perfect crystalline compounds also have zero entropy at $T = 0$ (because the change in entropy that accompanies the formation of the compounds, like the entropy of all transformations at that temperature, is zero). This conclusion is summarized by the **Third Law of thermodynamics**:

The entropy of all perfect crystalline substances is zero at $T = 0$.

As far as thermodynamics is concerned, choosing this common value as zero is then a matter of convenience. The molecular interpretation of entropy, however, justifies the value $S = 0$ at $T = 0$.

Molecular interpretation 3.3 *The statistical view of the Third Law of thermodynamics*

We saw in *Molecular interpretation 3.1* that, according to the Boltzmann formula, the entropy is zero if there is only one accessible microstate ($W = 1$). In most cases, $W = 1$ at $T = 0$ because there is only one way of achieving the lowest total energy: put all the molecules into the same, lowest state. Therefore, $S = 0$ at $T = 0$, in accord with the Third Law of thermodynamics. In certain cases, though, W may differ from 1 at $T = 0$. This is the case if there is no energy advantage in adopting a particular orientation even at absolute zero. For instance, for a diatomic molecule AB there may be almost no energy difference between the arrangements . . . AB AB AB . . . and . . . BA AB BA . . . , so $W > 1$ even at $T = 0$. If $S > 0$ at $T = 0$ we say that the substance has a **residual entropy**. Ice has a residual entropy of $3.4 \text{ J K}^{-1} \text{ mol}^{-1}$. It stems from the arrangement of the hydrogen bonds between neighbouring water molecules: a given O atom has two short O—H bonds and two long O···H bonds to its neighbours, but there is a degree of randomness in which two bonds are short and which two are long.

(b) Third-Law entropies

Entropies reported on the basis that $S(0) = 0$ are called **Third-Law entropies** (and often just ‘entropies’). When the substance is in its standard state at the temperature T , the **standard (Third-Law) entropy** is denoted $S^\circ(T)$. A list of values at 298 K is given in Table 3.3.

The **standard reaction entropy**, $\Delta_r S^\circ$, is defined, like the standard reaction enthalpy, as the difference between the molar entropies of the pure, separated products and the pure, separated reactants, all substances being in their standard states at the specified temperature:

$$\Delta_r S^\circ = \sum_{\text{Products}} \nu S_m^\circ - \sum_{\text{Reactants}} \nu S_m^\circ \quad (3.21)$$

In this expression, each term is weighted by the appropriate stoichiometric coefficient. Standard reaction entropies are likely to be positive if there is a net formation of gas in a reaction, and are likely to be negative if there is a net consumption of gas.

Synoptic Table 3.3* Standard Third-Law entropies at 298 K

| | $S_m^\circ / (\text{J K}^{-1} \text{ mol}^{-1})$ |
|--|--|
| <i>Solids</i> | |
| Graphite, C(s) | 5.7 |
| Diamond, C(s) | 2.4 |
| Sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s})$ | 360.2 |
| Iodine, $\text{I}_2(\text{s})$ | 116.1 |
| <i>Liquids</i> | |
| Benzene, $\text{C}_6\text{H}_6(\text{l})$ | 173.3 |
| Water, $\text{H}_2\text{O}(\text{l})$ | 69.9 |
| Mercury, $\text{Hg}(\text{l})$ | 76.0 |
| <i>Gases</i> | |
| Methane, $\text{CH}_4(\text{g})$ | 186.3 |
| Carbon dioxide, $\text{CO}_2(\text{g})$ | 213.7 |
| Hydrogen, $\text{H}_2(\text{g})$ | 130.7 |
| Helium, He | 126.2 |
| Ammonia, $\text{NH}_3(\text{g})$ | 126.2 |

* More values are given in the *Data section*.

Illustration 3.6 Calculating a standard reaction entropy

To calculate the standard reaction entropy of $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$ at 25°C , we use the data in Table 2.7 of the *Data Section* to write

$$\begin{aligned}\Delta_{\text{r}}S^\ominus &= S_{\text{m}}^\ominus(\text{H}_2\text{O}, \text{l}) - \{S_{\text{m}}^\ominus(\text{H}_2, \text{g}) + \tfrac{1}{2}S_{\text{m}}^\ominus(\text{O}_2, \text{g})\} \\ &= 69.9 \text{ J K}^{-1} \text{ mol}^{-1} - \{130.7 + \tfrac{1}{2}(205.0)\} \text{ J K}^{-1} \text{ mol}^{-1} \\ &= -163.4 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

The negative value is consistent with the conversion of two gases to a compact liquid.

A note on good practice Do not make the mistake of setting the standard molar entropies of elements equal to zero: they have non-zero values (provided $T > 0$), as we have already discussed.

Self-test 3.6 Calculate the standard reaction entropy for the combustion of methane to carbon dioxide and liquid water at 25°C . [$-243 \text{ J K}^{-1} \text{ mol}^{-1}$]

Just as in the discussion of enthalpies in Section 2.8, where we acknowledged that solutions of cations cannot be prepared in the absence of anions, the standard molar entropies of ions in solution are reported on a scale in which the standard entropy of the H^+ ions in water is taken as zero at all temperatures:

$$S^\ominus(\text{H}^+, \text{aq}) = 0 \quad [3.22]$$

The values based on this choice are listed in Table 2.7 in the *Data section*.⁵ Because the entropies of ions in water are values relative to the hydrogen ion in water, they may be either positive or negative. A positive entropy means that an ion has a higher molar entropy than H^+ in water and a negative entropy means that the ion has a lower molar entropy than H^+ in water. For instance, the standard molar entropy of $\text{Cl}^-(\text{aq})$ is $+57 \text{ J K}^{-1} \text{ mol}^{-1}$ and that of $\text{Mg}^{2+}(\text{aq})$ is $-128 \text{ J K}^{-1} \text{ mol}^{-1}$. Ion entropies vary as expected on the basis that they are related to the degree to which the ions order the water molecules around them in the solution. Small, highly charged ions induce local structure in the surrounding water, and the disorder of the solution is decreased more than in the case of large, singly charged ions. The absolute, Third-Law standard molar entropy of the proton in water can be estimated by proposing a model of the structure it induces, and there is some agreement on the value $-21 \text{ J K}^{-1} \text{ mol}^{-1}$. The negative value indicates that the proton induces order in the solvent.

Concentrating on the system

Entropy is the basic concept for discussing the direction of natural change, but to use it we have to analyse changes in both the system and its surroundings. We have seen that it is always very simple to calculate the entropy change in the surroundings, and we shall now see that it is possible to devise a simple method for taking that contribution into account automatically. This approach focuses our attention on the system

⁵ In terms of the language to be introduced in Section 5.1, the entropies of ions in solution are actually *partial molar entropies*, for their values include the consequences of their presence on the organization of the solvent molecules around them.

and simplifies discussions. Moreover, it is the foundation of all the applications of chemical thermodynamics that follow.

3.5 The Helmholtz and Gibbs energies

Consider a system in thermal equilibrium with its surroundings at a temperature T . When a change in the system occurs and there is a transfer of energy as heat between the system and the surroundings, the Clausius inequality, eqn 3.12, reads

$$dS - \frac{dq}{T} \geq 0 \quad (3.23)$$

We can develop this inequality in two ways according to the conditions (of constant volume or constant pressure) under which the process occurs.

(a) Criteria for spontaneity

First, consider heating at constant volume. Then, in the absence of non-expansion work, we can write $dq_V = dU$; consequently

$$dS - \frac{dU}{T} \geq 0 \quad (3.24)$$

The importance of the inequality in this form is that it expresses the criterion for spontaneous change solely in terms of the state functions of the system. The inequality is easily rearranged to

$$TdS \geq dU \quad (\text{constant } V, \text{ no additional work})^6 \quad (3.25)$$

At either constant internal energy ($dU = 0$) or constant entropy ($dS = 0$), this expression becomes, respectively,

$$dS_{U,V} \geq 0 \quad dU_{S,V} \leq 0 \quad (3.26)$$

where the subscripts indicate the constant conditions.

Equation 3.26 expresses the criteria for spontaneous change in terms of properties relating to the system. The first inequality states that, in a system at constant volume and constant internal energy (such as an isolated system), the entropy increases in a spontaneous change. That statement is essentially the content of the Second Law. The second inequality is less obvious, for it says that, if the entropy and volume of the system are constant, then the internal energy must decrease in a spontaneous change. Do not interpret this criterion as a tendency of the system to sink to lower energy. It is a disguised statement about entropy, and should be interpreted as implying that, if the entropy of the system is unchanged, then there must be an increase in entropy of the surroundings, which can be achieved only if the energy of the system decreases as energy flows out as heat.

When energy is transferred as heat at constant pressure, and there is no work other than expansion work, we can write $dq_p = dH$ and obtain

$$TdS \geq dH \quad (\text{constant } p, \text{ no additional work}) \quad (3.27)$$

At either constant enthalpy or constant entropy this inequality becomes, respectively,

$$dS_{H,p} \geq 0 \quad dH_{S,p} \leq 0 \quad (3.28)$$

The interpretations of these inequalities are similar to those of eqn 3.26. The entropy of the system at constant pressure must increase if its enthalpy remains constant (for

⁶ Recall that 'additional work' is work other than expansion work.

there can then be no change in entropy of the surroundings). Alternatively, the enthalpy must decrease if the entropy of the system is constant, for then it is essential to have an increase in entropy of the surroundings.

Because eqns 3.25 and 3.27 have the forms $dU - TdS \leq 0$ and $dH - TdS \leq 0$, respectively, they can be expressed more simply by introducing two more thermodynamic quantities. One is the **Helmholtz energy**, A , which is defined as

$$A = U - TS \quad [3.29]$$

The other is the **Gibbs energy**, G :

$$G = H - TS \quad [3.30]$$

All the symbols in these two definitions refer to the system.

When the state of the system changes at constant temperature, the two properties change as follows:

$$(a) \, dA = dU - TdS \quad (b) \, dG = dH - TdS \quad [3.31]$$

When we introduce eqns 3.25 and 3.27, respectively, we obtain the criteria of spontaneous change as

$$(a) \, dA_{T,V} \leq 0 \quad (b) \, dG_{T,p} \leq 0 \quad [3.32]$$

These inequalities are the most important conclusions from thermodynamics for chemistry. They are developed in subsequent sections and chapters.

(b) Some remarks on the Helmholtz energy

A change in a system at constant temperature and volume is spontaneous if $dA_{T,V} \leq 0$. That is, a change under these conditions is spontaneous if it corresponds to a decrease in the Helmholtz energy. Such systems move spontaneously towards states of lower A if a path is available. The criterion of equilibrium, when neither the forward nor reverse process has a tendency to occur, is

$$dA_{T,V} = 0 \quad [3.33]$$

The expressions $dA = dU - TdS$ and $dA < 0$ are sometimes interpreted as follows. A negative value of dA is favoured by a negative value of dU and a positive value of TdS . This observation suggests that the tendency of a system to move to lower A is due to its tendency to move towards states of lower internal energy and higher entropy. However, this interpretation is false (even though it is a good rule of thumb for remembering the expression for dA) because the tendency to lower A is solely a tendency towards states of greater overall entropy. Systems change spontaneously if in doing so the total entropy of the system and its surroundings increases, not because they tend to lower internal energy. The form of dA may give the impression that systems favour lower energy, but that is misleading: dS is the entropy change of the system, $-dU/T$ is the entropy change of the surroundings (when the volume of the system is constant), and their total tends to a maximum.

(c) Maximum work

It turns out that A carries a greater significance than being simply a signpost of spontaneous change: *the change in the Helmholtz function is equal to the maximum work accompanying a process*:

$$dw_{\max} = dA \quad [3.34]$$

As a result, A is sometimes called the ‘maximum work function’, or the ‘work function’.⁷

⁷ *Arbeit* is the German word for work; hence the symbol A .

Justification 3.2 *Maximum work*

To demonstrate that maximum work can be expressed in terms of the changes in Helmholtz energy, we combine the Clausius inequality $dS \geq dq/T$ in the form $TdS \geq dq$ with the First Law, $dU = dq + dw$, and obtain

$$dU \leq TdS + dw$$

(dU is smaller than the term on the right because we are replacing dq by TdS , which in general is larger.) This expression rearranges to

$$dw \geq dU - TdS$$

It follows that the most negative value of dw , and therefore the maximum energy that can be obtained from the system as work, is given by

$$dw_{\max} = dU - TdS$$

and that this work is done only when the path is traversed reversibly (because then the equality applies). Because at constant temperature $dA = dU - TdS$, we conclude that $dw_{\max} = dA$.

When a macroscopic isothermal change takes place in the system, eqn 3.34 becomes

$$w_{\max} = \Delta A \quad (3.35)$$

with

$$\Delta A = \Delta U - T\Delta S \quad (3.36)$$

This expression shows that in some cases, depending on the sign of $T\Delta S$, not all the change in internal energy may be available for doing work. If the change occurs with a decrease in entropy (of the system), in which case $T\Delta S < 0$, then the right-hand side of this equation is not as negative as ΔU itself, and consequently the maximum work is less than ΔU . For the change to be spontaneous, some of the energy must escape as heat in order to generate enough entropy in the surroundings to overcome the reduction in entropy in the system (Fig. 3.15). In this case, Nature is demanding a tax on the internal energy as it is converted into work. This is the origin of the alternative name ‘Helmholtz free energy’ for A , because ΔA is that part of the change in internal energy that we are free to use to do work.

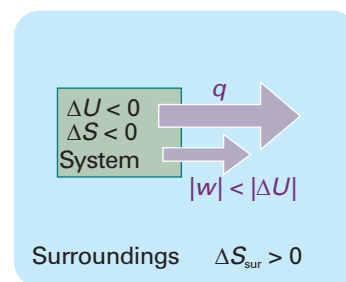


Fig. 3.15 In a system not isolated from its surroundings, the work done may be different from the change in internal energy. Moreover, the process is spontaneous if overall the entropy of the global, isolated system increases. In the process depicted here, the entropy of the system decreases, so that of the surroundings must increase in order for the process to be spontaneous, which means that energy must pass from the system to the surroundings as heat. Therefore, less work than ΔU can be obtained.

Molecular interpretation 3.4 *Maximum work and the Helmholtz energy*

Further insight into the relation between the work that a system can do and the Helmholtz energy is obtained by recalling that work is energy transferred to the surroundings as the uniform motion of atoms. We can interpret the expression $A = U - TS$ as showing that A is the total internal energy of the system, U , less a contribution that is stored as energy of thermal motion (the quantity TS). Because energy stored in random thermal motion cannot be used to achieve uniform motion in the surroundings, only the part of U that is not stored in that way, the quantity $U - TS$, is available for conversion into work.

If the change occurs with an increase of entropy of the system (in which case $T\Delta S > 0$), the right-hand side of the equation is more negative than ΔU . In this case, the maximum work that can be obtained from the system is greater than ΔU . The explanation of this apparent paradox is that the system is not isolated and energy may

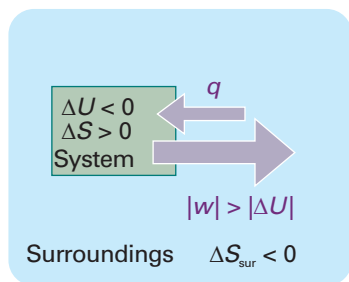


Fig. 3.16 In this process, the entropy of the system increases; hence we can afford to lose some entropy of the surroundings. That is, some of their energy may be lost as heat to the system. This energy can be returned to them as work. Hence the work done can exceed ΔU .

flow in as heat as work is done. Because the entropy of the system increases, we can afford a reduction of the entropy of the surroundings yet still have, overall, a spontaneous process. Therefore, some energy (no more than the value of $T\Delta S$) may leave the surroundings as heat and contribute to the work the change is generating (Fig. 3.16). Nature is now providing a tax refund.

Example 3.4 Calculating the maximum available work

When 1.000 mol $\text{C}_6\text{H}_{12}\text{O}_6$ (glucose) is oxidized to carbon dioxide and water at 25°C according to the equation $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6 \text{O}_2(\text{g}) \rightarrow 6 \text{CO}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{l})$, calorimetric measurements give $\Delta_r U^\circ = -2808 \text{ kJ mol}^{-1}$ and $\Delta_r S = +182.4 \text{ J K}^{-1} \text{ mol}^{-1}$ at 25°C . How much of this energy change can be extracted as (a) heat at constant pressure, (b) work?

Method We know that the heat released at constant pressure is equal to the value of ΔH , so we need to relate $\Delta_r H^\circ$ to $\Delta_r U^\circ$, which is given. To do so, we suppose that all the gases involved are perfect, and use eqn 2.21 in the form $\Delta_r H = \Delta_r U + \Delta v_g RT$. For the maximum work available from the process we use eqn 3.34.

Answer (a) Because $\Delta v_g = 0$, we know that $\Delta_r H^\circ = \Delta_r U^\circ = -2808 \text{ kJ mol}^{-1}$. Therefore, at constant pressure, the energy available as heat is 2808 kJ mol^{-1} . (b) Because $T = 298 \text{ K}$, the value of $\Delta_r A^\circ$ is

$$\Delta_r A^\circ = \Delta_r U^\circ - T\Delta_r S^\circ = -2862 \text{ kJ mol}^{-1}$$

Therefore, the combustion of 1.000 mol $\text{C}_6\text{H}_{12}\text{O}_6$ can be used to produce up to 2862 kJ of work. The maximum work available is greater than the change in internal energy on account of the positive entropy of reaction (which is partly due to the generation of a large number of small molecules from one big one). The system can therefore draw in energy from the surroundings (so reducing their entropy) and make it available for doing work.

Self-test 3.7 Repeat the calculation for the combustion of 1.000 mol $\text{CH}_4(\text{g})$ under the same conditions, using data from Table 2.5. [$|q_p| = 890 \text{ kJ}$, $|w_{\max}| = 813 \text{ kJ}$]

(d) Some remarks on the Gibbs energy

The Gibbs energy (the ‘free energy’) is more common in chemistry than the Helmholtz energy because, at least in laboratory chemistry, we are usually more interested in changes occurring at constant pressure than at constant volume. The criterion $dG_{T,p} \leq 0$ carries over into chemistry as the observation that, *at constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy*. Therefore, if we want to know whether a reaction is spontaneous, the pressure and temperature being constant, we assess the change in the Gibbs energy. If G decreases as the reaction proceeds, then the reaction has a spontaneous tendency to convert the reactants into products. If G increases, then the reverse reaction is spontaneous.

The existence of spontaneous endothermic reactions provides an illustration of the role of G . In such reactions, H increases, the system rises spontaneously to states of higher enthalpy, and $dH > 0$. Because the reaction is spontaneous we know that $dG < 0$ despite $dH > 0$; it follows that the entropy of the system increases so much that TdS outweighs dH in $dG = dH - TdS$. Endothermic reactions are therefore driven by the increase of entropy of the system, and this entropy change overcomes the reduction of entropy brought about in the surroundings by the inflow of heat into the system ($dS_{\text{sur}} = -dH/T$ at constant pressure).

(e) Maximum non-expansion work

The analogue of the maximum work interpretation of ΔA , and the origin of the name ‘free energy’, can be found for ΔG . In the *Justification* below, we show that, at constant temperature and pressure, the maximum additional (non-expansion) work, $w_{\text{add,max}}$, is given by the change in Gibbs energy:

$$dw_{\text{add,max}} = dG \quad (3.37)$$

The corresponding expression for a measurable change is

$$w_{\text{add,max}} = \Delta G \quad (3.38)$$

This expression is particularly useful for assessing the electrical work that may be produced by fuel cells and electrochemical cells, and we shall see many applications of it.

Justification 3.3 *Maximum non-expansion work*

Because $H = U + pV$, for a general change in conditions, the change in enthalpy is

$$dH = dq + dw + d(pV)$$

The corresponding change in Gibbs energy ($G = H - TS$) is

$$dG = dH - TdS - SdT = dq + dw + d(pV) - TdS - SdT$$

When the change is isothermal we can set $dT = 0$; then

$$dG = dq + dw + d(pV) - TdS$$

When the change is reversible, $dw = dw_{\text{rev}}$ and $dq = dq_{\text{rev}} = TdS$, so for a reversible, isothermal process

$$dG = TdS + dw_{\text{rev}} + d(pV) - TdS = dw_{\text{rev}} + d(pV)$$

The work consists of expansion work, which for a reversible change is given by $-pdV$, and possibly some other kind of work (for instance, the electrical work of pushing electrons through a circuit or of raising a column of liquid); this additional work we denote dw_{add} . Therefore, with $d(pV) = pdV + Vdp$,

$$dG = (-pdV + dw_{\text{add,rev}}) + pdV + Vdp = dw_{\text{add,rev}} + Vdp$$

If the change occurs at constant pressure (as well as constant temperature), we can set $dp = 0$ and obtain $dG = dw_{\text{add,rev}}$. Therefore, at constant temperature and pressure, $dw_{\text{add,rev}} = dG$. However, because the process is reversible, the work done must now have its maximum value, so eqn 3.37 follows.

Example 3.5 *Calculating the maximum non-expansion work of a reaction*

How much energy is available for sustaining muscular and nervous activity from the combustion of 1.00 mol of glucose molecules under standard conditions at 37°C (blood temperature)? The standard entropy of reaction is $+182.4 \text{ J K}^{-1} \text{ mol}^{-1}$.

Method The non-expansion work available from the reaction is equal to the change in standard Gibbs energy for the reaction ($\Delta_r G^\circ$, a quantity defined more fully below). To calculate this quantity, it is legitimate to ignore the temperature-dependence of the reaction enthalpy, to obtain $\Delta_r H^\circ$ from Table 2.5, and to substitute the data into $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$.

Answer Because the standard reaction enthalpy is $-2808 \text{ kJ mol}^{-1}$, it follows that the standard reaction Gibbs energy is

$$\Delta_r G^\circ = -2808 \text{ kJ mol}^{-1} - (310 \text{ K}) \times (182.4 \text{ J K}^{-1} \text{ mol}^{-1}) = -2865 \text{ kJ mol}^{-1}$$

Therefore, $w_{\text{add,max}} = -2865 \text{ kJ}$ for the combustion of 1 mol glucose molecules, and the reaction can be used to do up to 2865 kJ of non-expansion work. To place this result in perspective, consider that a person of mass 70 kg needs to do 2.1 kJ of work to climb vertically through 3.0 m; therefore, at least 0.13 g of glucose is needed to complete the task (and in practice significantly more).

Self-test 3.8 How much non-expansion work can be obtained from the combustion of 1.00 mol $\text{CH}_4(\text{g})$ under standard conditions at 298 K? Use $\Delta_r S^\ominus = -243 \text{ J K}^{-1} \text{ mol}^{-1}$. [818 kJ]

3.6 Standard reaction Gibbs energies

Standard entropies and enthalpies of reaction can be combined to obtain the **standard Gibbs energy of reaction** (or 'standard reaction Gibbs energy'), $\Delta_r G^\ominus$:

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus \quad [3.39]$$

The standard Gibbs energy of reaction is the difference in standard molar Gibbs energies of the products and reactants in their standard states at the temperature specified for the reaction as written. As in the case of standard reaction enthalpies, it is convenient to define the **standard Gibbs energies of formation**, $\Delta_f G^\ominus$, the standard reaction Gibbs energy for the formation of a compound from its elements in their reference states.⁸ Standard Gibbs energies of formation of the elements in their reference states are zero, because their formation is a 'null' reaction. A selection of values for compounds is given in Table 3.4. From the values there, it is a simple matter to obtain the standard Gibbs energy of reaction by taking the appropriate combination:

$$\Delta_r G^\ominus = \sum_{\text{Products}} \nu \Delta_f G^\ominus - \sum_{\text{Reactants}} \nu \Delta_f G^\ominus \quad (3.40)$$

with each term weighted by the appropriate stoichiometric coefficient.

Illustration 3.7 Calculating a standard Gibbs energy of reaction

To calculate the standard Gibbs energy of the reaction $\text{CO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$ at 25°C, we write

$$\begin{aligned} \Delta_r G^\ominus &= \Delta_f G^\ominus(\text{CO}_2, \text{g}) - \{\Delta_f G^\ominus(\text{CO}, \text{g}) + \tfrac{1}{2} \Delta_f G^\ominus(\text{O}_2, \text{g})\} \\ &= -394.4 \text{ kJ mol}^{-1} - \{(-137.2) + \tfrac{1}{2}(0)\} \text{ kJ mol}^{-1} \\ &= -257.2 \text{ kJ mol}^{-1} \end{aligned}$$

Self-test 3.9 Calculate the standard reaction Gibbs energy for the combustion of $\text{CH}_4(\text{g})$ at 298 K. [−818 kJ mol^{−1}]

Synoptic Table 3.4* Standard Gibbs energies of formation (at 298 K)

| | $\Delta_f G^\ominus / (\text{kJ mol}^{-1})$ |
|---|---|
| Diamond, C(s) | +2.9 |
| Benzene, $\text{C}_6\text{H}_6(\text{l})$ | +124.3 |
| Methane, $\text{CH}_4(\text{g})$ | −50.7 |
| Carbon dioxide, $\text{CO}_2(\text{g})$ | −394.4 |
| Water, $\text{H}_2\text{O}(\text{l})$ | −237.1 |
| Ammonia, $\text{NH}_3(\text{g})$ | −16.5 |
| Sodium chloride, $\text{NaCl}(\text{s})$ | −384.1 |

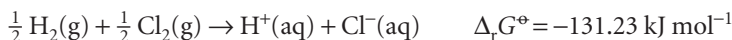
* More values are given in the *Data section*.

Just as we did in Section 2.8, where we acknowledged that solutions of cations cannot be prepared without their accompanying anions, we define one ion, conventionally the hydrogen ion, to have zero standard Gibbs energy of formation at all temperatures:

$$\Delta_f G^\ominus(\text{H}^+, \text{aq}) = 0 \quad [3.41]$$

⁸ The reference state of an element was defined in Section 2.7.

In essence, this definition adjusts the actual values of the Gibbs energies of formation of ions by a fixed amount, which is chosen so that the standard value for one of them, $\text{H}^+(\text{aq})$, has the value zero. Then for the reaction



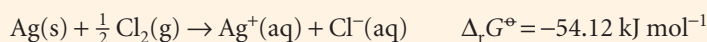
we can write

$$\Delta_r G^\ominus = \Delta_f G^\ominus(\text{H}^+, \text{aq}) + \Delta_f G^\ominus(\text{Cl}^-, \text{aq}) = \Delta_f G^\ominus(\text{Cl}^-, \text{aq})$$

and hence identify $\Delta_f G^\ominus(\text{Cl}^-, \text{aq})$ as $-131.23 \text{ kJ mol}^{-1}$. All the Gibbs energies of formation of ions tabulated in the *Data section* were calculated in the same way.

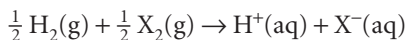
Illustration 3.8 Calculating the standard Gibbs energy of formation of an ion

With the value of $\Delta_f G^\ominus(\text{Cl}^-, \text{aq})$ established, we can find the value of $\Delta_f G^\ominus(\text{Ag}^+, \text{aq})$ from



which leads to $\Delta_f G^\ominus(\text{Ag}^+, \text{aq}) = +77.11 \text{ kJ mol}^{-1}$.

The factors responsible for the magnitude of the Gibbs energy of formation of an ion in solution can be identified by analysing it in terms of a thermodynamic cycle. As an illustration, we consider the standard Gibbs energies of formation of Cl^- in water, which is -131 kJ mol^{-1} . We do so by treating the formation reaction



as the outcome of the sequence of steps shown in Fig. 3.17 (with values taken from the *Data section*). The sum of the Gibbs energies for all the steps around a closed cycle is zero, so

$$\Delta_f G^\ominus(\text{Cl}^-, \text{aq}) = 1272 \text{ kJ mol}^{-1} + \Delta_{\text{solv}} G^\ominus(\text{H}^+) + \Delta_{\text{solv}} G^\ominus(\text{Cl}^-)$$

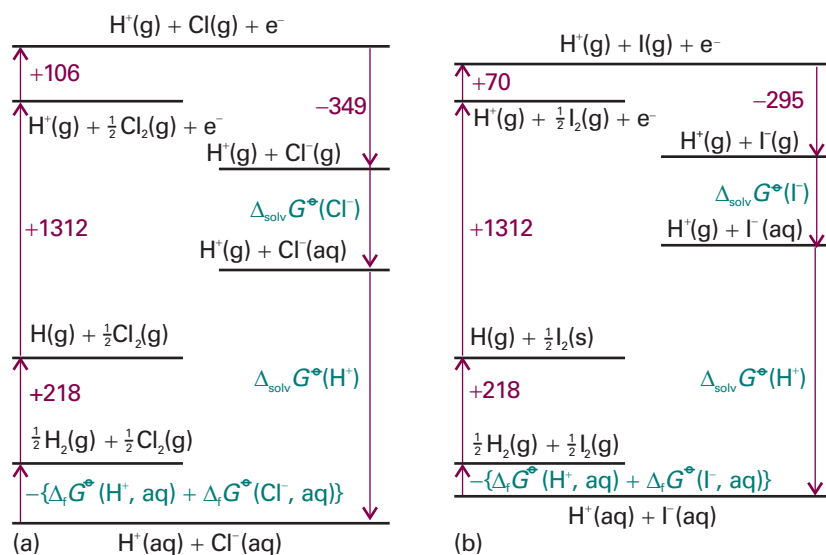


Fig. 3.17 The thermodynamic cycles for the discussion of the Gibbs energies of solvation (hydration) and formation of (a) chloride ions, (b) iodide ions in aqueous solution. The sum of the changes in Gibbs energies around the cycle sum to zero because G is a state function.

Comment 3.2

The standard Gibbs energies of formation of the gas-phase ions are unknown. We have therefore used ionization energies (the energies associated with the removal of electrons from atoms or cations in the gas phase) or electron affinities (the energies associated with the uptake of electrons by atoms or anions in the gas phase) and have assumed that any differences from the Gibbs energies arising from conversion to enthalpy and the inclusion of entropies to obtain Gibbs energies in the formation of H^+ are cancelled by the corresponding terms in the electron gain of X . The conclusions from the cycles are therefore only approximate.

An important point to note is that the value of $\Delta_f G^\circ$ of an ion X is not determined by the properties of X alone but includes contributions from the dissociation, ionization, and hydration of hydrogen.

Gibbs energies of solvation of individual ions may be estimated from an equation derived by Max Born, who identified $\Delta_{\text{solv}} G^\circ$ with the electrical work of transferring an ion from a vacuum into the solvent treated as a continuous dielectric of relative permittivity ϵ_r . The resulting **Born equation**, which is derived in *Further information 3.1*, is

$$\Delta_{\text{solv}} G^\circ = -\frac{z_i^2 e^2 N_A}{8\pi\epsilon_0 r_i} \left(1 - \frac{1}{\epsilon_r}\right) \quad (3.42a)$$

where z_i is the charge number of the ion and r_i its radius (N_A is Avogadro's constant). Note that $\Delta_{\text{solv}} G^\circ < 0$, and that $\Delta_{\text{solv}} G^\circ$ is strongly negative for small, highly charged ions in media of high relative permittivity. For water at 25°C,

$$\Delta_{\text{solv}} G^\circ = -\frac{z_i^2}{(r_i/\text{pm})} \times (6.86 \times 10^4 \text{ kJ mol}^{-1}) \quad (3.42b)$$

Illustration 3.9 Using the Born equation

To see how closely the Born equation reproduces the experimental data, we calculate the difference in the values of $\Delta_f G^\circ$ for Cl^- and I^- in water, for which $\epsilon_r = 78.54$ at 25°C, given their radii as 181 pm and 220 pm (Table 20.3), respectively, is

$$\begin{aligned} \Delta_{\text{solv}} G^\circ(\text{Cl}^-) - \Delta_{\text{solv}} G^\circ(\text{I}^-) &= -\left(\frac{1}{181} - \frac{1}{220}\right) \times (6.86 \times 10^4 \text{ kJ mol}^{-1}) \\ &= -67 \text{ kJ mol}^{-1} \end{aligned}$$

This estimated difference is in good agreement with the experimental difference, which is -61 kJ mol^{-1} .

Self-test 3.10 Estimate the value of $\Delta_{\text{solv}} G^\circ(\text{Cl}^-, \text{aq}) - \Delta_{\text{solv}} G^\circ(\text{Br}^-, \text{aq})$ from experimental data and from the Born equation.

[-26 kJ mol^{-1} experimental; -29 kJ mol^{-1} calculated]

Comment 3.3

The *NIST WebBook* is a good source of links to online databases of thermochemical data.

Calorimetry (for ΔH directly, and for S via heat capacities) is only one of the ways of determining Gibbs energies. They may also be obtained from equilibrium constants and electrochemical measurements (Chapter 7), and for gases they may be calculated using data from spectroscopic observations (Chapter 17).

Combining the First and Second Laws

The First and Second Laws of thermodynamics are both relevant to the behaviour of matter, and we can bring the whole force of thermodynamics to bear on a problem by setting up a formulation that combines them.

3.7 The fundamental equation

We have seen that the First Law of thermodynamics may be written $dU = dq + dw$. For a reversible change in a closed system of constant composition, and in the absence of

any additional (non-expansion) work, we may set $dw_{\text{rev}} = -pdV$ and (from the definition of entropy) $dq_{\text{rev}} = TdS$, where p is the pressure of the system and T its temperature. Therefore, for a reversible change in a closed system,

$$dU = TdS - pdV \quad (3.43)$$

However, because dU is an exact differential, its value is independent of path. Therefore, the same value of dU is obtained whether the change is brought about irreversibly or reversibly. Consequently, *eqn 3.43 applies to any change—reversible or irreversible—of a closed system that does no additional (non-expansion) work*. We shall call this combination of the First and Second Laws the **fundamental equation**.

The fact that the fundamental equation applies to both reversible and irreversible changes may be puzzling at first sight. The reason is that only in the case of a reversible change may TdS be identified with dq and $-pdV$ with dw . When the change is irreversible, $TdS > dq$ (the Clausius inequality) and $-pdV > dw$. The sum of dw and dq remains equal to the sum of TdS and $-pdV$, provided the composition is constant.

3.8 Properties of the internal energy

Equation 3.43 shows that the internal energy of a closed system changes in a simple way when either S or V is changed ($dU \propto dS$ and $dU \propto dV$). These simple proportionalities suggest that U should be regarded as a function of S and V . We could regard U as a function of other variables, such as S and p or T and V , because they are all interrelated; but the simplicity of the fundamental equation suggests that $U(S, V)$ is the best choice.

The *mathematical* consequence of U being a function of S and V is that we can express an infinitesimal change dU in terms of changes dS and dV by

$$dU = \left(\frac{\partial U}{\partial S} \right)_V dS + \left(\frac{\partial U}{\partial V} \right)_S dV \quad (3.44)$$

The two partial derivatives are the slopes of the plots of U against S and V , respectively. When this expression is compared to the *thermodynamic* relation, eqn 3.43, we see that, for systems of constant composition,

$$\left(\frac{\partial U}{\partial S} \right)_V = T \quad \left(\frac{\partial U}{\partial V} \right)_S = -p \quad (3.45)$$

The first of these two equations is a purely thermodynamic definition of temperature (a Zeroth-Law concept) as the ratio of the changes in the internal energy (a First-Law concept) and entropy (a Second-Law concept) of a constant-volume, closed, constant-composition system. We are beginning to generate relations between the properties of a system and to discover the power of thermodynamics for establishing unexpected relations.

(a) The Maxwell relations

An infinitesimal change in a function $f(x, y)$ can be written $df = gdx + hdy$ where g and h are functions of x and y . The mathematical criterion for df being an exact differential (in the sense that its integral is independent of path) is that

$$\left(\frac{\partial g}{\partial y} \right)_x = \left(\frac{\partial h}{\partial x} \right)_y \quad (3.46)$$

Because the fundamental equation, eqn 3.43, is an expression for an exact differential, the functions multiplying dS and dV (namely T and $-p$) must pass this test. Therefore, it must be the case that

Comment 3.4

Partial derivatives were introduced in *Comment 2.5* and are reviewed in *Appendix 2*. The type of result in eqn 3.44 was first obtained in Section 2.11, where we treated U as a function of T and V .

Comment 3.5

To illustrate the criterion set by eqn 3.46, let's test whether $df = 2xydx + x^2dy$ is an exact differential. We identify $g = 2xy$ and $h = x^2$ and form

$$\left(\frac{\partial g}{\partial y} \right)_x = \left(\frac{\partial(2xy)}{\partial y} \right)_x = 2x$$

$$\left(\frac{\partial h}{\partial x} \right)_y = \left(\frac{\partial x^2}{\partial x} \right)_y = 2x$$

Because these two coefficients are equal, df is exact.

Table 3.5 The Maxwell relations

| | |
|------------|--|
| From U : | $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$ |
| From H : | $\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$ |
| From A : | $\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$ |
| From G : | $\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$ |

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \quad (3.47)$$

We have generated a relation between quantities that, at first sight, would not seem to be related.

Equation 3.47 is an example of a **Maxwell relation**. However, apart from being unexpected, it does not look particularly interesting. Nevertheless, it does suggest that there may be other similar relations that are more useful. Indeed, we can use the fact that H , G , and A are all state functions to derive three more Maxwell relations. The argument to obtain them runs in the same way in each case: because H , G , and A are state functions, the expressions for dH , dG , and dA satisfy relations like eqn 3.47. All four relations are listed in Table 3.5 and we put them to work later in the chapter.

(b) The variation of internal energy with volume

The quantity $\pi_T = (\partial U / \partial V)_T$, which represents how the internal energy changes as the volume of a system is changed isothermally, played a central role in the manipulation of the First Law, and in *Further information 2.2* we used the relation

$$\pi_T = T \left(\frac{\partial p}{\partial T}\right)_V - p \quad (3.48)$$

This relation is called a **thermodynamic equation of state** because it is an expression for pressure in terms of a variety of thermodynamic properties of the system. We are now ready to derive it by using a Maxwell relation.

Justification 3.4 The thermodynamic equation of state

We obtain an expression for the coefficient π_T by dividing both sides of eqn 3.43 by dV , imposing the constraint of constant temperature, which gives

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_T + \left(\frac{\partial U}{\partial V}\right)_S$$

Next, we introduce the two relations in eqn 3.45 and the definition of π_T to obtain

$$\pi_T = T \left(\frac{\partial S}{\partial V}\right)_T - p$$

The third Maxwell relation in Table 3.5 turns $(\partial S / \partial V)_T$ into $(\partial p / \partial T)_V$, which completes the proof of eqn 3.48.

Example 3.6 Deriving a thermodynamic relation

Show thermodynamically that $\pi_T = 0$ for a perfect gas, and compute its value for a van der Waals gas.

Method Proving a result ‘thermodynamically’ means basing it entirely on general thermodynamic relations and equations of state, without drawing on molecular arguments (such as the existence of intermolecular forces). We know that for a perfect gas, $p = nRT/V$, so this relation should be used in eqn 3.48. Similarly, the van der Waals equation is given in Table 1.7, and for the second part of the question it should be used in eqn 3.48.

Answer For a perfect gas we write

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial(nRT/V)}{\partial T}\right)_V = \frac{nR}{V}$$

Then, eqn 3.48 becomes

$$\pi_T = \frac{nRT}{V} - p = 0$$

The equation of state of a van der Waals gas is

$$p = \frac{nRT}{V - nb} - a\frac{n^2}{V^2}$$

Because a and b are independent of temperature,

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V - nb}$$

Therefore, from eqn 3.48,

$$\pi_T = \frac{nRT}{V - nb} - \frac{nRT}{V - nb} + a\frac{n^2}{V^2} = a\frac{n^2}{V^2}$$

This result for π_T implies that the internal energy of a van der Waals gas increases when it expands isothermally (that is, $(\partial U/\partial V)_T > 0$), and that the increase is related to the parameter a , which models the attractive interactions between the particles. A larger molar volume, corresponding to a greater average separation between molecules, implies weaker mean intermolecular attractions, so the total energy is greater.

Self-test 3.11 Calculate π_T for a gas that obeys the virial equation of state (Table 1.7).
 $[\pi_T = RT^2(\partial B/\partial T)_V/V_m^2 + \dots]$

3.9 Properties of the Gibbs energy

The same arguments that we have used for U can be used for the Gibbs energy $G = H - TS$. They lead to expressions showing how G varies with pressure and temperature that are important for discussing phase transitions and chemical reactions.

(a) General considerations

When the system undergoes a change of state, G may change because H , T , and S all change. As in *Justification 2.1*, we write for infinitesimal changes in each property

$$dG = dH - d(TS) = dH - TdS - SdT$$

Because $H = U + pV$, we know that

$$dH = dU + d(pV) = dU + pdV + Vdp$$

and therefore

$$dG = dU + pdV + Vdp - TdS - SdT$$

For a closed system doing no non-expansion work, we can replace dU by the fundamental equation $dU = TdS - pdV$ and obtain

$$dG = TdS - pdV + pdV + Vdp - TdS - SdT$$

Four terms now cancel on the right, and we conclude that, for a closed system in the absence of non-expansion work and at constant composition,

$$dG = Vdp - SdT \quad (3.49)$$

This expression, which shows that a change in G is proportional to a change in p or T , suggests that G may be best regarded as a function of p and T . It confirms that G is an important quantity in chemistry because the pressure and temperature are usually the variables under our control. In other words, G carries around the combined consequences of the First and Second Laws in a way that makes it particularly suitable for chemical applications.

The same argument that led to eqn 3.45, when applied to the exact differential $dG = Vdp - SdT$, now gives

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \quad \left(\frac{\partial G}{\partial p}\right)_T = V \quad (3.50)$$

These relations show how the Gibbs energy varies with temperature and pressure (Fig. 3.18). The first implies that:

- Because $S > 0$ for all substances, G always *decreases* when the temperature is raised (at constant pressure and composition).
- Because $(\partial G/\partial T)_p$ becomes more negative as S increases, G decreases most sharply when the entropy of the system is large.

Therefore, the Gibbs energy of the gaseous phase of a substance, which has a high molar entropy, is more sensitive to temperature than its liquid and solid phases (Fig. 3.19). Similarly, the second relation implies that:

- Because $V > 0$ for all substances, G always *increases* when the pressure of the system is increased (at constant temperature and composition).

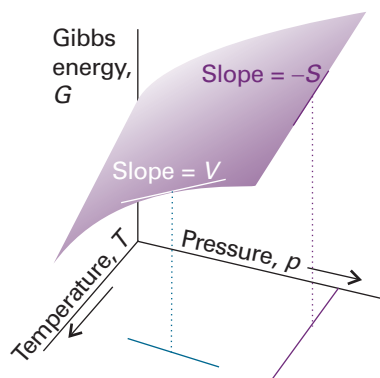


Fig. 3.18 The variation of the Gibbs energy of a system with (a) temperature at constant pressure and (b) pressure at constant temperature. The slope of the former is equal to the negative of the entropy of the system and that of the latter is equal to the volume.

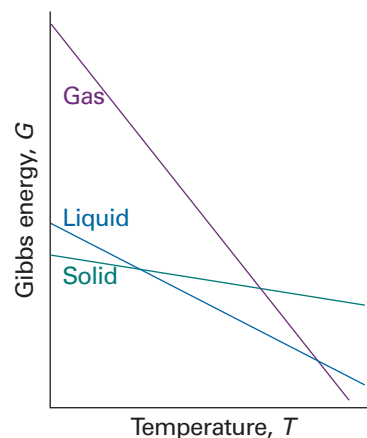


Fig. 3.19 The variation of the Gibbs energy with the temperature is determined by the entropy. Because the entropy of the gaseous phase of a substance is greater than that of the liquid phase, and the entropy of the solid phase is smallest, the Gibbs energy changes most steeply for the gas phase, followed by the liquid phase, and then the solid phase of the substance.

• Because $(\partial G/\partial p)_T$ increases with V , G is more sensitive to pressure when the volume of the system is large.

Because the molar volume of the gaseous phase of a substance is greater than that of its condensed phases, the molar Gibbs energy of a gas is more sensitive to pressure than its liquid and solid phases (Fig. 3.20).

(b) The variation of the Gibbs energy with temperature

As we remarked in the introduction, because the equilibrium composition of a system depends on the Gibbs energy, to discuss the response of the composition to temperature we need to know how G varies with temperature.

The first relation in eqn 3.50, $(\partial G/\partial T)_p = -S$, is our starting point for this discussion. Although it expresses the variation of G in terms of the entropy, we can express it in terms of the enthalpy by using the definition of G to write $S = (H - G)/T$. Then

$$\left(\frac{\partial G}{\partial T}\right)_p = \frac{G - H}{T} \quad (3.51)$$

We shall see later that the equilibrium constant of a reaction is related to G/T rather than to G itself,⁹ and it is easy to deduce from the last equation (see the *Justification* below) that

$$\left(\frac{\partial}{\partial T} \frac{G}{T}\right)_p = -\frac{H}{T^2} \quad (3.52)$$

This expression is called the **Gibbs–Helmholtz equation**. It shows that if we know the enthalpy of the system, then we know how G/T varies with temperature.

Justification 3.5 The Gibbs–Helmholtz equation

First, we note that

$$\left(\frac{\partial}{\partial T} \frac{G}{T}\right)_p = \frac{1}{T} \left(\frac{\partial G}{\partial T}\right)_p + G \frac{d}{dT} \frac{1}{T} = \frac{1}{T} \left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T^2} = \frac{1}{T} \left\{ \left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T} \right\}$$

Then we use eqn 3.51 in the form

$$\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T} = -\frac{H}{T}$$

It follows that

$$\left(\frac{\partial}{\partial T} \frac{G}{T}\right)_p = \frac{1}{T} \left\{ -\frac{H}{T} \right\} = -\frac{H}{T^2}$$

which is eqn 3.52.

The Gibbs–Helmholtz equation is most useful when it is applied to changes, including changes of physical state and chemical reactions at constant pressure. Then, because $\Delta G = G_f - G_i$ for the change of Gibbs energy between the final and initial states and because the equation applies to both G_f and G_i , we can write

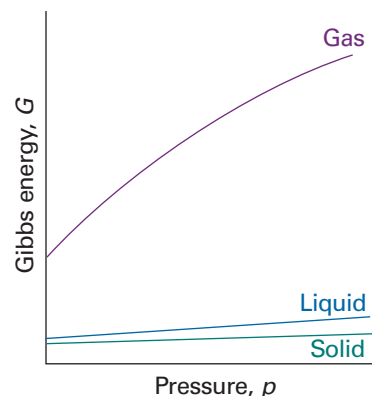


Fig. 3.20 The variation of the Gibbs energy with the pressure is determined by the volume of the sample. Because the volume of the gaseous phase of a substance is greater than that of the same amount of liquid phase, and the entropy of the solid phase is smallest (for most substances), the Gibbs energy changes most steeply for the gas phase, followed by the liquid phase, and then the solid phase of the substance. Because the volumes of the solid and liquid phases of a substance are similar, their molar Gibbs energies vary by similar amounts as the pressure is changed.

Comment 3.6

For this step, we use the rule for differentiating a product of functions (which is valid for partial derivatives as well as ordinary derivatives):

$$\frac{d(uv)}{dx} = u \frac{dv}{dx} + v \frac{du}{dx}$$

For instance, to differentiate $x^2 e^{ax}$, we write

$$\begin{aligned} \frac{d(x^2 e^{ax})}{dx} &= x^2 \frac{de^{ax}}{dx} + e^{ax} \frac{dx^2}{dx} \\ &= ax^2 e^{ax} + 2xe^{ax} \end{aligned}$$

⁹ In Section 7.2b we derive the result that the equilibrium constant for a reaction is related to its standard reaction Gibbs energy by $\Delta_r G^\circ/T = -R \ln K$.

$$\left(\frac{\partial}{\partial T} \frac{\Delta G}{T}\right)_p = -\frac{\Delta H}{T^2} \quad (3.53)$$

This equation shows that, if we know the change in enthalpy of a system that is undergoing some kind of transformation (such as vaporization or reaction), then we know how the corresponding change in Gibbs energy varies with temperature. As we shall see, this is a crucial piece of information in chemistry.

(c) The variation of the Gibbs energy with pressure

To find the Gibbs energy at one pressure in terms of its value at another pressure, the temperature being constant, we set $dT = 0$ in eqn 3.49, which gives $dG = Vdp$, and integrate:

$$G(p_f) = G(p_i) + \int_{p_i}^{p_f} V dp \quad (3.54a)$$

For molar quantities,

$$G_m(p_f) = G_m(p_i) + \int_{p_i}^{p_f} V_m dp \quad (3.54b)$$

This expression is applicable to any phase of matter, but to evaluate it we need to know how the molar volume, V_m , depends on the pressure.

The molar volume of a condensed phase changes only slightly as the pressure changes (Fig. 3.21), so we can treat V_m as a constant and take it outside the integral:

$$G_m(p_f) = G_m(p_i) + V_m \int_{p_i}^{p_f} dp = G_m(p_i) + (p_f - p_i) V_m \quad (3.55)$$

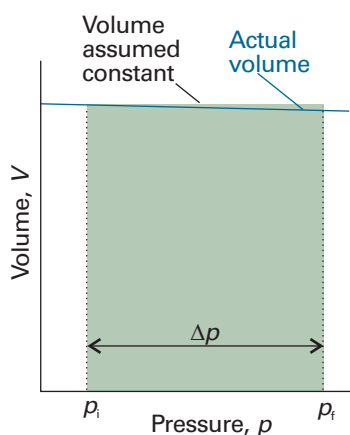


Fig. 3.21 The difference in Gibbs energy of a solid or liquid at two pressures is equal to the rectangular area shown. We have assumed that the variation of volume with pressure is negligible.

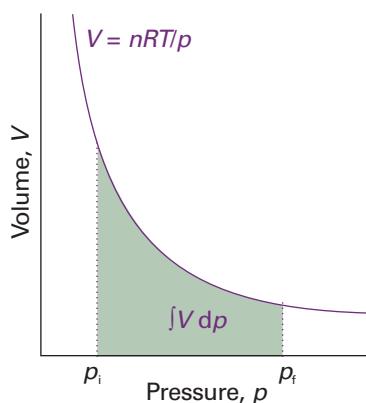


Fig. 3.22 The difference in Gibbs energy for a perfect gas at two pressures is equal to the area shown below the perfect-gas isotherm.

Self-test 3.12 Calculate the change in G_m for ice at -10°C , with density 917 kg m^{-3} , when the pressure is increased from 1.0 bar to 2.0 bar. [+2.0 J mol⁻¹]

Under normal laboratory conditions $(p_f - p_i)V_m$ is very small and may be neglected. Hence, we may usually suppose that the Gibbs energies of solids and liquids are independent of pressure. However, if we are interested in geophysical problems, then because pressures in the Earth's interior are huge, their effect on the Gibbs energy cannot be ignored. If the pressures are so great that there are substantial volume changes over the range of integration, then we must use the complete expression, eqn 3.54.

Illustration 3.10 Gibbs energies at high pressures

Suppose that for a certain phase transition of a solid $\Delta_{\text{trs}}V = +1.0 \text{ cm}^3 \text{ mol}^{-1}$ independent of pressure. Then, for an increase in pressure to 3.0 Mbar ($3.0 \times 10^{11} \text{ Pa}$) from 1.0 bar ($1.0 \times 10^5 \text{ Pa}$), the Gibbs energy of the transition changes from $\Delta_{\text{trs}}G(1 \text{ bar})$ to

$$\begin{aligned} \Delta_{\text{trs}}G(3 \text{ Mbar}) &= \Delta_{\text{trs}}G(1 \text{ bar}) + (1.0 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}) \times (3.0 \times 10^{11} \text{ Pa} - 1.0 \times 10^5 \text{ Pa}) \\ &= \Delta_{\text{trs}}G(1 \text{ bar}) + 3.0 \times 10^2 \text{ kJ mol}^{-1} \end{aligned}$$

where we have used $1 \text{ Pa m}^3 = 1 \text{ J}$.

The molar volumes of gases are large, so the Gibbs energy of a gas depends strongly on the pressure. Furthermore, because the volume also varies markedly with the pressure, we cannot treat it as a constant in the integral in eqn 3.54b (Fig. 3.22).

For a perfect gas we substitute $V_m = RT/p$ into the integral, treat RT as a constant, and find

$$G_m(p_f) = G_m(p_i) + RT \int_{p_i}^{p_f} \frac{dp}{p} = G_m(p_i) + RT \ln \frac{p_f}{p_i} \quad (3.56)^\circ$$

This expression shows that when the pressure is increased tenfold at room temperature, the molar Gibbs energy increases by $RT \ln 10 \approx 6 \text{ kJ mol}^{-1}$. It also follows from this equation that, if we set $p_i = p^\circ$ (the standard pressure of 1 bar), then the molar Gibbs energy of a perfect gas at a pressure p (set $p_f = p$) is related to its standard value by

$$G_m(p) = G_m^\circ + RT \ln \frac{p}{p^\circ} \quad (3.57)^\circ$$

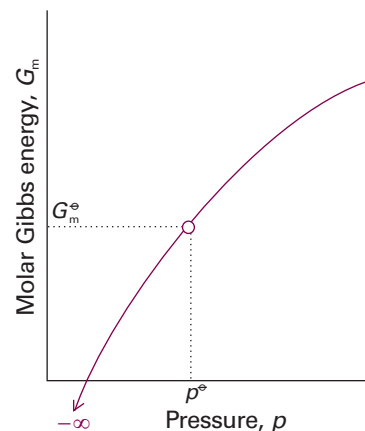


Fig. 3.23 The molar Gibbs energy potential of a perfect gas is proportional to $\ln p$, and the standard state is reached at p° . Note that, as $p \rightarrow 0$, the molar Gibbs energy becomes negatively infinite.

Exploration Show how the first derivative of G , $(\partial G/\partial p)_T$, varies with pressure, and plot the resulting expression over a pressure range. What is the physical significance of $(\partial G/\partial p)_T$?

Self-test 3.13 Calculate the change in the molar Gibbs energy of water vapour (treated as a perfect gas) when the pressure is increased isothermally from 1.0 bar to 2.0 bar at 298 K. Note that, whereas the change in molar Gibbs energy for a condensed phase (Self-test 3.12) is a few joules per mole, the answer you should get for a gas is of the order of kilojoules per mole. [+1.7 kJ mol⁻¹]

The logarithmic dependence of the molar Gibbs energy on the pressure predicted by eqn 3.57 is illustrated in Fig. 3.23. This very important expression, the consequences of which we unfold in the following chapters, applies to perfect gases (which is usually a good enough approximation). *Further information 3.2* describes how to take into account gas imperfections.

Checklist of key ideas

- | | |
|--|---|
| <ul style="list-style-type: none"> <input type="checkbox"/> 1. Kelvin statement of the Second Law of thermodynamics: No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work. <input type="checkbox"/> 2. The Second Law in terms of entropy: The entropy of an isolated system increases in the course of a spontaneous change: $\Delta S_{\text{tot}} > 0$. <input type="checkbox"/> 3. The thermodynamic definition of entropy is $dS = dq_{\text{rev}}/T$. The statistical definition of entropy is given by the Boltzmann formula, $S = k \ln W$. <input type="checkbox"/> 4. A Carnot cycle is a cycle composed of a sequence of isothermal and adiabatic reversible expansions and compressions. <input type="checkbox"/> 5. The efficiency of a heat engine is $\varepsilon = w /q_h$. The Carnot efficiency is $\varepsilon_{\text{rev}} = 1 - T_c/T_h$. <input type="checkbox"/> 6. The Kelvin scale is a thermodynamic temperature scale in which the triple point of water defines the point 273.16 K. <input type="checkbox"/> 7. The Clausius inequality is $dS \geq dq/T$. <input type="checkbox"/> 8. The normal transition temperature, T_{trs}, is the temperature at which two phases are in equilibrium at 1 atm. The entropy of transition at the transition temperature, $\Delta_{\text{trs}}S = \Delta_{\text{trs}}H/T_{\text{trs}}$. | <ul style="list-style-type: none"> <input type="checkbox"/> 9. Trouton's rule states that many normal liquids have approximately the same standard entropy of vaporization (about $85 \text{ J K}^{-1} \text{ mol}^{-1}$). <input type="checkbox"/> 10. The variation of entropy with temperature is given by $S(T_f) = S(T_i) + \int_{T_i}^{T_f} (C_p/T) dT.$ <input type="checkbox"/> 11. The entropy of a substance is measured from the area under a graph of C_p/T against T, using the Debye extrapolation at low temperatures, $C_p = aT^3$ as $T \rightarrow 0$. <input type="checkbox"/> 12. The Nernst heat theorem states that the entropy change accompanying any physical or chemical transformation approaches zero as the temperature approaches zero: $\Delta S \rightarrow 0$ as $T \rightarrow 0$ provided all the substances involved are perfectly ordered. <input type="checkbox"/> 13. Third Law of thermodynamics: The entropy of all perfect crystalline substances is zero at $T = 0$. <input type="checkbox"/> 14. The standard reaction entropy is calculated from $\Delta_r S^\circ = \sum_{\text{Products}} \nu S_m^\circ - \sum_{\text{Reactants}} \nu S_m^\circ.$ <input type="checkbox"/> 15. The standard molar entropies of ions in solution are reported on a scale in which $S^\circ(\text{H}^+, \text{aq}) = 0$ at all temperatures. |
|--|---|

- 16. The Helmholtz energy is $A = U - TS$. The Gibbs energy is $G = H - TS$.
- 17. The criteria of spontaneity may be written as: (a) $dS_{U,V} \geq 0$ and $dU_{S,V} \leq 0$, or (b) $dA_{T,V} \leq 0$ and $dG_{T,p} \leq 0$.
- 18. The criterion of equilibrium at constant temperature and volume, $dA_{T,V} = 0$. The criterion of equilibrium at constant temperature and pressure, $dG_{T,p} = 0$.
- 19. The maximum work and the Helmholtz energy are related by $w_{\max} = \Delta A$. The maximum additional (non-expansion) work and the Gibbs energy are related by $w_{\text{add,max}} = \Delta G$.
- 20. The standard Gibbs energy of reaction is given by $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ = \sum_{\text{Products}} \nu G_m^\circ - \sum_{\text{Reactants}} \nu G_m^\circ$.
- 21. The standard Gibbs energy of formation ($\Delta_f G^\circ$) is the standard reaction Gibbs energy for the formation of a compound from its elements in their reference states.
- 22. The standard Gibbs energy of reaction may be expressed in terms of $\Delta_f G^\circ$, $\Delta_r G^\circ = \sum_{\text{Products}} \nu \Delta_f G^\circ - \sum_{\text{Reactants}} \nu \Delta_f G^\circ$.
- 23. The standard Gibbs energies of formation of ions are reported on a scale in which $\Delta_f G^\circ(\text{H}^+, \text{aq}) = 0$ at all temperatures.
- 24. The fundamental equation is $dU = TdS - pdV$.
- 25. The Maxwell relations are listed in Table 3.5.
- 26. A thermodynamic equation of state is an expression for pressure in terms of thermodynamic quantities, $\pi_T = T(\partial p/\partial T)_V - p$.
- 27. The Gibbs energy is best described as a function of pressure and temperature, $dG = Vdp - SdT$. The variation of Gibbs energy with pressure and temperature are, respectively, $(\partial G/\partial p)_T = V$ and $(\partial G/\partial T)_p = -S$.
- 28. The temperature dependence of the Gibbs energy is given by the Gibbs–Helmholtz equation, $(\partial(G/T)/\partial T)_p = -H/T^2$.
- 29. For a condensed phase, the Gibbs energy varies with pressure as $G(p_f) = G(p_i) + V_m \Delta p$. For a perfect gas, $G(p_f) = G(p_i) + nRT \ln(p_f/p_i)$.

Further reading¹⁰

Articles and texts

- N.C. Craig, Entropy analyses of four familiar processes. *J. Chem. Educ.* **65**, 760 (1988).
- J.B. Fenn, *Engines, energy, and entropy*. W.H. Freeman and Co., New York (1982).
- F.J. Hale, Heat engines and refrigerators. In *Encyclopedia of applied physics* (ed. G.L. Trigg), **7**, 303. VCH, New York (1993).
- D. Kondepudi and I. Prigogine, *Modern thermodynamics: from heat engines to dissipative structures*. Wiley, New York (1998).

P.G. Nelson, Derivation of the Second Law of thermodynamics from Boltzmann's distribution law. *J. Chem. Educ.* **65**, 390 (1988).

Sources of data and information

- M.W. Chase, Jr. (ed.), *NIST–JANAF thermochemical tables*. Published as *J. Phys. Chem. Ref. Data, Monograph no. 9*. American Institute of Physics, New York (1998).
- R.C. Weast (ed.), *Handbook of chemistry and physics*, Vol. 81. CRC Press, Boca Raton (2004).

Further information

Further information 3.1 The Born equation

The electrical concepts required in this derivation are reviewed in *Appendix 3*. The strategy of the calculation is to identify the Gibbs energy of solvation with the work of transferring an ion from a vacuum into the solvent. That work is calculated by taking the difference of the work of charging an ion when it is in the solution and the work of charging the same ion when it is in a vacuum.

The Coulomb interaction between two charges q_1 and q_2 separated by a distance r is described by the *Coulombic potential energy*:

$$V = \frac{q_1 q_2}{4\pi\epsilon r}$$

where ϵ is the medium's permittivity. The permittivity of vacuum is $\epsilon_0 = 8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$. The relative permittivity (formerly

called the 'dielectric constant') of a substance is defined as $\epsilon_r = \epsilon/\epsilon_0$. Ions do not interact as strongly in a solvent of high relative permittivity (such as water, with $\epsilon_r = 80$ at 293 K) as they do in a solvent of lower relative permittivity (such as ethanol, with $\epsilon_r = 25$ at 293 K). See Chapter 18 for more details. The potential energy of a charge q_1 in the presence of a charge q_2 can be expressed in terms of the *Coulomb potential*, ϕ :

$$V = q_1 \phi \quad \phi = \frac{q_2}{4\pi\epsilon r}$$

We model an ion as a sphere of radius r_i immersed in a medium of permittivity ϵ . It turns out that, when the charge of the sphere is q , the electric potential, ϕ , at its surface is the same as the potential due to a point charge at its centre, so we can use the last expression and write

¹⁰ See *Further reading* in Chapter 2 for additional articles, texts, and sources of thermochemical data.

$$\phi = \frac{q}{4\pi\epsilon r_i}$$

The work of bringing up a charge dq to the sphere is ϕdq . Therefore, the total work of charging the sphere from 0 to $z_i e$ is

$$w = \int_0^{z_i e} \phi dq = \frac{1}{4\pi\epsilon r_i} \int_0^{z_i e} q dq = \frac{z_i^2 e^2}{8\pi\epsilon r_i}$$

This electrical work of charging, when multiplied by Avogadro's constant, is the molar Gibbs energy for charging the ions.

The work of charging an ion in a vacuum is obtained by setting $\epsilon = \epsilon_0$, the vacuum permittivity. The corresponding value for charging the ion in a medium is obtained by setting $\epsilon = \epsilon_r \epsilon_0$, where ϵ_r is the relative permittivity of the medium. It follows that the change in molar Gibbs energy that accompanies the transfer of ions from a vacuum to a solvent is the difference of these two quantities:

$$\Delta_{\text{solv}} G^\ominus = \frac{z_i^2 e^2 N_A}{8\pi\epsilon r_i} - \frac{z_i^2 e^2 N_A}{8\pi\epsilon_0 r_i} = \frac{z_i^2 e^2 N_A}{8\pi\epsilon_r \epsilon_0 r_i} - \frac{z_i^2 e^2 N_A}{8\pi\epsilon_0 r_i} = -\frac{z_i^2 e^2 N_A}{8\pi\epsilon_0 r_i} \left(1 - \frac{1}{\epsilon_r}\right)$$

which is eqn 3.42.

Further information 3.2 Real gases: the fugacity

At various stages in the development of physical chemistry it is necessary to switch from a consideration of idealized systems to real systems. In many cases it is desirable to preserve the form of the expressions that have been derived for an idealized system. Then deviations from the idealized behaviour can be expressed most simply. For instance, the pressure-dependence of the molar Gibbs energy of a real gas might resemble that shown in Fig. 3.24. To adapt eqn 3.57 to this case, we replace the true pressure, p , by an effective pressure, called the **fugacity**,¹¹ f , and write

$$G_m = G_m^\ominus + RT \ln \frac{f}{p^\ominus} \quad [3.58]$$

The fugacity, a function of the pressure and temperature, is defined so that this relation is exactly true. Although thermodynamic expressions in terms of fugacities derived from this expression are exact, they are useful only if we know how to interpret fugacities in terms of actual pressures. To develop this relation we write the fugacity as

$$f = \phi p \quad [3.59]$$

where ϕ is the dimensionless **fugacity coefficient**, which in general depends on the temperature, the pressure, and the identity of the gas.

Equation 3.54b is true for all gases whether real or perfect.

Expressing it in terms of the fugacity by using eqn 3.58 turns it into

$$\begin{aligned} \int_{p'}^p V_m dp &= G_m(p) - G_m(p') = \left\{ G_m^\ominus + RT \ln \frac{f}{p^\ominus} \right\} - \left\{ G_m^\ominus + RT \ln \frac{f'}{p^\ominus} \right\} \\ &= RT \ln \frac{f}{f'} \end{aligned}$$

In this expression, f is the fugacity when the pressure is p and f' is the fugacity when the pressure is p' . If the gas were perfect, we would write

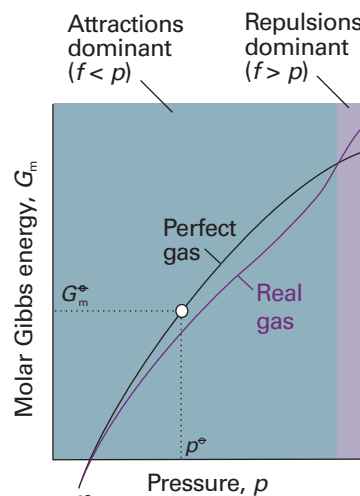


Fig. 3.24 The molar Gibbs energy of a real gas. As $p \rightarrow 0$, the molar Gibbs energy coincides with the value for a perfect gas (shown by the black line). When attractive forces are dominant (at intermediate pressures), the molar Gibbs energy is less than that of a perfect gas and the molecules have a lower ‘escaping tendency’. At high pressures, when repulsive forces are dominant, the molar Gibbs energy of a real gas is greater than that of a perfect gas. Then the ‘escaping tendency’ is increased.

$$\int_{p'}^p V_{\text{perfect, m}} dp = RT \ln \frac{p}{p'}$$

The difference between the two equations is

$$\begin{aligned} \int_{p'}^p (V_m - V_{\text{perfect, m}}) dp &= RT \left(\ln \frac{f}{f'} - \ln \frac{p}{p'} \right) = RT \ln \left(\frac{f/f'}{p/p'} \right) \\ &= RT \ln \left(\frac{f}{f'} \times \frac{p'}{p} \right) \end{aligned}$$

which can be rearranged into

$$\ln \left(\frac{f}{p} \times \frac{p'}{f'} \right) = \frac{1}{RT} \int_{p'}^p (V_m - V_{\text{perfect, m}}) dp$$

When $p' \rightarrow 0$, the gas behaves perfectly and f' becomes equal to the pressure, p' . Therefore, $f'/p' \rightarrow 1$ as $p' \rightarrow 0$. If we take this limit, which means setting $f'/p' = 1$ on the left and $p' = 0$ on the right, the last equation becomes

$$\ln \frac{f}{p} = \frac{1}{RT} \int_0^p (V_m - V_{\text{perfect, m}}) dp$$

Then, with $\phi = f/p$,

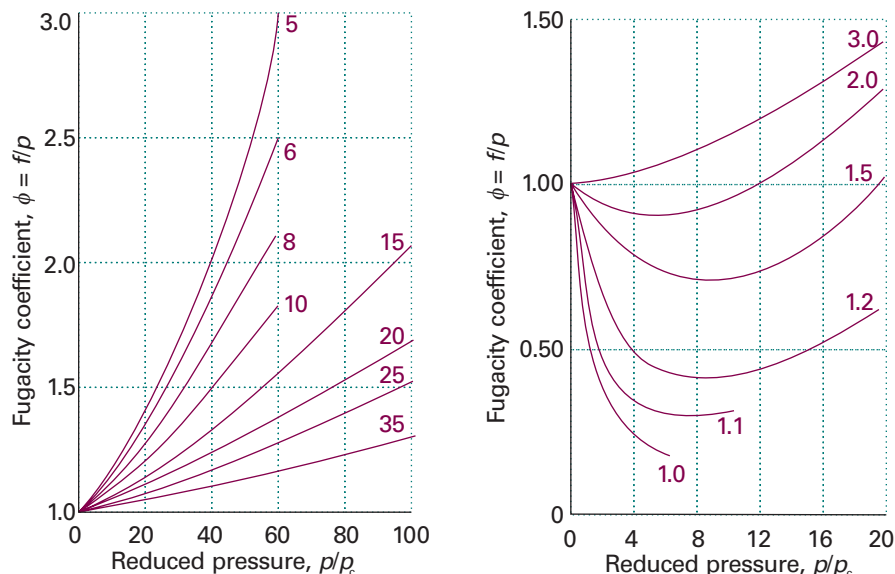
$$\ln \phi = \frac{1}{RT} \int_0^p (V_m - V_{\text{perfect, m}}) dp$$

For a perfect gas, $V_{\text{perfect, m}} = RT/p$. For a real gas, $V_m = RTZ/p$, where Z is the compression factor of the gas (Section 1.3). With these two substitutions, we obtain

¹¹ The name ‘fugacity’ comes from the Latin for ‘fleetness’ in the sense of ‘escaping tendency’; fugacity has the same dimensions as pressure.

Fig. 3.25 The fugacity coefficient of a van der Waals gas plotted using the reduced variables of the gas. The curves are labelled with the reduced temperature $T_r = T/T_c$.

Exploration Evaluate the fugacity coefficient as a function of the reduced volume of a van der Waals gas and plot the outcome for a selection of reduced temperatures over the range $0.8 \leq T_r \leq 3$.



$$\ln \phi = \int_0^p \frac{Z - 1}{p} dp \quad (3.60)$$

Provided we know how Z varies with pressure up to the pressure of interest, this expression enables us to determine the fugacity coefficient and hence, through eqn 3.59, to relate the fugacity to the pressure of the gas.

We see from Fig. 1.14 that for most gases $Z < 1$ up to moderate pressures, but that $Z > 1$ at higher pressures. If $Z < 1$ throughout the range of integration, then the integrand in eqn 3.60 is negative and $\phi < 1$. This value implies that $f < p$ (the molecules tend to stick together) and that the molar Gibbs energy of the gas is less than that of a perfect gas. At higher pressures, the range over which $Z > 1$ may dominate the range over which $Z < 1$. The integral is then positive, $\phi > 1$, and $f > p$ (the repulsive interactions are dominant and tend to drive the particles apart). Now the molar Gibbs energy of the gas is greater than that of the perfect gas at the same pressure.

Figure 3.25, which has been calculated using the full van der Waals equation of state, shows how the fugacity coefficient depends on the

Synoptic table 3.6* The fugacity of nitrogen at 273 K

| p/atm | f/atm |
|----------------|----------------|
| 1 | 0.999 55 |
| 10 | 9.9560 |
| 100 | 97.03 |
| 1000 | 1839 |

* More values are given in the *Data section*.

pressure in terms of the reduced variables (Section 1.5). Because critical constants are available in Table 1.6, the graphs can be used for quick estimates of the fugacities of a wide range of gases. Table 3.6 gives some explicit values for nitrogen.

Discussion questions

3.1 The evolution of life requires the organization of a very large number of molecules into biological cells. Does the formation of living organisms violate the Second Law of thermodynamics? State your conclusion clearly and present detailed arguments to support it.

3.2 You received an unsolicited proposal from a self-declared inventor who is seeking investors for the development of his latest idea: a device that uses heat extracted from the ground by a heat pump to boil water into steam that is used to heat a home and to power a steam engine that drives the heat pump. This procedure is potentially very lucrative because, after an initial extraction of energy from the ground, no fossil fuels would be required to keep the device running indefinitely. Would you invest in this idea? State your conclusion clearly and present detailed arguments to support it.

3.3 The following expressions have been used to establish criteria for spontaneous change: $\Delta S_{\text{tot}} > 0$, $dS_{U,V} \geq 0$ and $dU_{S,V} \leq 0$, $dA_{T,V} \leq 0$,

and $dG_{T,p} \leq 0$. Discuss the origin, significance, and applicability of each criterion.

3.4 The following expressions have been used to establish criteria for reversibility: $dA_{T,V} = 0$ and $dG_{T,p} = 0$. Discuss the origin, significance, and applicability of each criterion.

3.5 Discuss the physical interpretation of any one Maxwell relation.

3.6 Account for the dependence of π_r of a van der Waals gas in terms of the significance of the parameters a and b .

3.7 Suggest a physical interpretation of the dependence of the Gibbs energy on the pressure.

3.8 Suggest a physical interpretation of the dependence of the Gibbs energy on the temperature.

Exercises

Assume that all gases are perfect and that data refer to 298.15 K unless otherwise stated.

3.1(a) Calculate the change in entropy when 25 kJ of energy is transferred reversibly and isothermally as heat to a large block of iron at (a) 0°C, (b) 100°C.

3.1(b) Calculate the change in entropy when 50 kJ of energy is transferred reversibly and isothermally as heat to a large block of copper at (a) 0°C, (b) 70°C.

3.2(a) Calculate the molar entropy of a constant-volume sample of neon at 500 K given that it is $146.22 \text{ J K}^{-1} \text{ mol}^{-1}$ at 298 K.

3.2(b) Calculate the molar entropy of a constant-volume sample of argon at 250 K given that it is $154.84 \text{ J K}^{-1} \text{ mol}^{-1}$ at 298 K.

3.3(a) Calculate ΔS (for the system) when the state of 3.00 mol of perfect gas atoms, for which $C_{p,m} = \frac{5}{2}R$, is changed from 25°C and 1.00 atm to 125°C and 5.00 atm. How do you rationalize the sign of ΔS ?

3.3(b) Calculate ΔS (for the system) when the state of 2.00 mol diatomic perfect gas molecules, for which $C_{p,m} = \frac{7}{2}R$, is changed from 25°C and 1.50 atm to 135°C and 7.00 atm. How do you rationalize the sign of ΔS ?

3.4(a) A sample consisting of 3.00 mol of diatomic perfect gas molecules at 200 K is compressed reversibly and adiabatically until its temperature reaches 250 K. Given that $C_{v,m} = 27.5 \text{ J K}^{-1} \text{ mol}^{-1}$, calculate q , w , ΔU , ΔH , and ΔS .

3.4(b) A sample consisting of 2.00 mol of diatomic perfect gas molecules at 250 K is compressed reversibly and adiabatically until its temperature reaches 300 K. Given that $C_{v,m} = 27.5 \text{ J K}^{-1} \text{ mol}^{-1}$, calculate q , w , ΔU , ΔH , and ΔS .

3.5(a) Calculate ΔH and ΔS_{tot} when two copper blocks, each of mass 10.0 kg, one at 100°C and the other at 0°C, are placed in contact in an isolated container. The specific heat capacity of copper is $0.385 \text{ J K}^{-1} \text{ g}^{-1}$ and may be assumed constant over the temperature range involved.

3.5(b) Calculate ΔH and ΔS_{tot} when two iron blocks, each of mass 1.00 kg, one at 200°C and the other at 25°C, are placed in contact in an isolated container. The specific heat capacity of iron is $0.449 \text{ J K}^{-1} \text{ g}^{-1}$ and may be assumed constant over the temperature range involved.

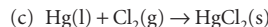
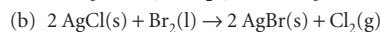
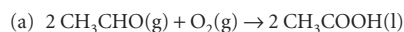
3.6(a) Consider a system consisting of 2.0 mol $\text{CO}_2(\text{g})$, initially at 25°C and 10 atm and confined to a cylinder of cross-section 10.0 cm^2 . It is allowed to expand adiabatically against an external pressure of 1.0 atm until the piston has moved outwards through 20 cm. Assume that carbon dioxide may be considered a perfect gas with $C_{v,m} = 28.8 \text{ J K}^{-1} \text{ mol}^{-1}$ and calculate (a) q , (b) w , (c) ΔU , (d) ΔT , (e) ΔS .

3.6(b) Consider a system consisting of 1.5 mol $\text{CO}_2(\text{g})$, initially at 15°C and 9.0 atm and confined to a cylinder of cross-section 100.0 cm^2 . The sample is allowed to expand adiabatically against an external pressure of 1.5 atm until the piston has moved outwards through 15 cm. Assume that carbon dioxide may be considered a perfect gas with $C_{v,m} = 28.8 \text{ J K}^{-1} \text{ mol}^{-1}$, and calculate (a) q , (b) w , (c) ΔU , (d) ΔT , (e) ΔS .

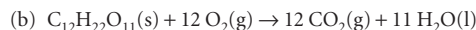
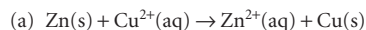
3.7(a) The enthalpy of vaporization of chloroform (CHCl_3) is 29.4 kJ mol^{-1} at its normal boiling point of 334.88 K. Calculate (a) the entropy of vaporization of chloroform at this temperature and (b) the entropy change of the surroundings.

3.7(b) The enthalpy of vaporization of methanol is $35.27 \text{ kJ mol}^{-1}$ at its normal boiling point of 64.1°C. Calculate (a) the entropy of vaporization of methanol at this temperature and (b) the entropy change of the surroundings.

3.8(a) Calculate the standard reaction entropy at 298 K of



3.8(b) Calculate the standard reaction entropy at 298 K of



3.9(a) Combine the reaction entropies calculated in Exercise 3.8a with the reaction enthalpies, and calculate the standard reaction Gibbs energies at 298 K.

3.9(b) Combine the reaction entropies calculated in Exercise 3.8b with the reaction enthalpies, and calculate the standard reaction Gibbs energies at 298 K.

3.10(a) Use standard Gibbs energies of formation to calculate the standard reaction Gibbs energies at 298 K of the reactions in Exercise 3.8a.

3.10(b) Use standard Gibbs energies of formation to calculate the standard reaction Gibbs energies at 298 K of the reactions in Exercise 3.8b.

3.11(a) Calculate the standard Gibbs energy of the reaction $4 \text{HCl}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{Cl}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$ at 298 K, from the standard entropies and enthalpies of formation given in the *Data section*.

3.11(b) Calculate the standard Gibbs energy of the reaction $\text{CO}(\text{g}) + \text{CH}_3\text{OH}(\text{l}) \rightarrow \text{CH}_3\text{COOH}(\text{l})$ at 298 K, from the standard entropies and enthalpies of formation given in the *Data section*.

3.12(a) The standard enthalpy of combustion of solid phenol ($\text{C}_6\text{H}_5\text{OH}$) is $-3054 \text{ kJ mol}^{-1}$ at 298 K and its standard molar entropy is $144.0 \text{ J K}^{-1} \text{ mol}^{-1}$. Calculate the standard Gibbs energy of formation of phenol at 298 K.

3.12(b) The standard enthalpy of combustion of solid urea ($\text{CO}(\text{NH}_2)_2$) is -632 kJ mol^{-1} at 298 K and its standard molar entropy is $104.60 \text{ J K}^{-1} \text{ mol}^{-1}$. Calculate the standard Gibbs energy of formation of urea at 298 K.

3.13(a) Calculate the change in the entropies of the system and the surroundings, and the total change in entropy, when a sample of nitrogen gas of mass 14 g at 298 K and 1.00 bar doubles its volume in (a) an isothermal reversible expansion, (b) an isothermal irreversible expansion against $p_{\text{ex}} = 0$, and (c) an adiabatic reversible expansion.

3.13(b) Calculate the change in the entropies of the system and the surroundings, and the total change in entropy, when the volume of a sample of argon gas of mass 21 g at 298 K and 1.50 bar increases from 1.20 dm^3 to 4.60 dm^3 in (a) an isothermal reversible expansion, (b) an isothermal irreversible expansion against $p_{\text{ex}} = 0$, and (c) an adiabatic reversible expansion.

3.14(a) Calculate the maximum non-expansion work per mole that may be obtained from a fuel cell in which the chemical reaction is the combustion of methane at 298 K.

3.14(b) Calculate the maximum non-expansion work per mole that may be obtained from a fuel cell in which the chemical reaction is the combustion of propane at 298 K.

3.15(a) (a) Calculate the Carnot efficiency of a primitive steam engine operating on steam at 100°C and discharging at 60°C. (b) Repeat the calculation for a modern steam turbine that operates with steam at 300°C and discharges at 80°C.

3.15(b) A certain heat engine operates between 1000 K and 500 K. (a) What is the maximum efficiency of the engine? (b) Calculate the maximum work that can be done by for each 1.0 kJ of heat supplied by the hot source. (c) How much heat is discharged into the heat sink in a reversible process for each 1.0 kJ supplied by the hot source?

3.16(a) Suppose that 3.0 mmol $\text{N}_2(\text{g})$ occupies 36 cm^3 at 300 K and expands to 60 cm^3 . Calculate ΔG for the process.

3.16(b) Suppose that 2.5 mmol $\text{Ar}(\text{g})$ occupies 72 dm^3 at 298 K and expands to 100 dm^3 . Calculate ΔG for the process.

3.17(a) The change in the Gibbs energy of a certain constant-pressure process was found to fit the expression $\Delta G/\text{J} = -85.40 + 36.5(T/\text{K})$. Calculate the value of ΔS for the process.

3.17(b) The change in the Gibbs energy of a certain constant-pressure process was found to fit the expression $\Delta G/\text{J} = -73.1 + 42.8(T/\text{K})$. Calculate the value of ΔS for the process.

3.18(a) Calculate the change in Gibbs energy of 35 g of ethanol (mass density 0.789 g cm^{-3}) when the pressure is increased isothermally from 1 atm to 3000 atm.

3.18(b) Calculate the change in Gibbs energy of 25 g of methanol (mass density 0.791 g cm^{-3}) when the pressure is increased isothermally from 100 kPa to 100 MPa.

3.19(a) Calculate the change in chemical potential of a perfect gas when its pressure is increased isothermally from 1.8 atm to 29.5 atm at 40°C .

3.19(b) Calculate the change in chemical potential of a perfect gas when its pressure is increased isothermally from 92.0 kPa to 252.0 kPa at 50°C .

3.20(a) The fugacity coefficient of a certain gas at 200 K and 50 bar is 0.72. Calculate the difference of its molar Gibbs energy from that of a perfect gas in the same state.

3.20(b) The fugacity coefficient of a certain gas at 290 K and 2.1 MPa is 0.68. Calculate the difference of its molar Gibbs energy from that of a perfect gas in the same state.

3.21(a) Estimate the change in the Gibbs energy of 1.0 dm^3 of benzene when the pressure acting on it is increased from 1.0 atm to 100 atm.

3.21(b) Estimate the change in the Gibbs energy of 1.0 dm^3 of water when the pressure acting on it is increased from 100 kPa to 300 kPa.

3.22(a) Calculate the change in the molar Gibbs energy of hydrogen gas when its pressure is increased isothermally from 1.0 atm to 100.0 atm at 298 K.

3.22(b) Calculate the change in the molar Gibbs energy of oxygen when its pressure is increased isothermally from 50.0 kPa to 100.0 kPa at 500 K.

Problems*

Assume that all gases are perfect and that data refer to 298 K unless otherwise stated.

Numerical problems

3.1 Calculate the difference in molar entropy (a) between liquid water and ice at -5°C , (b) between liquid water and its vapour at 95°C and 1.00 atm. The differences in heat capacities on melting and on vaporization are $37.3 \text{ J K}^{-1} \text{ mol}^{-1}$ and $-41.9 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. Distinguish between the entropy changes of the sample, the surroundings, and the total system, and discuss the spontaneity of the transitions at the two temperatures.

3.2 The heat capacity of chloroform (trichloromethane, CHCl_3) in the range 240 K to 330 K is given by $C_{p,m}/(\text{J K}^{-1} \text{ mol}^{-1}) = 91.47 + 7.5 \times 10^{-2}(T/\text{K})$. In a particular experiment, 1.00 mol CHCl_3 is heated from 273 K to 300 K. Calculate the change in molar entropy of the sample.

3.3 A block of copper of mass 2.00 kg ($C_{p,m} = 24.44 \text{ J K}^{-1} \text{ mol}^{-1}$) and temperature 0°C is introduced into an insulated container in which there is 1.00 mol $\text{H}_2\text{O}(\text{g})$ at 100°C and 1.00 atm. (a) Assuming all the steam is condensed to water, what will be the final temperature of the system, the heat transferred from water to copper, and the entropy change of the water, copper, and the total system? (b) In fact, some water vapour is present at equilibrium. From the vapour pressure of water at the temperature calculated in (a), and assuming that the heat capacities of both gaseous and liquid water are constant and given by their values at that temperature, obtain an improved value of the final temperature, the heat transferred, and the various entropies. (Hint. You will need to make plausible approximations.)

3.4 Consider a perfect gas contained in a cylinder and separated by a frictionless adiabatic piston into two sections A and B. All changes in B isothermal; that is, a thermostat surrounds B to keep its temperature constant. There is 2.00 mol of the gas in each section. Initially, $T_A = T_B = 300 \text{ K}$, $V_A = V_B$

$= 2.00 \text{ dm}^3$. Energy is supplied as heat to Section A and the piston moves to the right reversibly until the final volume of Section B is 1.00 dm^3 . Calculate (a) ΔS_A and ΔS_B , (b) ΔA_A and ΔA_B , (c) ΔG_A and ΔG_B , (d) ΔS of the total system and its surroundings. If numerical values cannot be obtained, indicate whether the values should be positive, negative, or zero or are indeterminate from the information given. (Assume $C_{V,m} = 20 \text{ J K}^{-1} \text{ mol}^{-1}$.)

3.5 A Carnot cycle uses 1.00 mol of a monatomic perfect gas as the working substance from an initial state of 10.0 atm and 600 K. It expands isothermally to a pressure of 1.00 atm (Step 1), and then adiabatically to a temperature of 300 K (Step 2). This expansion is followed by an isothermal compression (Step 3), and then an adiabatic compression (Step 4) back to the initial state. Determine the values of q , w , ΔU , ΔH , ΔS , ΔS_{tot} , and ΔG for each stage of the cycle and for the cycle as a whole. Express your answer as a table of values.

3.6 1.00 mol of perfect gas molecules at 27°C is expanded isothermally from an initial pressure of 3.00 atm to a final pressure of 1.00 atm in two ways: (a) reversibly, and (b) against a constant external pressure of 1.00 atm. Determine the values of q , w , ΔU , ΔH , ΔS , ΔS_{sur} , ΔS_{tot} for each path.

3.7 The standard molar entropy of $\text{NH}_3(\text{g})$ is $192.45 \text{ J K}^{-1} \text{ mol}^{-1}$ at 298 K, and its heat capacity is given by eqn 2.25 with the coefficients given in Table 2.2. Calculate the standard molar entropy at (a) 100°C and (b) 500°C .

3.8 A block of copper of mass 500 g and initially at 293 K is in thermal contact with an electric heater of resistance $1.00 \text{ k}\Omega$ and negligible mass. A current of 1.00 A is passed for 15.0 s. Calculate the change in entropy of the copper, taking $C_{p,m} = 24.4 \text{ J K}^{-1} \text{ mol}^{-1}$. The experiment is then repeated with the copper immersed in a stream of water that maintains its temperature at 293 K. Calculate the change in entropy of the copper and the water in this case.

3.9 Find an expression for the change in entropy when two blocks of the same substance and of equal mass, one at the temperature T_1 and the other at T_2 , are brought into thermal contact and allowed to reach equilibrium. Evaluate the

* Problems denoted with the symbol ‡ were supplied by Charles Trapp, Carmen Giunta, and Marshall Cady.

change for two blocks of copper, each of mass 500 g, with $C_{p,m} = 24.4 \text{ J K}^{-1} \text{ mol}^{-1}$, taking $T_h = 500 \text{ K}$ and $T_c = 250 \text{ K}$.

3.10 A gaseous sample consisting of 1.00 mol molecules is described by the equation of state $pV_m = RT(1 + Bp)$. Initially at 373 K, it undergoes Joule–Thomson expansion from 100 atm to 1.00 atm. Given that $C_{p,m} = \frac{5}{2}R$, $\mu = 0.21 \text{ K atm}^{-1}$, $B = -0.525(\text{K/T}) \text{ atm}^{-1}$, and that these are constant over the temperature range involved, calculate ΔT and ΔS for the gas.

3.11 The molar heat capacity of lead varies with temperature as follows:

| | | | | | | |
|--|------|------|------|------|------|------|
| T/K | 10 | 15 | 20 | 25 | 30 | 50 |
| $C_{p,m}/(\text{J K}^{-1} \text{ mol}^{-1})$ | 2.8 | 7.0 | 10.8 | 14.1 | 16.5 | 21.4 |
| T/K | 70 | 100 | 150 | 200 | 250 | 298 |
| $C_{p,m}/(\text{J K}^{-1} \text{ mol}^{-1})$ | 23.3 | 24.5 | 25.3 | 25.8 | 26.2 | 26.6 |

Calculate the standard Third-Law entropy of lead at (a) 0°C and (b) 25°C.

3.12 From standard enthalpies of formation, standard entropies, and standard heat capacities available from tables in the *Data section*, calculate the standard enthalpies and entropies at 298 K and 398 K for the reaction $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$. Assume that the heat capacities are constant over the temperature range involved.

3.13 The heat capacity of anhydrous potassium hexacyanoferrate(II) varies with temperature as follows:

| | | | |
|--------------|--|--------------|--|
| T/K | $C_{p,m}/(\text{J K}^{-1} \text{ mol}^{-1})$ | T/K | $C_{p,m}/(\text{J K}^{-1} \text{ mol}^{-1})$ |
| 10 | 2.09 | 100 | 179.6 |
| 20 | 14.43 | 110 | 192.8 |
| 30 | 36.44 | 150 | 237.6 |
| 40 | 62.55 | 160 | 247.3 |
| 50 | 87.03 | 170 | 256.5 |
| 60 | 111.0 | 180 | 265.1 |
| 70 | 131.4 | 190 | 273.0 |
| 80 | 149.4 | 200 | 280.3 |
| 90 | 165.3 | | |

Calculate the molar enthalpy relative to its value at $T = 0$ and the Third-Law entropy at each of these temperatures.

3.14 The compound 1,3,5-trichloro-2,4,6-trifluorobenzene is an intermediate in the conversion of hexachlorobenzene to hexafluorobenzene, and its thermodynamic properties have been examined by measuring its heat capacity over a wide temperature range (R.L. Andon and J.F. Martin, *J. Chem. Soc. Faraday Trans. I* 871 (1973)). Some of the data are as follows:

| | | | | | | |
|--|--------|--------|--------|--------|--------|--------|
| T/K | 14.14 | 16.33 | 20.03 | 31.15 | 44.08 | 64.81 |
| $C_{p,m}/(\text{J K}^{-1} \text{ mol}^{-1})$ | 9.492 | 12.70 | 18.18 | 32.54 | 46.86 | 66.36 |
| T/K | 100.90 | 140.86 | 183.59 | 225.10 | 262.99 | 298.06 |
| $C_{p,m}/(\text{J K}^{-1} \text{ mol}^{-1})$ | 95.05 | 121.3 | 144.4 | 163.7 | 180.2 | 196.4 |

Calculate the molar enthalpy relative to its value at $T = 0$ and the Third-Law molar entropy of the compound at these temperatures.

3.15† Given that $S_m^\circ = 29.79 \text{ J K}^{-1} \text{ mol}^{-1}$ for bismuth at 100 K and the following tabulated heat capacities data (D.G. Archer, *J. Chem. Eng. Data* 40, 1015 (1995)), compute the standard molar entropy of bismuth at 200 K.

| | | | | | | | |
|--|-------|-------|-------|-------|-------|-------|-------|
| T/K | 100 | 120 | 140 | 150 | 160 | 180 | 200 |
| $C_{p,m}/(\text{J K}^{-1} \text{ mol}^{-1})$ | 23.00 | 23.74 | 24.25 | 24.44 | 24.61 | 24.89 | 25.11 |

Compare the value to the value that would be obtained by taking the heat capacity to be constant at $24.44 \text{ J K}^{-1} \text{ mol}^{-1}$ over this range.

3.16 Calculate $\Delta_r G^\circ(375 \text{ K})$ for the reaction $2 \text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{CO}_2(\text{g})$ from the value of $\Delta_r G^\circ(298 \text{ K})$, $\Delta_r H^\circ(298 \text{ K})$, and the Gibbs–Helmholtz equation.

3.17 Estimate the standard reaction Gibbs energy of $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightarrow 2 \text{NH}_3(\text{g})$ at (a) 500 K, (b) 1000 K from their values at 298 K.

3.18 At 200 K, the compression factor of oxygen varies with pressure as shown below. Evaluate the fugacity of oxygen at this temperature and 100 atm.

| | | | | | | | |
|----------------|--------|---------|---------|---------|--------|--------|--------|
| p/atm | 1.0000 | 4.00000 | 7.00000 | 10.0000 | 40.00 | 70.00 | 100.0 |
| Z | 0.9971 | 0.98796 | 0.97880 | 0.96956 | 0.8734 | 0.7764 | 0.6871 |

Theoretical problems

3.19 Represent the Carnot cycle on a temperature–entropy diagram and show that the area enclosed by the cycle is equal to the work done.

3.20 Prove that two reversible adiabatic paths can never cross. Assume that the energy of the system under consideration is a function of temperature only. (*Hint*. Suppose that two such paths can intersect, and complete a cycle with the two paths plus one isothermal path. Consider the changes accompanying each stage of the cycle and show that they conflict with the Kelvin statement of the Second Law.)

3.21 Prove that the perfect gas temperature scale and the thermodynamic temperature scale based on the Second Law of thermodynamics differ from each other by at most a constant numerical factor.

3.22 The molar Gibbs energy of a certain gas is given by $G_m = RT \ln p + A + Bp + \frac{1}{2}Cp^2 + \frac{1}{3}Dp^3$, where A , B , C , and D are constants. Obtain the equation of state of the gas.

3.23 Evaluate $(\partial S/\partial V)_T$ for (a) a van der Waals gas, (b) a Dieterici gas (Table 1.7). For an isothermal expansion, for which kind of gas (and a perfect gas) will ΔS be greatest? Explain your conclusion.

3.24 Show that, for a perfect gas, $(\partial U/\partial S)_V = T$ and $(\partial U/\partial V)_S = -p$.

3.25 Two of the four Maxwell relations were derived in the text, but two were not. Complete their derivation by showing that $(\partial S/\partial T)_V = (\partial p/\partial T)_V$ and $(\partial T/\partial p)_S = (\partial V/\partial S)_p$.

3.26 Use the Maxwell relations to express the derivatives (a) $(\partial S/\partial V)_T$ and $(\partial V/\partial S)_p$ and (b) $(\partial p/\partial S)_V$ and $(\partial V/\partial S)_p$ in terms of the heat capacities, the expansion coefficient α , and the isothermal compressibility, κ_T .

3.27 Use the Maxwell relations to show that the entropy of a perfect gas depends on the volume as $S \propto R \ln V$.

3.28 Derive the thermodynamic equation of state

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_p$$

Derive an expression for $(\partial H/\partial p)_T$ for (a) a perfect gas and (b) a van der Waals gas. In the latter case, estimate its value for 1.0 mol Ar(g) at 298 K and 10 atm. By how much does the enthalpy of the argon change when the pressure is increased isothermally to 11 atm?

3.29 Show that if $B(T)$ is the second virial coefficient of a gas, and $\Delta B = B(T'') - B(T')$, $\Delta T = T'' - T'$, and T is the mean of T'' and T' , then $\pi_T \approx RT^2 \Delta B/V_m^2 \Delta T$. Estimate π_T for argon given that $B(250 \text{ K}) = -28.0 \text{ cm}^3 \text{ mol}^{-1}$ and $B(300 \text{ K}) = -15.6 \text{ cm}^3 \text{ mol}^{-1}$ at 275 K at (a) 1.0 atm, (b) 10.0 atm.

3.30 The Joule coefficient, μ_J , is defined as $\mu_J = (\partial T/\partial V)_U$. Show that $\mu_J C_V = p - \alpha T/\kappa_T$.

3.31 Evaluate π_T for a Dieterici gas (Table 1.7). Justify physically the form of the expression obtained.

3.32 The adiabatic compressibility, κ_S , is defined like κ_T (eqn 2.44) but at constant entropy. Show that for a perfect gas $p\gamma\kappa_S = 1$ (where γ is the ratio of heat capacities).

3.33 Suppose that S is regarded as a function of p and T . Show that $TdS = C_p dT - \alpha TV dp$. Hence, show that the energy transferred as heat when the pressure on an incompressible liquid or solid is increased by Δp is equal to $-\alpha TV \Delta p$. Evaluate q when the pressure acting on 100 cm³ of mercury at 0°C is increased by 1.0 kbar. ($\alpha = 1.82 \times 10^{-4} \text{ K}^{-1}$.)

3.34 Suppose that (a) the attractive interactions between gas particles can be neglected, (b) the attractive interaction is dominant in a van der Waals gas, and the pressure is low enough to make the approximation $4ap/(RT)^2 \ll 1$. Find expressions for the fugacity of a van der Waals gas in terms of the pressure and estimate its value for ammonia at 10.00 atm and 298.15 K in each case.

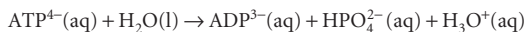
3.35 Find an expression for the fugacity coefficient of a gas that obeys the equation of state $pV_m = RT(1 + B/V_m + C/V_m^2)$. Use the resulting expression to estimate the fugacity of argon at 1.00 atm and 100 K using $B = -21.13 \text{ cm}^3 \text{ mol}^{-1}$ and $C = 1054 \text{ cm}^6 \text{ mol}^{-2}$.

Applications: to biology, environmental science, polymer science, and engineering

3.36 The protein lysozyme unfolds at a transition temperature of 75.5°C and the standard enthalpy of transition is 509 kJ mol⁻¹. Calculate the entropy of unfolding of lysozyme at 25.0°C, given that the difference in the constant-pressure heat capacities upon unfolding is 6.28 kJ K⁻¹ mol⁻¹ and can be assumed to be independent of temperature. *Hint.* Imagine that the transition at 25.0°C occurs in three steps: (i) heating of the folded protein from 25.0°C to the transition temperature, (ii) unfolding at the transition temperature, and (iii) cooling of the unfolded protein to 25.0°C. Because the entropy is a state function, the entropy change at 25.0°C is equal to the sum of the entropy changes of the steps.

3.37 At 298 K the standard enthalpy of combustion of sucrose is -5797 kJ mol⁻¹ and the standard Gibbs energy of the reaction is -6333 kJ mol⁻¹. Estimate the additional non-expansion work that may be obtained by raising the temperature to blood temperature, 37°C.

3.38 In biological cells, the energy released by the oxidation of foods (*Impact on Biology I2.2*) is stored in adenosine triphosphate (ATP or ATP⁴⁻). The essence of ATP's action is its ability to lose its terminal phosphate group by hydrolysis and to form adenosine diphosphate (ADP or ADP³⁻):



At pH = 7.0 and 37°C (310 K, blood temperature) the enthalpy and Gibbs energy of hydrolysis are $\Delta_r H = -20 \text{ kJ mol}^{-1}$ and $\Delta_r G = -31 \text{ kJ mol}^{-1}$, respectively. Under these conditions, the hydrolysis of 1 mol ATP⁴⁻(aq) results in the extraction of up to 31 kJ of energy that can be used to do non-expansion work, such as the synthesis of proteins from amino acids, muscular contraction, and the activation of neuronal circuits in our brains. (a) Calculate and account for the sign of the entropy of hydrolysis of ATP at pH = 7.0 and 310 K. (b) Suppose that the radius of a typical biological cell is 10 μm and that inside it 10⁶ ATP molecules are hydrolysed each second. What is the power density of the cell in watts per cubic metre (1 W = 1 J s⁻¹)? A computer battery delivers about 15 W and has a volume of 100 cm³. Which has the greater power density, the cell or the battery? (c) The formation of glutamine from glutamate and ammonium ions requires 14.2 kJ mol⁻¹ of energy input. It is driven by the hydrolysis of ATP to ADP mediated by the enzyme glutamine synthetase. How many moles of ATP must be hydrolysed to form 1 mol glutamine?

3.39† In 1995, the Intergovernmental Panel on Climate Change (IPCC) considered a global average temperature rise of 1.0–3.5°C likely by the year 2100, with 2.0°C its best estimate. Because water vapour is itself a greenhouse gas, the increase in water vapour content of the atmosphere is of some concern to climate change experts. Predict the relative increase in water

vapour in the atmosphere based on a temperature rises of 2.0 K, assuming that the relative humidity remains constant. (The present global mean temperature is 290 K, and the equilibrium vapour pressure of water at that temperature is 0.0189 bar.)

3.40† Nitric acid hydrates have received much attention as possible catalysts for heterogeneous reactions that bring about the Antarctic ozone hole. Worsnop *et al.* investigated the thermodynamic stability of these hydrates under conditions typical of the polar winter stratosphere (D. R. Worsnop, L.E. Fox, M.S. Zahniser, and S.C. Wofsy, *Science* **259**, 71 (1993)). They report thermodynamic data for the sublimation of mono-, di-, and trihydrates to nitric acid and water vapours, $\text{HNO}_3 \cdot n\text{H}_2\text{O}(\text{s}) \rightarrow \text{HNO}_3(\text{g}) + n\text{H}_2\text{O}(\text{g})$, for $n = 1, 2$, and 3. Given $\Delta_r G^\circ$ and $\Delta_r H^\circ$ for these reactions at 220 K, use the Gibbs–Helmholtz equation to compute $\Delta_r G^\circ$ at 190 K.

| n | 1 | 2 | 3 |
|---|------|------|------|
| $\Delta_r G^\circ/(\text{kJ mol}^{-1})$ | 46.2 | 69.4 | 93.2 |
| $\Delta_r H^\circ/(\text{kJ mol}^{-1})$ | 127 | 188 | 237 |

3.41† J. Gao and J. H. Weiner in their study of the origin of stress on the atomic level in dense polymer systems (*Science* **266**, 748 (1994)), observe that the tensile force required to maintain the length, l , of a long linear chain of N freely jointed links each of length a , can be interpreted as arising from an entropic spring. For such a chain, $S(l) = -3kl^2/2Na^2 + C$, where k is the Boltzmann constant and C is a constant. Using thermodynamic relations of this and previous chapters, show that the tensile force obeys Hooke's law, $f = -k_t l$, if we assume that the energy U is independent of l .

3.42 Suppose that an internal combustion engine runs on octane, for which the enthalpy of combustion is -5512 kJ mol⁻¹ and take the mass of 1 gallon of fuel as 3 kg. What is the maximum height, neglecting all forms of friction, to which a car of mass 1000 kg can be driven on 1.00 gallon of fuel given that the engine cylinder temperature is 2000°C and the exit temperature is 800°C?

3.43 The cycle involved in the operation of an internal combustion engine is called the *Otto cycle*. Air can be considered to be the working substance and can be assumed to be a perfect gas. The cycle consists of the following steps: (1) reversible adiabatic compression from A to B, (2) reversible constant-volume pressure increase from B to C due to the combustion of a small amount of fuel, (3) reversible adiabatic expansion from C to D, and (4) reversible and constant-volume pressure decrease back to state A. Determine the change in entropy (of the system and of the surroundings) for each step of the cycle and determine an expression for the efficiency of the cycle, assuming that the heat is supplied in Step 2. Evaluate the efficiency for a compression ratio of 10:1. Assume that, in state A, $V = 4.00 \text{ dm}^3$, $p = 1.00 \text{ atm}$, and $T = 300 \text{ K}$, that $V_A = 10V_B$, $p_C/p_B = 5$, and that $C_{p,m} = \frac{7}{2}R$.

3.44 To calculate the work required to lower the temperature of an object, we need to consider how the coefficient of performance changes with the temperature of the object. (a) Find an expression for the work of cooling an object from T_i to T_f when the refrigerator is in a room at a temperature T_h . *Hint.* Write $dw = dq/c(T)$, relate dq to dT through the heat capacity C_p , and integrate the resulting expression. Assume that the heat capacity is independent of temperature in the range of interest. (b) Use the result in part (a) to calculate the work needed to freeze 250 g of water in a refrigerator at 293 K. How long will it take when the refrigerator operates at 100 W?

3.45 The expressions that apply to the treatment of refrigerators also describe the behaviour of heat pumps, where warmth is obtained from the back of a refrigerator while its front is being used to cool the outside world. Heat pumps are popular home heating devices because they are very efficient. Compare heating of a room at 295 K by each of two methods: (a) direct conversion of 1.00 kJ of electrical energy in an electrical heater, and (b) use of 1.00 kJ of electrical energy to run a reversible heat pump with the outside at 260 K. Discuss the origin of the difference in the energy delivered to the interior of the house by the two methods.