3 The Second Law

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 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.

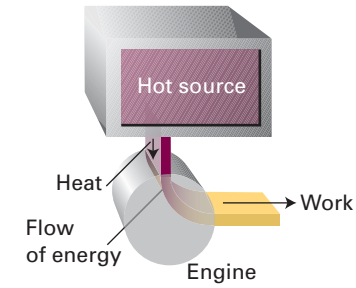

Fig. 3.1 The Kelvin statement of the Second Law denies the possibility of the process illustrated here, in which heat is changed completely into work, there being no other change. The process is not in conflict with the First Law because energy is conserved.

3.1 The dispersal of energy

Key point **During a spontaneous change in an isolated system the total energy is dispersed into random thermal motion of the particles in the system.**

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 disorderly 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

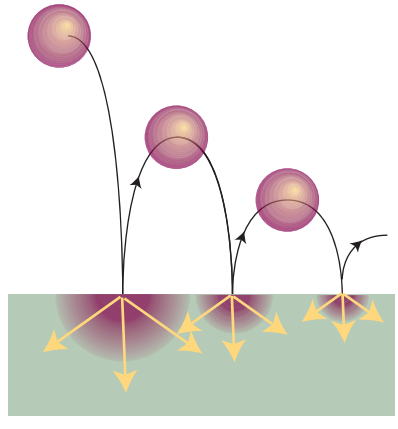

Fig. 3.2 The direction of spontaneous change for a ball bouncing on a floor. On each bounce some of its energy is degraded into the thermal motion of the atoms of the floor, and that energy disperses. The reverse has never been observed to take place on a macroscopic scale.

[1] Concerted motion, but on a much smaller scale, is observed as *Brownian motion,* the jittering motion of small particles suspended in a liquid or gas.

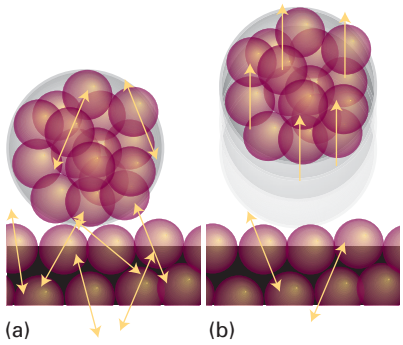

Fig. 3.3 The molecular interpretation of the irreversibility expressed by the Second Law. (a) A ball resting on a warm surface; the atoms are undergoing thermal motion (vibration, in this instance), as indicated by the arrows. (b) For the ball to fly upwards, some of the random vibrational motion would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

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 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 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

Key points **The entropy acts as a signpost of spontaneous change. (a) Entropy change is defined in terms of heat transactions (the Clausius definition). (b) Absolute entropies are defined in terms of the number of ways of achieving a configuration (the Boltzmann formula). (c) The Carnot cycle is used to prove that entropy is a state function. (d) The efficiency of a heat engine is the basis of the definition of the thermodynamic temperature scale and one realization, the Kelvin scale. (e) The Clausius inequality is used to show that the entropy increases in a spontaneous change and therefore that the Clausius definition is consistent with the Second Law.**

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, $\mathrm{d}S$, 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

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

Definition of entropy change

where q_{rev} is the heat supplied reversibly. For a measurable change between two states i and f this expression integrates to

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

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.

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 ($J\,K^{-1}\,mol^{-1}$). The units of entropy are the same as those of the gas constant, R, and molar heat capacities. Molar entropy is an intensive property.

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 $q_{rev} = -w_{rev}$ 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

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

From eqn 2.10, we know that

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

It follows that

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

• A brief illustration

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

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

Self-test 3.1 Calculate the change in entropy when the pressure of a fixed amount of perfect gas is changed isothermally from p_i to p_f. What is this change due to?

[$\Delta S = nR \ln(p_i/p_f)$; the change in volume when the gas is compressed]

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 the internal energy of the surroundings, dU_{sur}.[2] 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, delete the constraint 'reversible', and write

$$dS_{sur} = \frac{dq_{sur,rev}}{T_{sur}} = \frac{dq_{sur}}{T_{sur}} \qquad \text{Entropy change of the surroundings} \qquad (3.3a)$$

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

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

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, $q_{sur} = 0$, so

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

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.

• A brief illustration

To calculate the entropy change in the surroundings when 1.00 mol $H_2O(l)$ is formed from its elements under standard conditions at 298 K, we use $\Delta H^{\ominus} = -286$ kJ from Table 2.8. The energy released as heat is supplied to the surroundings, now regarded as being at constant pressure, so $q_{sur} = +286$ kJ. Therefore,

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

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 $N_2O_4(g)$ is formed from 2.00 mol $NO_2(g)$ under standard conditions at 298 K.
[-192 J K^{-1}]

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

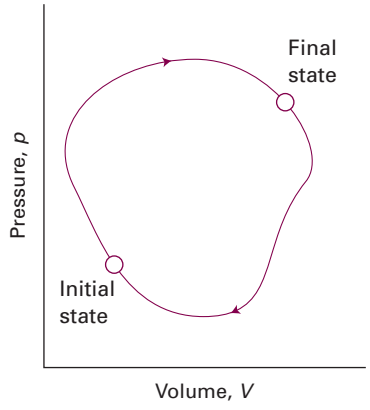

Fig. 3.5 In a thermodynamic cycle, the overall change in a state function (from the initial state to the final state and then back to the initial state again) is zero.

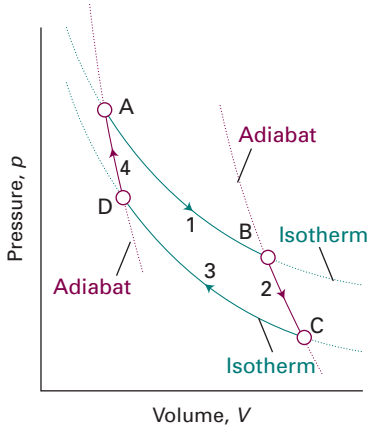

Fig. 3.6 The basic structure of a Carnot cycle. In Step 1, there is an isothermal reversible expansion at the temperature T_h. Step 2 is a reversible adiabatic expansion in which the temperature falls from T_h to T_c. In Step 3 there is an isothermal reversible compression at T_c, and that isothermal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

(c) 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

$$\oint \frac{dq_{rev}}{T_{sur}} = 0 \qquad (3.6)$$

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 the sum of the changes in each of these four steps:

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

However, we show in the following *Justification* that for a perfect gas

$$\frac{q_h}{q_c} = -\frac{T_h}{T_c} \qquad (3.7)$$

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

Justification 3.1 *Heating accompanying reversible adiabatic expansion*

This *Justification* is based on two features of the cycle. One feature is that the two temperatures T_h and T_c in eqn 3.7 lie on the same adiabat in Fig. 3.6. The second feature is that the energies transferred as heat during the two isothermal stages are

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

We now show that the two volume ratios are related in a very simple way. From the relation between temperature and volume for reversible adiabatic processes (VT^c = constant, eqn 2.28):

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

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, on cancellation of the temperatures, simplifies to

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

With this relation established, we can write

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

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 3.6 applies to any material, not just a perfect gas (which is why, in anticipation, we have not labelled it with a °). We begin this step of the argument by introducing the **efficiency**, η (eta), of a heat engine:

$$\eta = \frac{\text{work performed}}{\text{heat absorbed from hot source}} = \frac{|w|}{|q_h|} \qquad \text{Definition of efficiency} \qquad [3.8]$$

We are using modulus signs to avoid complications with signs: all efficiencies are positive numbers. 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:

$$\eta = \frac{|q_h| - |q_c|}{|q_h|} = 1 - \frac{|q_c|}{|q_h|} \qquad (3.9)$$

It then follows from eqn 3.7 (noting that the modulus signs remove the minus sign) that

$$\eta = 1 - \frac{T_c}{T_h} \qquad \text{Carnot efficiency} \qquad (3.10)_{rev}$$

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 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

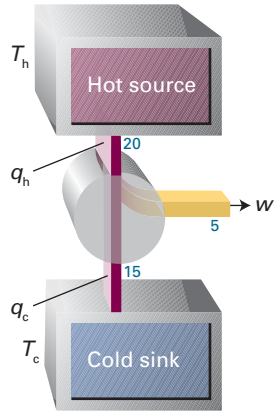

Fig. 3.7 Suppose an energy q_h (for example, 20 kJ) is supplied to the engine and q_c is lost from the engine (for example, $q_c = -15$ kJ) and discarded into the cold reservoir. The work done by the engine is equal to $q_h + q_c$ (for example, 20 kJ + (−15 kJ) = 5 kJ). The efficiency is the work done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

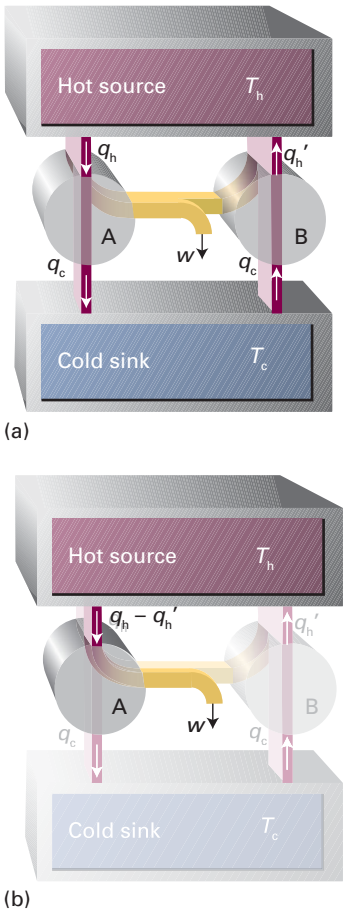

Fig. 3.8 (a) The demonstration of the equivalence of the efficiencies of all reversible engines working between the same thermal reservoirs is based on the flow of energy represented in this diagram. (b) The net effect of the processes is the conversion of heat into work without there being a need for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

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 3.10 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 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.

(d) 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

$$T = (1 - \eta)T_h \tag{3.11}$$

This expression enabled Kelvin to define the **thermodynamic temperature scale** in terms of the efficiency of a heat engine: we construct an engine in which the hot source is at a known temperature and the cold sink is the object of interest. The temperature of the latter can then be inferred from the measured efficiency of the engine. The **Kelvin scale** (which is a special case of the thermodynamic temperature scale) is defined by using water at its triple point as the notional hot source and defining that temperature as 273.16 K exactly. For instance, if it is found that the efficiency of such an engine is 0.20, then the temperature of the cold sink is $0.80 \times 273.16\ \text{K} = 220\ \text{K}$. This result is independent of the working substance of the engine.

(e) The Clausius inequality

We now show that the definition of entropy is consistent with the Second Law. To begin, we recall that more work is done when a change is reversible than when it is irreversible. That is, $|\mathrm{d}w_{\text{rev}}| \geq |\mathrm{d}w|$. Because d$w$ and dw_{rev} are negative when energy leaves the system as work, this expression is the same as $-\mathrm{d}w_{\text{rev}} \geq -\mathrm{d}w$, and hence $\mathrm{d}w - \mathrm{d}w_{\text{rev}} \geq 0$. 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:

$$\mathrm{d}U = \mathrm{d}q + \mathrm{d}w = \mathrm{d}q_{\text{rev}} + \mathrm{d}w_{\text{rev}}$$

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

$$dS \geq \frac{dq}{T} \qquad \text{Clausius inequality} \qquad (3.12)$$

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.

• A brief illustration

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. 3.10). 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

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

which is positive (because $dq_c > 0$ and $T_h > T_c$). 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

$$dS \geq 0 \qquad (3.13)$$

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.

IMPACT ON ENGINEERING

I3.1 Refrigeration

The same argument that we have used to discuss the efficiency of a heat engine can be used to discuss the efficiency of a refrigerator, a device for transferring energy as heat from a cold object (the contents of the refrigerator) to a warm sink (typically, the room in which the refrigerator stands). The less work we have to do to bring this transfer about, the more efficient is the refrigerator.

When an energy $|q_c|$ migrates from a cool source at a temperature T_c into a warmer sink at a temperature T_h, the change in entropy is

$$\Delta S = -\frac{|q_c|}{T_c} + \frac{|q_c|}{T_h} < 0 \qquad (3.14)$$

The process is not spontaneous because not enough entropy is generated in the warm sink to overcome the entropy loss from the cold source (Fig. 3.11). 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:

$$c = \frac{\text{energy transferred as heat}}{\text{energy transferred as work}} = \frac{|q_c|}{|w|} \qquad \text{Definition of coefficient of performance} \qquad [3.15]$$

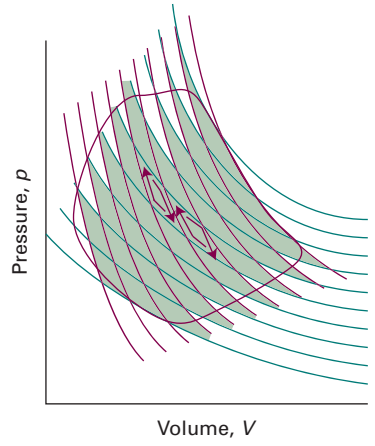

Fig. 3.9 A general cycle can be divided into small Carnot cycles. The match is exact in the limit of infinitesimally small cycles. Paths cancel in the interior of the collection, and only the perimeter, an increasingly good approximation to the true cycle as the number of cycles increases, survives.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

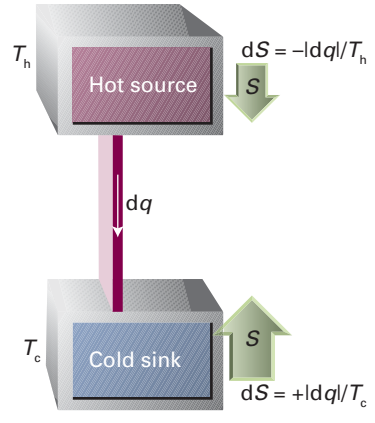

Fig. 3.10 When energy leaves a hot reservoir as heat, the entropy of the reservoir decreases. When the same quantity of energy enters a cooler reservoir, the entropy increases by a larger amount. Hence, overall there is an increase in entropy and the process is spontaneous. Relative changes in entropy are indicated by the sizes of the arrows.

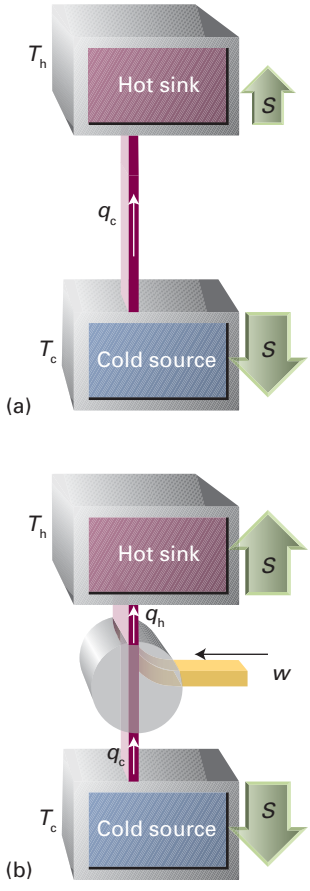

Fig. 3.11 (a) The flow of energy as heat from a cold source to a hot sink is not spontaneous. As shown here, the entropy increase of the hot sink is smaller than the entropy decrease of the cold source, so there is a net decrease in entropy. (b) The process becomes feasible if work is provided to add to the energy stream. Then the increase in entropy of the hot sink can be made to cancel the entropy decrease of the cold source.

The less the work that is required to achieve a given transfer, the greater the coefficient of performance and the more efficient is the refrigerator. For some of this development it will prove best to work with $1/c$.

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,

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

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

$$\frac{1}{c} = \frac{T_h}{T_c} - 1 = \frac{T_h - T_c}{T_c}$$

and therefore

$$c = \frac{T_c}{T_h - T_c} \qquad (3.16)_{rev}$$

for the thermodynamically optimum coefficient of performance.

• A brief illustration

For a refrigerator withdrawing heat from ice-cold water (T_c = 273 K) in a typical environment (T_h = 293 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. •

3.3 Entropy changes accompanying specific processes

Key points **(a) The entropy of a perfect gas increases when it expands isothermally. (b) The change in entropy of a substance accompanying a change of state at its transition temperature is calculated from its enthalpy of transition. (c) The increase in entropy when a substance is heated is expressed in terms of its heat capacity. (d) The entropy of a substance at a given temperature is determined from measurements of its heat capacity from $T = 0$ up to the temperature of interest, allowing for phase transitions in that range.**

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

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

Entropy change for the isothermal expansion of a perfect gas (3.17)°

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 the energy lost as heat from the system is acquired by the

surroundings, so $dq_{sur} = -dq$. For a reversible change we use the expression in Example 3.1 ($q_{rev} = nRT \ln(V_f/V_i)$); consequently, from eqn 3.3b

$$\Delta S_{sur} = \frac{q_{sur}}{T} = -\frac{q_{rev}}{T} = -nR \ln \frac{V_f}{V_i} \qquad (3.18)^\circ_{rev}$$

This change is the negative of the change in the system, so we can conclude that $\Delta S_{tot} = 0$, which is what we should expect for a reversible process. If, on the other hand, the isothermal expansion occurs freely ($w = 0$), then $q = 0$ (because $\Delta U = 0$). Consequently, $\Delta S_{sur} = 0$, and the total entropy change is given by eqn 3.17 itself:

$$\Delta S_{tot} = nR \ln \frac{V_f}{V_i} \qquad (3.19)^\circ$$

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

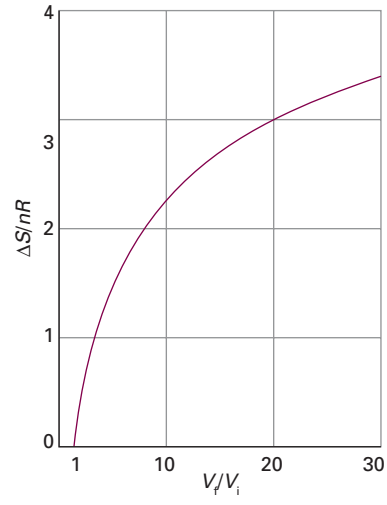

Fig. 3.12 The logarithmic increase in entropy of a perfect gas as it expands isothermally.

interActivity Evaluate the change in expansion of 1.00 mol CO_2 (g) from 0.001 m^3 to 0.010 m^3 at 298 K, treated as a van der Waals gas.

(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 liquid 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 because the two phases in the system are in equilibrium. Because at constant pressure $q = \Delta_{trs}H$, the change in molar entropy *of the system* is[3]

$$\Delta_{trs}S = \frac{\Delta_{trs}H}{T_{trs}} \qquad \text{Entropy of phase transition} \qquad (3.20)$$

If the phase transition is exothermic ($\Delta_{trs}H < 0$, as in freezing or condensing), then the entropy change of the system is negative. This decrease in entropy is consistent with the increased order of a solid compared with a liquid and with the increased order of a liquid compared with a gas. The change in entropy of the surroundings, however, is positive because energy is released as heat into them, and at the transition temperature the total change in entropy is zero. If the transition is endothermic ($\Delta_{trs}H > 0$, as in melting and vaporization), then the entropy change of the system is positive, which is consistent with dispersal of matter in the system. The entropy of the surroundings decreases by the same amount, and overall the total change in entropy is zero.

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 $J\,K^{-1}\,mol^{-1}$): this empirical observation is called **Trouton's rule**. The explanation of Trouton's rule is that a comparable change in volume occurs when any liquid evaporates and becomes a gas. Hence, all

[3] Recall from Section 2.6 that $\Delta_{trs}H$ is an enthalpy change per mole of substance; so $\Delta_{trs}S$ is also a molar quantity.

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

	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 1.8 K and 30 bar)	19.9 (at 4.22 K)

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

Table 3.2* The standard entropies of vaporization of liquids

	$\Delta_{vap}H^{\ominus}/(kJ\,mol^{-1})$	$\theta_b/°C$	$\Delta_{vap}S^{\ominus}/(J\,K^{-1}\,mol^{-1})$
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*.

liquids can be expected to have similar standard entropies of vaporization. Liquids that show significant deviations from Trouton's rule do so on account of strong molecular interactions that result in a partial ordering of their molecules. As a result, there is a greater change in disorder when the liquid turns into a vapour than for a fully disordered liquid. 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 J K^{-1} mol^{-1} at 298 K); the entropy of N_2 under the same conditions is 192 J K^{-1} mol^{-1}. As we shall see in Chapter 12, fewer rotational states are accessible at room temperature for light molecules than for heavy molecules.

• A brief illustration

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 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

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

Substitution of the data then gives

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

The experimental value is +29.45 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 another temperature T_i and the heat supplied to change its temperature from one value to the other:

$$S(T_f) = S(T_i) + \int_{T_i}^{T_f} \frac{dq_{rev}}{T} \tag{3.21}$$

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, written as $dq_{rev} = C_p dT$). Consequently, at constant pressure:

$$S(T_f) = S(T_i) + \int_{T_i}^{T_f} \frac{C_p dT}{T} \tag{3.22}$$

Entropy variation with temperature

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

$$S(T_f) = S(T_i) + C_p \int_{T_i}^{T_f} \frac{dT}{T} = S(T_i) + C_p \ln \frac{T_f}{T_i} \tag{3.23}$$

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 dm^3 is allowed to expand to 1.000 dm^3 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 3.17 and that of the second step, provided C_V is independent of temperature, by eqn 3.23 (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 molar 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 those in Table 2.8, converting to the value at constant volume by using the relation $C_{p,m} - C_{V,m} = R$.)

Answer From eqn 3.17 the entropy change of the isothermal expansion from V_i to V_f is

$$\Delta S(\text{Step 1}) = nR \ln \frac{V_f}{V_i}$$

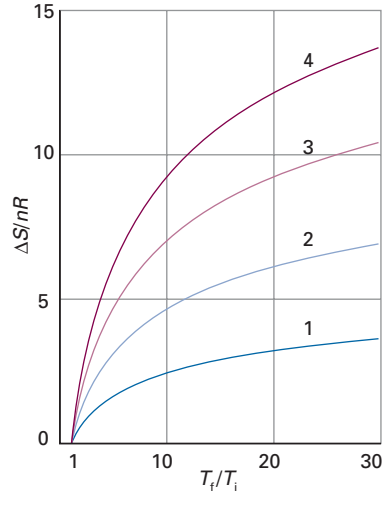

Fig. 3.13 The logarithmic increase in entropy of a substance as it is heated at constant volume. Different curves correspond to different values of the constant-volume heat capacity (which is assumed constant over the temperature range) expressed as $C_{V,m}/R$.

interActivity 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.

From eqn 3.23, the entropy change in the second step, from T_i to T_f at constant volume, is

$$\Delta S(\text{Step 2}) = nC_{V,m} \ln \frac{T_f}{T_i} = \frac{3}{2} nR \ln \frac{T_f}{T_i} = nR \ln \left(\frac{T_f}{T_i} \right)^{3/2}$$

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

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

(We have used $\ln x + \ln y = \ln xy$.) Now we substitute $n = p_i V_i / RT_i$ and obtain

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

At this point we substitute the data:

$$\Delta S = \frac{(1.00 \times 10^5 \text{ Pa}) \times (0.500 \times 10^{-3} \text{ m}^3)}{298 \text{ K}} \times \ln \left\{ \frac{1.000}{0.500} \left(\frac{373}{298} \right)^{3/2} \right\}$$

$$= +0.173 \text{ J K}^{-1}$$

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 dm^3 and cooled to −25°C. [−0.43 J K^{-1}]

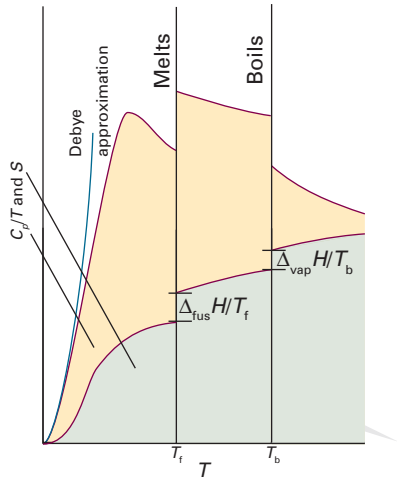

Fig. 3.14 The variation of C_p/T with the temperature for a sample is used to evaluate the entropy, which is equal to the area beneath the upper curve up to the corresponding temperature, plus the entropy of each phase transition passed.

interActivity 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).

(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 3.22, taking care to add the entropy of transition ($\Delta_{trs}H/T_{trs}$) 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 molar entropy above its boiling temperature is given by

$$S_m(T) = S_m(0) + \int_0^{T_f} \frac{C_{p,m}(s,T)}{T} dT + \frac{\Delta_{fus}H}{T_f} + \int_{T_f}^{T_b} \frac{C_{p,m}(l,T)}{T} dT + \frac{\Delta_{vap}H}{T_b} + \int_{T_b}^{T} \frac{C_{p,m}(g,T)}{T} dT \qquad (3.24)$$

All the properties required, except $S_m(0)$, 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 $C_{p,m}/T$ against T is the integral required. Because $dT/T = d \ln T$, an alternative procedure is to evaluate the area under a plot of $C_{p,m}$ 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 7.1), 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 $C_{p,m} = aT^3$ is assumed valid down to $T = 0$.

A brief illustration

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

	$S_m^{\ominus}/(\text{J K}^{-1}\text{ mol}^{-1})$
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

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

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 J K^{-1} 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 3.22 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

$$S_m(T) = S_m(0) + \int_0^T \frac{aT^3}{T}\mathrm{d}T = S_m(0) + a\int_0^T T^2\mathrm{d}T$$

$$= S_m(0) + \tfrac{1}{3}aT^3 = S_m(0) + \tfrac{1}{3}C_{p,m}(T)$$

from which it follows that

$$S_m(4.2\text{ K}) = S_m(0) + 0.14\text{ J K}^{-1}\text{ mol}^{-1}$$

Self-test 3.5 For metals, there is also a contribution to the heat capacity from the electrons that 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

Key points **(a) The Nernst heat theorem implies the Third Law of thermodynamics. (b) The Third Law allows us to define absolute entropies of substances and to define the standard entropy of a reaction.**

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 (all molecules occupy 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: $\Delta S \to 0$ as $T \to 0$ provided all the substances involved are perfectly ordered.

Nernst heat theorem

• A brief illustration

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

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

The two individual entropies can also be determined by measuring the heat capacities from $T = 0$ up to $T = 369$ K. It is found that $S_m(\alpha) = S_m(\alpha, 0) + 37$ J K^{-1} mol^{-1} and $S_m(\beta) = S_m(\beta, 0) + 38$ J K^{-1} mol^{-1}. These two values imply that at the transition temperature

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

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 $T = 0$.

Third Law of thermodynamics

As far as thermodynamics is concerned, choosing this common value as zero is a matter of convenience. The molecular interpretation of entropy, however, justifies the value $S = 0$ at $T = 0$. We saw in Section 3.2b 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 J K^{-1} 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 $S^{\ominus}(T)$. A list of values at 298 K is given in Table 3.3.

The **standard reaction entropy**, $S^{\ominus}(T)$, 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:

$$\Delta_r S^{\ominus} = \sum_{\text{Products}} \nu S_m^{\ominus} - \sum_{\text{Reactants}} \nu S_m^{\ominus} \qquad \text{(3.25a)}$$

Definition of standard reaction entropy

In this expression, each term is weighted by the appropriate stoichiometric coefficient. A more sophisticated approach is to adopt the notation introduced in Section 2.8 and to write

$$\Delta_r S^{\ominus} = \sum_J \nu_J S_m^{\ominus}(J) \qquad \text{(3.25b)}$$

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.

Table 3.3* Standard Third-Law entropies at 298 K

	$S_m^{\ominus}/(\text{J K}^{-1}\text{ mol}^{-1})$
Solids	
Graphite, C(s)	5.7
Diamond, C(s)	2.4
Sucrose, $C_{12}H_{22}O_{11}$(s)	360.2
Iodine, I_2(s)	116.1
Liquids	
Benzene, C_6H_6(l)	173.3
Water, H_2O(l)	69.9
Mercury, Hg(l)	76.0
Gases	
Methane, CH_4(g)	186.3
Carbon dioxide, CO_2(g)	213.7
Hydrogen, H_2(g)	130.7
Helium, He	126.2
Ammonia, NH_3(g)	192.4

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

• A brief illustration

To calculate the standard reaction entropy of $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ at 25°C, we use the data in Table 2.8 of the *Data section* to write

$$\begin{aligned}\Delta_r S^{\ominus} &= S_m^{\ominus}(H_2O,1) - \{S_m^{\ominus}(H_2,g) + \tfrac{1}{2}S_m^{\ominus}(O_2,g)\} \\ &= 69.9\text{ J K}^{-1}\text{ mol}^{-1} - \{130.7 + \tfrac{1}{2}(205.0)\}\text{J K}^{-1}\text{ mol}^{-1} \\ &= -163.4\text{ J K}^{-1}\text{ mol}^{-1}\end{aligned}$$

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

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

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.

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:

$$S^{\ominus}(H^+, \text{aq}) = 0 \qquad [3.26]$$

Convention for ions in solution

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

3.5 The Helmholtz and Gibbs energies

Key points **(a) The Clausius inequality implies a number of criteria for spontaneous change under a variety of conditions that may be expressed in terms of the properties of the system alone; they are summarized by introducing the Helmholtz and Gibbs energies. (b) A spontaneous process at constant temperature and volume is accompanied by a decrease in the Helmholtz energy. (c) The change in the Helmholtz energy is equal to the maximum work accompanying a process at constant temperature. (d) A spontaneous process at constant temperature and pressure is accompanied by a decrease in the Gibbs energy. (e) The change in the Gibbs energy is equal to the maximum non-expansion work accompanying a process at constant temperature and pressure.**

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 ($\mathrm{d}S \geq \mathrm{d}q/T$, eqn 3.12) reads

$$\mathrm{d}S - \frac{\mathrm{d}q}{T} \geq 0 \tag{3.27}$$

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 $\mathrm{d}q_V = \mathrm{d}U$; consequently

$$\mathrm{d}S - \frac{\mathrm{d}U}{T} \geq 0 \tag{3.28}$$

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 into

$$T\mathrm{d}S \geq \mathrm{d}U \quad \text{(constant } V\text{, no additional work)}^5 \tag{3.29}$$

At either constant internal energy ($\mathrm{d}U = 0$) or constant entropy ($\mathrm{d}S = 0$), this expression becomes, respectively,

$$\mathrm{d}S_{U,V} \geq 0 \qquad \mathrm{d}U_{S,V} \leq 0 \tag{3.30}$$

where the subscripts indicate the constant conditions.

Equation 3.30 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

[5] Recall that 'additional work' is work other than expansion work.

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

$$T\mathrm{d}S \geq \mathrm{d}H \quad \text{(constant } p\text{, no additional work)} \tag{3.31}$$

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

$$\mathrm{d}S_{H,p} \geq 0 \qquad \mathrm{d}H_{S,p} \leq 0 \tag{3.32}$$

The interpretations of these inequalities are similar to those of eqn 3.30. The entropy of the system at constant pressure must increase if its enthalpy remains constant (for 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 3.29 and 3.31 have the forms $\mathrm{d}U - T\mathrm{d}S \leq 0$ and $\mathrm{d}H - T\mathrm{d}S \leq 0$, respectively, they can be expressed more simply by introducing two more thermodynamic quantities. One is the **Helmholtz energy**, A, which is defined as

$$A = U - TS \qquad \text{Definition of Helmholtz energy} \qquad [3.33]$$

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

$$G = H - TS \qquad \text{Definition of Gibbs energy} \qquad [3.34]$$

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:

$$\text{(a) } \mathrm{d}A = \mathrm{d}U - T\mathrm{d}S \qquad \text{(b) } \mathrm{d}G = \mathrm{d}H - T\mathrm{d}S \tag{3.35}$$

When we introduce eqns 3.29 and 3.31, respectively, we obtain the criteria of spontaneous change as

$$\text{(a) } \mathrm{d}A_{T,V} \leq 0 \qquad \text{(b) } \mathrm{d}G_{T,p} \leq 0 \tag{3.36}$$

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 $\mathrm{d}A_{T,V} \leq 0$. 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

$$dA_{T,V} = 0 \tag{3.37}$$

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, as we show in the following *Justification*, 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 at constant temperature*:

$$dw_{max} = dA \tag{3.38}$$

As a result, A is sometimes called the 'maximum work function', or the 'work function'.[6]

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 of 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 3.38 becomes

$$w_{max} = \Delta A \tag{3.39}$$

Relation between A and maximum work

with

$$\Delta A = \Delta U - T\Delta S \tag{3.40}$$

[6] *Arbeit* is the German word for work; hence the symbol A.

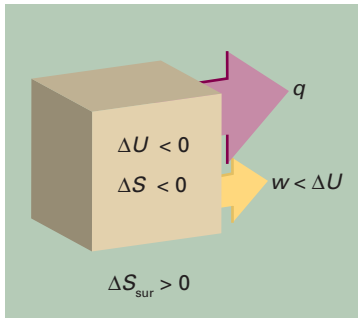

Fig. 3.16 In a system not isolated from its surroundings, the work done may be different from the change in internal energy. Moreover, the process is spontaneous if overall the entropy of the system and its surroundings increases. In the process depicted here, the entropy of the system decreases, so 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.

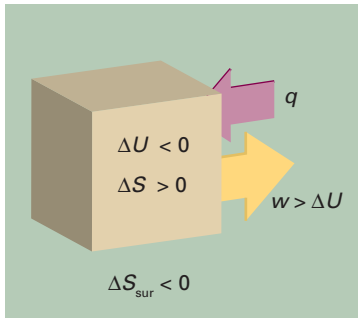

Fig. 3.17 In this process, the entropy of the system increases; hence we can afford to lose some entropy of the surroundings. That is, some of their energy may be lost as heat to the system. This energy can be returned to them as work. Hence the work done can exceed ΔU.

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. 3.16). 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.

Further insight into the relation between the work that a system can do and the Helmholtz energy is to recall 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 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. 3.17). Nature is now providing a tax refund.

Example 3.4 *Calculating the maximum available work*

When 1.000 mol $C_6H_{12}O_6$ (glucose) is oxidized to carbon dioxide and water at 25°C according to the equation $C_6H_{12}O_6(s) + 6\ O_2(g) \rightarrow 6\ CO_2(g) + 6\ H_2O(l)$, calorimetric measurements give $\Delta_r U^\ominus = -2808$ kJ mol^{-1} and $\Delta_r S^\ominus = +259.1$ J K^{-1} 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 $\Delta_r H^\ominus$ to $\Delta_r U^\ominus$, which is given. To do so, we suppose that all the gases involved are perfect, and use eqn 2.21 in the form $\Delta_r H = \Delta_r U + \Delta\nu_g RT$. For the maximum work available from the process we use eqn 3.39.

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

$$\Delta_r A^\ominus = \Delta_r U^\ominus - T\Delta_r S^\ominus = -2885 \text{ kJ mol}^{-1}$$

Therefore, the combustion of 1.000 mol $C_6H_{12}O_6$ can be used to produce up to 2885 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 $CH_4(g)$ under the same conditions, using data from Tables 2.6 and 2.8.

[$|q_p| = 890$ kJ, $|w_{max}| = 818$ 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 ($dS_{sur} = -dH/T$ 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 following *Justification*, we show that at constant temperature and pressure, the maximum additional (non-expansion) work, $w_{add,max}$, is given by the change in Gibbs energy:

$$dw_{add,max} = dG \tag{3.41a}$$

The corresponding expression for a measurable change is

$$w_{add,max} = \Delta G \tag{3.41b}$$

Relation between G and maximum non-expansion work

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, $dw = dw_{rev}$ and $dq = dq_{rev} = TdS$, so for a reversible, isothermal process

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

The work consists of expansion work, which for a reversible change is given by $-p\mathrm{d}V$, 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 $\mathrm{d}w_{\mathrm{add}}$. Therefore, with $\mathrm{d}(pV) = p\mathrm{d}V + V\mathrm{d}p$,

$$\mathrm{d}G = (-p\mathrm{d}V + \mathrm{d}w_{\mathrm{add,rev}}) + p\mathrm{d}V + V\mathrm{d}p = \mathrm{d}w_{\mathrm{add,rev}} + V\mathrm{d}p$$

If the change occurs at constant pressure (as well as constant temperature), we can set $\mathrm{d}p = 0$ and obtain $\mathrm{d}G = \mathrm{d}w_{\mathrm{add,rev}}$. Therefore, at constant temperature and pressure, $\mathrm{d}w_{\mathrm{add,rev}} = \mathrm{d}G$. However, because the process is reversible, the work done must now have its maximum value, so eqn 3.41 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 +259.1 J K^{-1} mol^{-1}.

Method The non-expansion work available from the reaction is equal to the change in standard Gibbs energy for the reaction ($\Delta_r G^\ominus$, a quantity defined more fully below). To calculate this quantity, it is legitimate to ignore the temperature-dependence of the reaction enthalpy, to obtain $\Delta_r H^\ominus$ from Tables 2.6 and 2.8, and to substitute the data into $\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$.

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

$$\Delta_r G^\ominus = -2808\ \mathrm{kJ\ mol^{-1}} - (310\ \mathrm{K}) \times (259.1\ \mathrm{J\ K^{-1}\ mol^{-1}}) = -2888\ \mathrm{kJ\ mol^{-1}}$$

Therefore, $w_{\mathrm{add,max}} = -2888$ kJ for the combustion of 1 mol glucose molecules, and the reaction can be used to do up to 2888 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 $CH_4(g)$ under standard conditions at 298 K? Use $\Delta_r S^\ominus = -243\ \mathrm{J\ K^{-1}\ mol^{-1}}$. [818 kJ]

3.6 Standard molar Gibbs energies

Key points **Standard Gibbs energies of formation are used to calculate the standard Gibbs energies of reactions. The Gibbs energies of formation of ions may be estimated from a thermodynamic cycle and the Born equation.**

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

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus \qquad \text{Definition of standard Gibbs energy of reaction} \qquad [3.42]$$

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.[7] 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:

$$\Delta_r G^\ominus = \sum_{\text{Products}} \nu \Delta_f G^\ominus - \sum_{\text{Reactants}} \nu \Delta_f G^\ominus \qquad (3.43a)$$

Procedure for calculating the standard Gibbs energy of reaction

In the notation introduced in Section 2.8,

$$\Delta_r G^\ominus = \sum_J \nu_J \Delta_f G^\ominus(J) \qquad (3.43b)$$

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

	$\Delta_f G^\ominus$/(kJ mol^{-1})
Diamond, C(s)	+2.9
Benzene, C_6H_6(l)	+124.3
Methane, CH_4(g)	−50.7
Carbon dioxide, CO_2(g)	−394.4
Water, H_2O(l)	−237.1
Ammonia, NH_3(g)	−16.5
Sodium chloride, NaCl(s)	−384.1

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

• A brief illustration

To calculate the standard Gibbs energy of the reaction $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$ at 25°C, we write

$$\begin{aligned}\Delta_r G^\ominus &= \Delta_f G^\ominus(CO_2,g) - \{\Delta_f G^\ominus(CO,g) + \tfrac{1}{2}\Delta_f G^\ominus(O_2,g)\} \\ &= -394.4 \text{ kJ mol}^{-1} - \{(-137.2) + \tfrac{1}{2}(0)\}\text{kJ mol}^{-1} \\ &= -257.2 \text{ kJ mol}^{-1}\end{aligned}$$ •

Self-test 3.9 Calculate the standard reaction Gibbs energy for the combustion of CH_4(g) at 298 K. [−818 kJ mol^{-1}]

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:

$$\Delta_f G^\ominus(H^+,aq) = 0 \qquad [3.44]$$

Convention for ions in solution

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

• A brief illustration

For the reaction

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) \rightarrow H^+(aq) + Cl^-(aq) \qquad \Delta_r G^\ominus = -131.23 \text{ kJ mol}^{-1}$$

we can write

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

and hence identify $\Delta_f G^\ominus(Cl^-,aq)$ as −131.23 kJ mol^{-1}. With the value of $\Delta_f G^\ominus(Cl^-,aq)$ established, we can find the value of $\Delta_f G^\ominus(Ag^+,aq)$ from

$$Ag(s) + \tfrac{1}{2}Cl_2(g) \rightarrow Ag^+(aq) + Cl^-(aq) \qquad \Delta_r G^\ominus = -54.12 \text{ kJ mol}^{-1}$$

which leads to $\Delta_f G^\ominus(Ag^+,aq) = +77.11$ kJ mol^{-1}. All the Gibbs energies of formation of ions tabulated in the *Data section* were calculated in the same way. •

[7] The reference state of an element was defined in Section 2.8.

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

Key point **The fundamental equation, a combination of the First and Second Laws, is an expression for the change in internal energy that accompanies changes in the volume and entropy of a system.**

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 $dw_{rev} = -pdV$ and (from the definition of entropy) $dq_{rev} = TdS$, where p is the pressure of the system and T its temperature. Therefore, for a reversible change in a closed system,

$$dU = TdS - pdV \qquad \text{The fundamental equation} \qquad (3.46)$$

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 3.46 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

Key points **Relations between thermodynamic properties are generated by combining thermodynamic and mathematical expressions for changes in their values. (a) The Maxwell relations are a series of relations between derivatives of thermodynamic properties based on criteria for changes in the properties being exact differentials. (b) The Maxwell relations are used to derive the thermodynamic equation of state and to determine how the internal energy of a substance varies with volume.**

Equation 3.46 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 is best 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

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \qquad (3.47)$$

A brief comment

Partial derivatives were introduced in *Mathematical background 2*. The type of result in eqn 3.47 was first obtained in Section 2.11, where we treated U as a function of T and V.

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 3.46, we see that, for systems of constant composition,

$$\left(\frac{\partial U}{\partial S}\right)_V = T \qquad \left(\frac{\partial U}{\partial V}\right)_S = -p \tag{3.48}$$

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 $\mathrm{d}f = g\mathrm{d}x + h\mathrm{d}y$ where g and h are functions of x and y. The mathematical criterion for $\mathrm{d}f$ being an exact differential (in the sense that its integral is independent of path) is that

$$\left(\frac{\partial g}{\partial y}\right)_x = \left(\frac{\partial h}{\partial x}\right)_y \tag{3.49}$$

This criterion is discussed in *Mathematical background 2*. Because the fundamental equation, eqn 3.46, is an expression for an exact differential, the functions multiplying $\mathrm{d}S$ and $\mathrm{d}V$ (namely T and $-p$) must pass this test. Therefore, it must be the case that

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \tag{3.50}$$

A Maxwell relation

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

Equation 3.50 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 $\mathrm{d}H$, $\mathrm{d}G$, and $\mathrm{d}A$ satisfy relations like eqn 3.49. All four relations are listed in Table 3.5 and we put them to work later in the chapter.

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

(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

$$\pi_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \tag{3.51}$$

A thermodynamic equation of state

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 3.47 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 3.48 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 3.51.

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 3.51. 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 3.51.

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 3.51 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,

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

Therefore, from eqn 3.51,

$$\pi_T = \frac{nRT}{V - nb} - p = \frac{nRT}{V - nb} - \left(\frac{nRT}{V - nb} - a\frac{n^2}{V^2}\right) = a\frac{n^2}{V^2}$$

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). $[\pi_T = RT^2(\partial B/\partial T)_V/V_m^2 + \cdots]$

3.9 Properties of the Gibbs energy

Key points **(a) The variation of the Gibbs energy of a system suggests that it is best regarded as a function of pressure and temperature. The Gibbs energy of a substance decreases with temperature and increases with pressure. (b) The variation of Gibbs energy with temperature is related to the enthalpy by the Gibbs–Helmholtz equation. (c) The Gibbs energies of solids and liquids are almost independent of pressure; those of gases vary linearly with the logarithm of the pressure.**

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

$$dG = Vdp - SdT \qquad \text{The fundamental equation of chemical thermodynamics} \qquad (3.52)$$

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 may be regarded as the **fundamental equation of chemical thermodynamics** as it is so central to the application of thermodynamics to chemistry: it suggests 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 3.48, when applied to the exact differential $dG = Vdp - SdT$, now gives

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \qquad \left(\frac{\partial G}{\partial p}\right)_T = V \qquad \text{The variation of } G \text{ with } T \text{ and } p \qquad (3.53)$$

These relations show how the Gibbs energy varies with temperature and pressure (Fig. 3.19). 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. 3.20). 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).
- 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. 3.21).

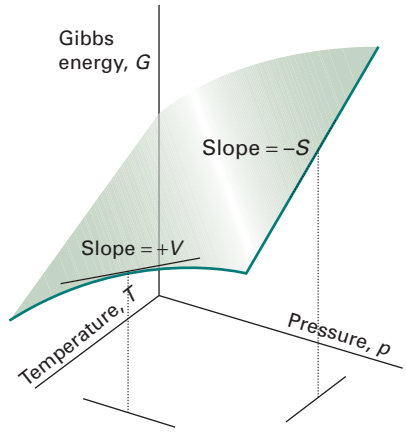

Fig. 3.19 The variation of the Gibbs energy of a system with (a) temperature at constant pressure and (b) pressure at constant temperature. The slope of the former is equal to the negative of the entropy of the system and that of the latter is equal to the volume.

(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 3.53, $(\partial G/\partial T)_p = -S$, 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

$$\left(\frac{\partial G}{\partial T}\right)_p = \frac{G - H}{T} \tag{3.54}$$

We shall see later that the equilibrium constant of a reaction is related to G/T rather than to G itself,[8] and it is easy to deduce from the last equation (see the following *Justification*) that

$$\left(\frac{\partial (G/T)}{\partial T}\right)_p = -\frac{H}{T^2} \tag{3.55}$$

Gibbs–Helmholtz equation

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.

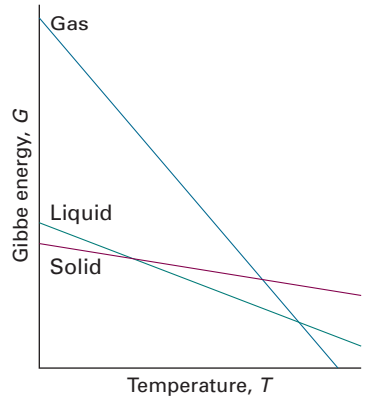

Fig. 3.20 The variation of the Gibbs energy with the temperature is determined by the entropy. Because the entropy of the gaseous phase of a substance is greater than that of the liquid phase, and the entropy of the solid phase is smallest, the Gibbs energy changes most steeply for the gas phase, followed by the liquid phase, and then the solid phase of the substance.

Justification 3.5 *The Gibbs–Helmholtz equation*

First, we note that

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

Then we use eqn 3.54 to write

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

When this expression is substituted in the preceding one, we obtain eqn 3.55.

[8] In Section 6.2b we derive the result that the equilibrium constant for a reaction is related to its standard reaction Gibbs energy by $\Delta_r G^\ominus/T = -R \ln K$.

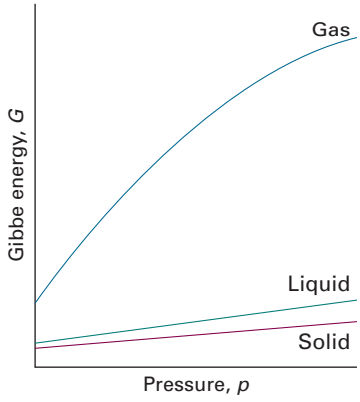

Fig. 3.21 The variation of the Gibbs energy with the pressure is determined by the volume of the sample. Because the volume of the gaseous phase of a substance is greater than that of the same amount of liquid phase, and the entropy of the solid phase is smallest (for most substances), the Gibbs energy 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.

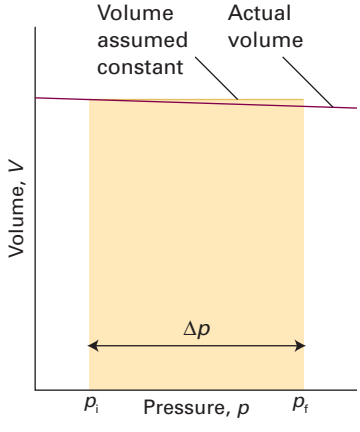

Fig. 3.22 The difference in Gibbs energy of a solid or liquid at two pressures is equal to the rectangular area shown. We have assumed that the variation of volume with pressure is negligible.

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

$$\left(\frac{\partial(\Delta G/T)}{\partial T}\right)_p = -\frac{\Delta H}{T^2} \tag{3.56}$$

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 3.52, which gives $dG = V dp$, and integrate:

$$G(p_f) = G(p_i) + \int_{p_i}^{p_f} V dp \tag{3.57a}$$

For molar quantities,

$$G_m(p_f) = G_m(p_i) + \int_{p_i}^{p_f} V_m \, dp \tag{3.57b}$$

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. 3.22), so we can treat V_m as a constant and take it outside the integral:

$$G_m(p_f) = G_m(p_i) + V_m \int_{p_i}^{p_f} dp = G_m(p_i) + (p_f - p_i)V_m \tag{3.58}$$

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 3.57.

• A brief illustration

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

$$\begin{aligned}\Delta_{trs}G(3\text{ Mbar}) &= \Delta_{trs}G(1\text{ bar}) + (1.0\times10^{-6}\text{ m}^3\text{ mol}^{-1}) \times (3.0\times10^{11}\text{ Pa} - 1.0\times10^5\text{ Pa}) \\ &= \Delta_{trs}G(1\text{ bar}) + 3.0\times10^2\text{ kJ mol}^{-1}\end{aligned}$$

where we have used 1 Pa m^3 = 1 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 3.57b (Fig. 3.23). For a perfect gas we substitute $V_m = RT/p$ into the integral, treat RT as a constant, and find

$$G_m(p_f) = G_m(p_i) + RT\int_{p_i}^{p_f}\frac{1}{p}\mathrm{d}p = G_m(p_i) + RT\ln\frac{p_f}{p_i} \qquad (3.59)^\circ$$

This expression shows that, when the pressure is increased tenfold at room temperature, the molar Gibbs energy increases by $RT \ln 10 \approx 6$ kJ mol^{-1}. It also follows from this equation that, if we set $p_i = p^\ominus$ (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

$$G_m(p) = G_m^\ominus + RT\ln\frac{p}{p^\ominus} \qquad (3.60)^\circ$$

The molar Gibbs energy of a perfect gas

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 3.60 is illustrated in Fig. 3.24. 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.

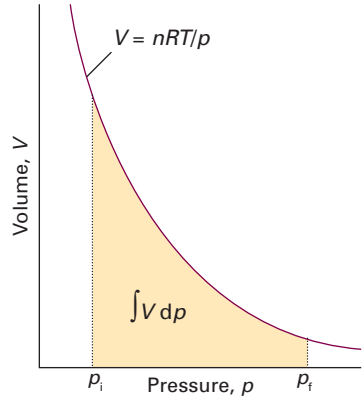

Fig. 3.23 The difference in Gibbs energy for a perfect gas at two pressures is equal to the area shown below the perfect-gas isotherm.

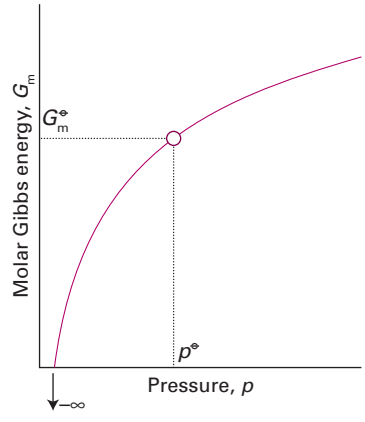

Fig. 3.24 The molar Gibbs energy of a perfect gas is proportional to ln p, and the standard state is reached at $p^\ominus$. Note that, as $p \to 0$, the molar Gibbs energy becomes negatively infinite.

interActivity 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 $(\partial G/\partial p)_T$?

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 J K^{-1} 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 J K^{-1} 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 $C_{V,m} = 27.5$ J K^{-1} 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 $C_{V,m} = 27.5$ J K^{-1} 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 J K^{-1} 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 J K^{-1} g^{-1} and may be assumed constant over the temperature range involved.

3.6(a) Consider a system consisting of 2.0 mol CO_2(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 $C_{V,m} = 28.8$ J K^{-1} 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 CO_2(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 $C_{V,m} = 28.8$ J K^{-1} 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 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

(a) $2\,CH_3CHO(g) + O_2(g) \rightarrow 2\,CH_3COOH(l)$

(b) $2\,AgCl(s) + Br_2(l) \rightarrow 2\,AgBr(s) + Cl_2(g)$

(c) $Hg(l) + Cl_2(g) \rightarrow HgCl_2(s)$

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

(a) $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

(b) $C_{12}H_{22}O_{11}(s) + 12\,O_2(g) \rightarrow 12\,CO_2(g) + 11\,H_2O(l)$

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 $4\,HCl(g) + O_2(g) \rightarrow 2\,Cl_2(g) + 2\,H_2O(l)$ 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 $CO(g) + CH_3OH(l) \rightarrow CH_3COOH(l)$ 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 (C_6H_5OH) is −3054 kJ mol^{-1} at 298 K and its standard molar entropy is 144.0 J K^{-1} 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 ($CO(NH_2)_2$) is −632 kJ mol^{-1} at 298 K and its standard molar entropy is 104.60 J K^{-1} 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 $p_{ex} = 0$, 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 $p_{ex} = 0$, 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 cold sink in a reversible process for each 1.0 kJ supplied by the hot source?

3.16(a) Suppose that 3.0 mmol $N_2(g)$ 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 Ar(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 $\Delta G/J = -85.40 + 36.5(T/K)$. 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 $\Delta G/J = -73.1 + 42.8(T/K)$. 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. Take $k_T = 1.26 \times 10^{-9}$ Pa^{-1}.

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 that 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 $J\,K^{-1}\,mol^{-1}$ and −41.9 $J\,K^{-1}\,mol^{-1}$, 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 $C_{p,m}/(J\,K^{-1}\,mol^{-1}) = 91.47 + 7.5 \times 10^{-2}\,(T/K)$. 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 ($C_{p,m} = 24.44\ J\,K^{-1}\,mol^{-1}$) and temperature 0°C is introduced into an insulated container in which there is 1.00 mol $H_2O(g)$ 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 are isothermal, that is, a thermostat surrounds B to keep its temperature constant. There is 2.00 mol of the gas in each section. Initially $T_A = T_B = 300$ K, $V_A = V_B = 2.00\ dm^3$. 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 $C_{V,m} = 20\ J\,K^{-1}\,mol^{-1}$.)

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 $NH_3(g)$ is 192.45 $J\,K^{-1}\,mol^{-1}$ 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 kΩ and negligible mass. A current of 1.00 A is passed for 15.0 s. Calculate the change in entropy of the copper, taking $C_{p,m} = 24.4\ J\,K^{-1}\,mol^{-1}$. 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_h and the other at T_c, 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.

Chapter 3

E3.1(a) (a) 92 J K^{-1} (b) 67 J K^{-1}

E3.2(a) 152.67 J K^{-1} mol^{-1}

E3.3(a) −22.1 J K^{-1}

E3.4(a) $q = 0, \Delta S = 0, \Delta U = +4.1$ kJ, $\Delta H = +5.4$ kJ

E3.5(a) $\Delta H = 0, \Delta H_{tot} = 0, \Delta S_{tot} = +93.4$ J K^{-1}

E3.6(a) (a) $q = 0$ (b) −20 J (c) −20 J (d) $-0.34\dot{7}$ K (e) +0.60 J K^{-1}

E3.7(a) (a) +87.8 J K^{-1} mol^{-1} (b) −87.8 J K^{-1} mol^{-1}

E3.8(a) (a) −386.1 J K^{-1} mol^{-1} (b) +92.6 J K^{-1} mol^{-1}
(c) −153.1 J K^{-1} mol^{-1}

E3.9(a) (a) −521.5 kJ mol^{-1} (b) +25.8 kJ mol^{-1} (c) −178.7 kJ mol^{-1}

E3.10(a) (a) −522.1 kJ mol^{-1} (b) +25.78 kJ mol^{-1} (c) −178.6 kJ mol^{-1}

E3.11(a) −93.05 kJ mol^{-1}

E3.12(a) −50 kJ mol^{-1}

E3.13(a) (a) $\Delta S(\text{gas}) = +2.9$ J K^{-1}, $\Delta S(\text{surroundings}) = -2.9$ J K^{-1}, $\Delta S(\text{total}) = 0$
(b) $\Delta S(\text{gas}) = +2.9$ J K^{-1}, $\Delta S(\text{surroundings}) = 0$, $\Delta S(\text{total}) = +2.9$ J K^{-1}
(c) $\Delta S(\text{gas}) = 0, \Delta S(\text{surroundings}) = 0, \Delta S(\text{total}) = 0$

E3.14(a) 817.90 kJ mol^{-1}

E3.15(a) $\eta = 1 - \dfrac{333\text{ K}}{373\text{ K}} = 0.11$, $\eta = 1 - \dfrac{353\text{ K}}{573\text{ K}} = 0.38$

E3.16(a) −3.8 J

E3.17(a) −36.5 J K^{-1}

E3.18(a) 12 kJ

E3.19(a) +7.3 kJ mol^{-1}

E3.20(a) −0.55 kJ mol^{-1}

E3.21(a) +10 kJ

E3.22(a) +11 kJ mol^{-1}