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The properties of gases

This chapter establishes the properties of gases that will be used throughout the text. It begins with an account of an idealized version of a gas, a perfect gas, and shows how its equation of state may be assembled experimentally. We then see how the properties of real gases differ from those of a perfect gas, and construct an equation of state that describes their properties.

The simplest state of matter is a **gas**, a form of matter that fills any container it occupies. Initially we consider only pure gases, but later in the chapter we see that the same ideas and equations apply to mixtures of gases too.

The perfect gas

We shall find it helpful to picture a gas as a collection of molecules (or atoms) in continuous random motion, with average speeds that increase as the temperature is raised. A gas differs from a liquid in that, except during collisions, the molecules of a gas are widely separated from one another and move in paths that are largely unaffected by intermolecular forces.

1.1 The states of gases

The **physical state** of a sample of a substance, its physical condition, is defined by its physical properties. Two samples of a substance that have the same physical properties are in the same state. The state of a pure gas, for example, is specified by giving its volume, V, amount of substance (number of moles), n, pressure, p, and temperature, T. However, it has been established experimentally that it is sufficient to specify only three of these variables, for then the fourth variable is fixed. That is, it is an experimental fact that each substance is described by an **equation of state**, an equation that interrelates these four variables.

The general form of an equation of state is

$$p = f(T,V,n) \tag{1.1}$$

This equation tells us that, if we know the values of T, V, and n for a particular substance, then the pressure has a fixed value. Each substance is described by its own equation of state, but we know the explicit form of the equation in only a few special cases. One very important example is the equation of state of a 'perfect gas', which has the form $p = nRT/V$, where R is a constant. Much of the rest of this chapter will examine the origin of this equation of state and its applications.

The perfect gas

Real gases

Table 1.1 Pressure units

Name	Symbol	Value
pascal	1 Pa	$1\ \mathrm{N\,m^{-2}}$, $1\ \mathrm{kg\,m^{-1}\,s^{-2}}$
bar	1 bar	10^5 Pa
atmosphere	1 atm	101.325 kPa
torr	1 Torr	(101 325/760) Pa = 133.32 . . . Pa
millimetres of mercury	1 mmHg	133.322 . . . Pa
pound per square inch	1 psi	6.894 757 . . . kPa

(a) Pressure

Pressure is defined as force divided by the area to which the force is applied. The greater the force acting on a given area, the greater the pressure. The origin of the force exerted by a gas is the incessant battering of the molecules on the walls of its container. The collisions are so numerous that they exert an effectively steady force, which is experienced as a steady pressure.

Comment 1.1

The International System of units (SI, from the French *Système International d'Unités*) is discussed in *Appendix* 1.

The SI unit of pressure, the *pascal* (Pa), is defined as 1 newton per metre-squared:

$$1\ \mathrm{Pa} = 1\ \mathrm{N\,m^{-2}} \qquad [1.2a]$$

In terms of base units,

$$1\ \mathrm{Pa} = 1\ \mathrm{kg\,m^{-1}\,s^{-2}} \qquad [1.2b]$$

Several other units are still widely used (Table 1.1); of these units, the most commonly used are atmosphere ($1\ \mathrm{atm} = 1.013\ 25 \times 10^5\ \mathrm{Pa}$ exactly) and bar ($1\ \mathrm{bar} = 10^5\ \mathrm{Pa}$). A pressure of 1 bar is the **standard pressure** for reporting data; we denote it $p^\ominus$.

Self-test 1.1 Calculate the pressure (in pascals and atmospheres) exerted by a mass of 1.0 kg pressing through the point of a pin of area $1.0 \times 10^{-2}\ \mathrm{mm^2}$ at the surface of the Earth. *Hint.* The force exerted by a mass m due to gravity at the surface of the Earth is mg, where g is the acceleration of free fall (see endpaper 2 for its standard value). [0.98 GPa, 9.7×10^3 atm]

If two gases are in separate containers that share a common movable wall (Fig. 1.1), the gas that has the higher pressure will tend to compress (reduce the volume of) the gas that has lower pressure. The pressure of the high-pressure gas will fall as it expands and that of the low-pressure gas will rise as it is compressed. There will come a stage when the two pressures are equal and the wall has no further tendency to move. This condition of equality of pressure on either side of a movable wall (a 'piston') is a state of **mechanical equilibrium** between the two gases. The pressure of a gas is therefore an indication of whether a container that contains the gas will be in mechanical equilibrium with another gas with which it shares a movable wall.

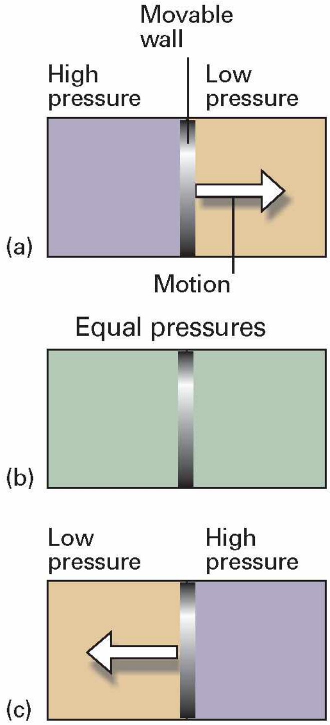


Fig. 1.1 When a region of high pressure is separated from a region of low pressure by a movable wall, the wall will be pushed into one region or the other, as in (a) and (c). However, if the two pressures are identical, the wall will not move (b). The latter condition is one of mechanical equilibrium between the two regions.

(b) The measurement of pressure

The pressure exerted by the atmosphere is measured with a **barometer**. The original version of a barometer (which was invented by Torricelli, a student of Galileo) was an inverted tube of mercury sealed at the upper end. When the column of mercury is in mechanical equilibrium with the atmosphere, the pressure at its base is equal to that exerted by the atmosphere. It follows that the height of the mercury column is proportional to the external pressure.

Example 1.1 *Calculating the pressure exerted by a column of liquid*

Derive an equation for the pressure at the base of a column of liquid of mass density ρ (rho) and height h at the surface of the Earth.

Method Pressure is defined as $p = F/A$ where F is the force applied to the area A, and $F = mg$. To calculate F we need to know the mass m of the column of liquid, which is its mass density, ρ, multiplied by its volume, V: $m = \rho V$. The first step, therefore, is to calculate the volume of a cylindrical column of liquid.

Answer Let the column have cross-sectional area A; then its volume is Ah and its mass is $m = \rho Ah$. The force the column of this mass exerts at its base is

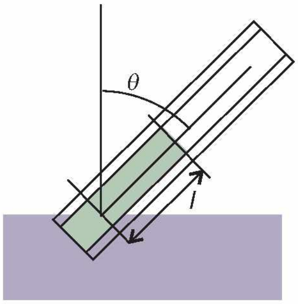
$$F = mg = \rho Ahg$$

The pressure at the base of the column is therefore

$$p = \frac{F}{A} = \frac{\rho Ahg}{A} = \rho gh \qquad (1.3)$$

Note that the pressure is independent of the shape and cross-sectional area of the column. The mass of the column of a given height increases as the area, but so does the area on which the force acts, so the two cancel.

Self-test 1.2 Derive an expression for the pressure at the base of a column of liquid of length l held at an angle θ (theta) to the vertical (**1**). [$p = \rho gl \cos\theta$]



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The pressure of a sample of gas inside a container is measured by using a pressure gauge, which is a device with electrical properties that depend on the pressure. For instance, a *Bayard–Alpert pressure gauge* is based on the ionization of the molecules present in the gas and the resulting current of ions is interpreted in terms of the pressure. In a *capacitance manometer*, the deflection of a diaphragm relative to a fixed electrode is monitored through its effect on the capacitance of the arrangement. Certain semiconductors also respond to pressure and are used as transducers in solid-state pressure gauges.

(c) Temperature

The concept of temperature springs from the observation that a change in physical state (for example, a change of volume) can occur when two objects are in contact with one another, as when a red-hot metal is plunged into water. Later (Section 2.1) we shall see that the change in state can be interpreted as arising from a flow of energy as heat from one object to another. The **temperature**, T, is the property that indicates the direction of the flow of energy through a thermally conducting, rigid wall. If energy flows from A to B when they are in contact, then we say that A has a higher temperature than B (Fig. 1.2).

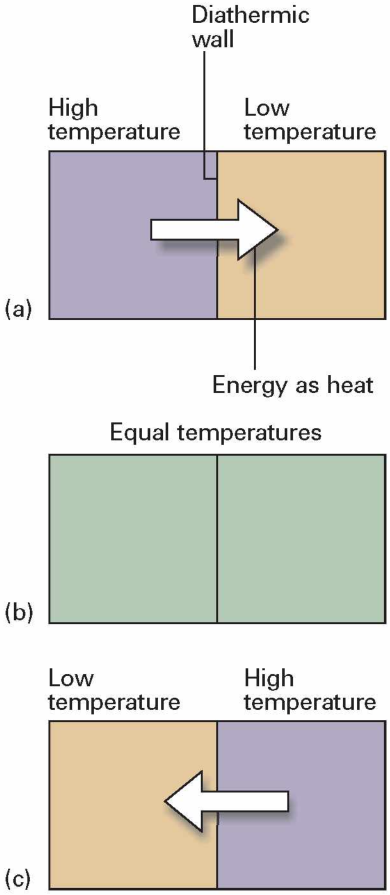

Fig. 1.2 Energy flows as heat from a region at a higher temperature to one at a lower temperature if the two are in contact through a diathermic wall, as in (a) and (c). However, if the two regions have identical temperatures, there is no net transfer of energy as heat even though the two regions are separated by a diathermic wall (b). The latter condition corresponds to the two regions being at thermal equilibrium.

It will prove useful to distinguish between two types of boundary that can separate the objects. A boundary is **diathermic** (thermally conducting) if a change of state is observed when two objects at different temperatures are brought into contact.[1] A

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[1] The word dia is from the Greek for 'through'.

metal container has diathermic walls. A boundary is **adiabatic** (thermally insulating) if no change occurs even though the two objects have different temperatures. A vacuum flask is an approximation to an adiabatic container.

The temperature is a property that indicates whether two objects would be in 'thermal equilibrium' if they were in contact through a diathermic boundary. **Thermal equilibrium** is established if no change of state occurs when two objects A to B are in contact through a diathermic boundary. Suppose an object A (which we can think of as a block of iron) is in thermal equilibrium with an object B (a block of copper), and that B is also in thermal equilibrium with another object C (a flask of water). Then it has been found experimentally that A and C will also be in thermal equilibrium when they are put in contact (Fig. 1.3). This observation is summarized by the **Zeroth Law of thermodynamics**:

> If A is in thermal equilibrium with B, and B is in thermal equilibrium with C, then C is also in thermal equilibrium with A.

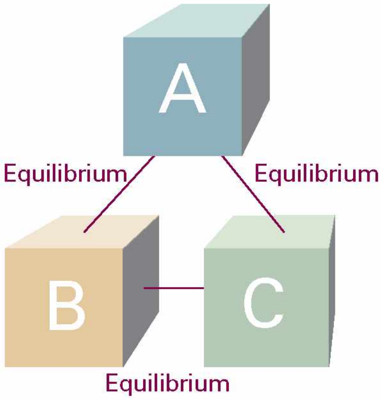

Fig. 1.3 The experience summarized by the Zeroth Law of thermodynamics is that, if an object A is in thermal equilibrium with B and B is in thermal equilibrium with C, then C is in thermal equilibrium with A.

The Zeroth Law justifies the concept of temperature and the use of a **thermometer**, a device for measuring the temperature. Thus, suppose that B is a glass capillary containing a liquid, such as mercury, that expands significantly as the temperature increases. Then, when A is in contact with B, the mercury column in the latter has a certain length. According to the Zeroth Law, if the mercury column in B has the same length when it is placed in thermal contact with another object C, then we can predict that no change of state of A and C will occur when they are in thermal contact. Moreover, we can use the length of the mercury column as a measure of the temperatures of A and C.

In the early days of thermometry (and still in laboratory practice today), temperatures were related to the length of a column of liquid, and the difference in lengths shown when the thermometer was first in contact with melting ice and then with boiling water was divided into 100 steps called 'degrees', the lower point being labelled 0. This procedure led to the **Celsius scale** of temperature. In this text, temperatures on the Celsius scale are denoted θ and expressed in *degrees Celsius* (°C). However, because different liquids expand to different extents, and do not always expand uniformly over a given range, thermometers constructed from different materials showed different numerical values of the temperature between their fixed points. The pressure of a gas, however, can be used to construct a **perfect-gas temperature scale** that is independent of the identity of the gas. The perfect-gas scale turns out to be identical to the **thermodynamic temperature scale** to be introduced in Section 3.2c, so we shall use the latter term from now on to avoid a proliferation of names. On the thermodynamic temperature scale, temperatures are denoted T and are normally reported in kelvins, K (not °K). Thermodynamic and Celsius temperatures are related by the exact expression

$$T/\mathrm{K} = \theta/^{\circ}\mathrm{C} + 273.15 \tag{1.4}$$

This relation, in the form $\theta/^{\circ}\mathrm{C} = T/\mathrm{K} - 273.15$, is the current definition of the Celsius scale in terms of the more fundamental **Kelvin scale**. It implies that a difference in temperature of 1°C is equivalent to a difference of 1 K.

A note on good practice We write $T = 0$, not $T = 0$ K for the zero temperature on the thermodynamic temperature scale. This scale is absolute, and the lowest temperature is 0 regardless of the size of the divisions on the scale (just as we write $p = 0$ for zero pressure, regardless of the size of the units we adopt, such as bar or pascal). However, we write 0°C because the Celsius scale is not absolute.

Illustration 1.1 *Converting temperatures*

To express 25.00°C as a temperature in kelvins, we use eqn 1.4 to write

$$T/\mathrm{K} = (25.00°\mathrm{C})/°\mathrm{C} + 273.15 = 25.00 + 273.15 = 298.15$$

Note how the units (in this case, °C) are cancelled like numbers. This is the procedure called 'quantity calculus' in which a physical quantity (such as the temperature) is the product of a numerical value (25.00) and a unit (1°C). Multiplication of both sides by the unit K then gives $T = 298.15$ K.

A note on good practice When the units need to be specified in an equation, the approved procedure, which avoids any ambiguity, is to write (physical quantity)/units, which is a dimensionless number, just as (25.00°C)/°C = 25.00 in this *Illustration*. Units may be multiplied and cancelled just like numbers.

1.2 The gas laws

The equation of state of a gas at low pressure was established by combining a series of empirical laws.

(a) The perfect gas law

We assume that the following individual gas laws are familiar:

Boyle's law: $pV = \text{constant}$, at constant n, T (1.5)°

Charles's law: $V = \text{constant} \times T$, at constant n, p (1.6a)°

$p = \text{constant} \times T$, at constant n, V (1.6b)°

Avogadro's principle:[2] $V = \text{constant} \times n$ at constant p, T (1.7)°

Boyle's and Charles's laws are examples of a **limiting law**, a law that is strictly true only in a certain limit, in this case $p \to 0$. Equations valid in this limiting sense will be signalled by a ° on the equation number, as in these expressions. Avogadro's principle is commonly expressed in the form 'equal volumes of gases at the same temperature and pressure contain the same numbers of molecules'. In this form, it is increasingly true as $p \to 0$. Although these relations are strictly true only at $p = 0$, they are reasonably reliable at normal pressures ($p \approx 1$ bar) and are used widely throughout chemistry.

Figure 1.4 depicts the variation of the pressure of a sample of gas as the volume is changed. Each of the curves in the graph corresponds to a single temperature and hence is called an **isotherm**. According to Boyle's law, the isotherms of gases are hyperbolas. An alternative depiction, a plot of pressure against 1/volume, is shown in Fig. 1.5. The linear variation of volume with temperature summarized by Charles's law is illustrated in Fig. 1.6. The lines in this illustration are examples of **isobars**, or lines showing the variation of properties at constant pressure. Figure 1.7 illustrates the linear variation of pressure with temperature. The lines in this diagram are **isochores**, or lines showing the variation of properties at constant volume.

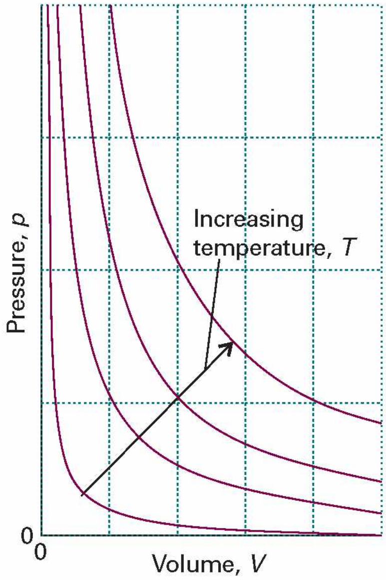

Fig. 1.4 The pressure–volume dependence of a fixed amount of perfect gas at different temperatures. Each curve is a hyperbola ($pV = \text{constant}$) and is called an *isotherm*.

Exploration[3] Explore how the pressure of 1.5 mol $CO_2(g)$ varies with volume as it is compressed at (a) 273 K, (b) 373 K from 30 dm^3 to 15 dm^3.

Comment 1.2

A hyperbola is a curve obtained by plotting y against x with $xy = \text{constant}$.

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[2] Avogadro's principle is a principle rather than a law (a summary of experience) because it depends on the validity of a model, in this case the existence of molecules. Despite there now being no doubt about the existence of molecules, it is still a model-based principle rather than a law.

[3] To solve this and other *Explorations*, use either mathematical software or the *Living graphs* from the text's web site.

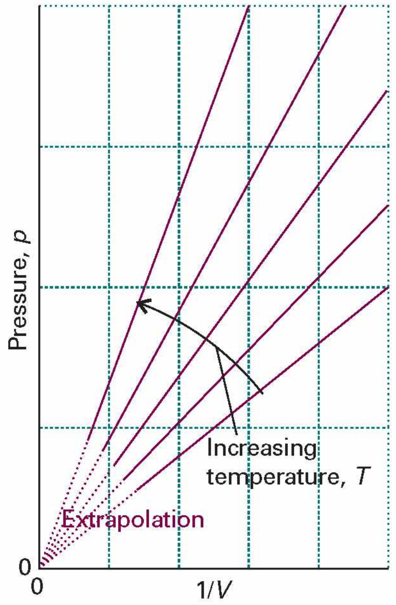

Fig. 1.5 Straight lines are obtained when the pressure is plotted against $1/V$ at constant temperature.

Exploration Repeat *Exploration 1.4*, but plot the data as p against $1/V$.

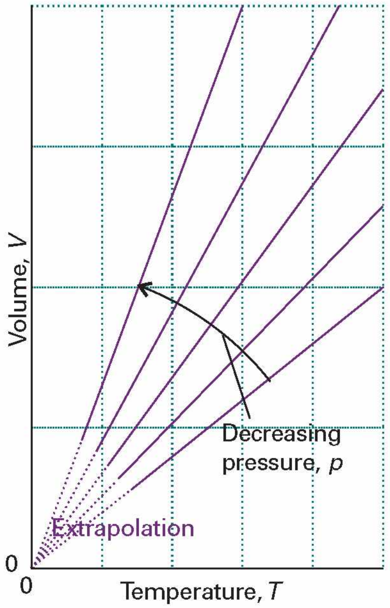

Fig. 1.6 The variation of the volume of a fixed amount of gas with the temperature at constant pressure. Note that in each case the isobars extrapolate to zero volume at $T = 0$, or $\theta = -273°\text{C}$.

Exploration Explore how the volume of 1.5 mol $CO_2(g)$ in a container maintained at (a) 1.00 bar, (b) 0.50 bar varies with temperature as it is cooled from 373 K to 273 K.

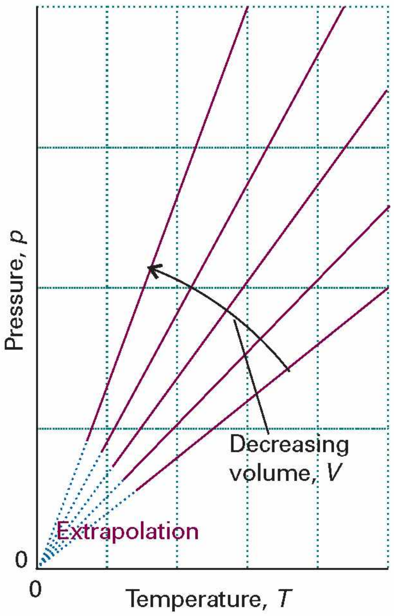

Fig. 1.7 The pressure also varies linearly with the temperature at constant volume, and extrapolates to zero at $T = 0$ (−273°C).

Exploration Explore how the pressure of 1.5 mol $CO_2(g)$ in a container of volume (a) 30 dm^3, (b) 15 dm^3 varies with temperature as it is cooled from 373 K to 273 K.

A note on good practice To test the validity of a relation between two quantities, it is best to plot them in such a way that they should give a straight line, for deviations from a straight line are much easier to detect than deviations from a curve.

The empirical observations summarized by eqns 1.5–7 can be combined into a single expression:

$$pV = \text{constant} \times nT$$

This expression is consistent with Boyle's law ($pV = \text{constant}$) when n and T are constant, with both forms of Charles's law ($p \propto T$, $V \propto T$) when n and either V or p are held constant, and with Avogadro's principle ($V \propto n$) when p and T are constant. The constant of proportionality, which is found experimentally to be the same for all gases, is denoted R and called the **gas constant**. The resulting expression

$$pV = nRT \tag*{(1.8)°}$$

is the **perfect gas equation**. It is the approximate equation of state of any gas, and becomes increasingly exact as the pressure of the gas approaches zero. A gas that obeys eqn 1.8 exactly under all conditions is called a **perfect gas** (or *ideal gas*). A **real gas**, an actual gas, behaves more like a perfect gas the lower the pressure, and is described exactly by eqn 1.8 in the limit of $p \to 0$. The gas constant R can be determined by evaluating $R = pV/nT$ for a gas in the limit of zero pressure (to guarantee that it is behaving perfectly). However, a more accurate value can be obtained by measuring the speed of sound in a low-pressure gas (argon is used in practice) and extrapolating its value to zero pressure. Table 1.2 lists the values of R in a variety of units.

Table 1.2 The gas constant

R	
8.314 47	$\mathrm{J\,K^{-1}\,mol^{-1}}$
$8.205\,74 \times 10^{-2}$	$\mathrm{dm^3\,atm\,K^{-1}\,mol^{-1}}$
$8.314\,47 \times 10^{-2}$	$\mathrm{dm^3\,bar\,K^{-1}\,mol^{-1}}$
8.314 47	$\mathrm{Pa\,m^3\,K^{-1}\,mol^{-1}}$
1 62.364	$\mathrm{dm^3\,Torr\,K^{-1}\,mol^{-1}}$
1.987 21	$\mathrm{cal\,K^{-1}\,mol^{-1}}$

Molecular interpretation 1.1 *The kinetic model of gases*

The molecular explanation of Boyle's law is that, if a sample of gas is compressed to half its volume, then twice as many molecules strike the walls in a given period of time than before it was compressed. As a result, the average force exerted on the walls is doubled. Hence, when the volume is halved the pressure of the gas is doubled, and $p \times V$ is a constant. Boyle's law applies to all gases regardless of their chemical identity (provided the pressure is low) because at low pressures the average separation of molecules is so great that they exert no influence on one another and hence travel independently. The molecular explanation of Charles's law lies in the fact that raising the temperature of a gas increases the average speed of its molecules. The molecules collide with the walls more frequently and with greater impact. Therefore they exert a greater pressure on the walls of the container.

These qualitative concepts are expressed quantitatively in terms of the kinetic model of gases, which is described more fully in Chapter 21. Briefly, the kinetic model is based on three assumptions:

1. The gas consists of molecules of mass m in ceaseless random motion.
2. The size of the molecules is negligible, in the sense that their diameters are much smaller than the average distance travelled between collisions.
3. The molecules interact only through brief, infrequent, and elastic collisions.

An *elastic collision* is a collision in which the total translational kinetic energy of the molecules is conserved. From the very economical assumptions of the kinetic model, it can be deduced (as we shall show in detail in Chapter 21) that the pressure and volume of the gas are related by

$$pV = \tfrac{1}{3}nMc^2 \qquad (1.9)^\circ$$

where $M = mN_A$, the molar mass of the molecules, and c is the *root mean square speed* of the molecules, the square root of the mean of the squares of the speeds, v, of the molecules:

$$c = \langle v^2 \rangle^{1/2} \qquad (1.10)$$

We see that, if the root mean square speed of the molecules depends only on the temperature, then at constant temperature

$$pV = \text{constant}$$

which is the content of Boyle's law. Moreover, for eqn 1.9 to be the equation of state of a perfect gas, its right-hand side must be equal to nRT. It follows that the root mean square speed of the molecules in a gas at a temperature T must be

$$c = \left(\frac{3RT}{M}\right)^{1/2} \qquad (1.11)^\circ$$

We can conclude that *the root mean square speed of the molecules of a gas is proportional to the square root of the temperature and inversely proportional to the square root of the molar mass*. That is, the higher the temperature, the higher the root mean square speed of the molecules, and, at a given temperature, heavy molecules travel more slowly than light molecules. The root mean square speed of N_2 molecules, for instance, is found from eqn 1.11 to be 515 m s^{-1} at 298 K.

Comment 1.3

For an object of mass m moving at a speed v, the kinetic energy is $E_K = \tfrac{1}{2}mv^2$. The potential energy, E_P or V, of an object is the energy arising from its position (not speed). No universal expression for the potential energy can be given because it depends on the type of interaction the object experiences.

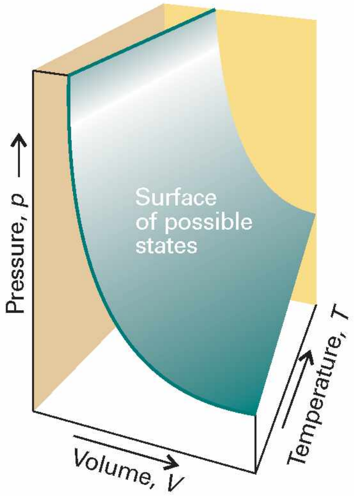

Fig. 1.8 A region of the p,V,T surface of a fixed amount of perfect gas. The points forming the surface represent the only states of the gas that can exist.

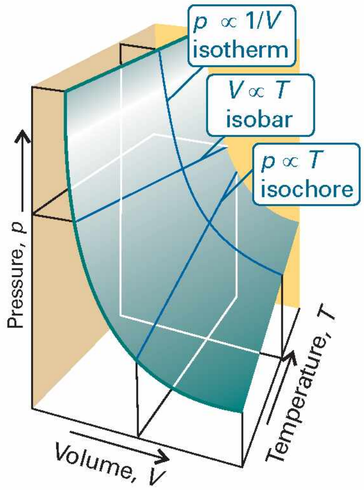

Fig. 1.9 Sections through the surface shown in Fig. 1.8 at constant temperature give the isotherms shown in Fig. 1.4 and the isobars shown in Fig. 1.6.

The surface in Fig. 1.8 is a plot of the pressure of a fixed amount of perfect gas against its volume and thermodynamic temperature as given by eqn 1.8. The surface depicts the only possible states of a perfect gas: the gas cannot exist in states that do not correspond to points on the surface. The graphs in Figs. 1.4 and 1.6 correspond to the sections through the surface (Fig. 1.9).

Example 1.2 *Using the perfect gas equation*

In an industrial process, nitrogen is heated to 500 K in a vessel of constant volume. If it enters the vessel at 100 atm and 300 K, what pressure would it exert at the working temperature if it behaved as a perfect gas?

Method We expect the pressure to be greater on account of the increase in temperature. The perfect gas law in the form $PV/nT = R$ implies that, if the conditions are changed from one set of values to another, then because PV/nT is equal to a constant, the two sets of values are related by the 'combined gas law':

$$\frac{p_1V_1}{n_1T_1} = \frac{p_2V_2}{n_2T_2} \qquad (1.12)°$$

The known and unknown data are summarized in (**2**).

	n	p	V	T
Initial	Same	100	Same	300
Final	Same	?	Same	500

2

Answer Cancellation of the volumes (because $V_1 = V_2$) and amounts (because $n_1 = n_2$) on each side of the combined gas law results in

$$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$

which can be rearranged into

$$p_2 = \frac{T_2}{T_1} \times p_1$$

Substitution of the data then gives

$$p_2 = \frac{500\ \text{K}}{300\ \text{K}} \times (100\ \text{atm}) = 167\ \text{atm}$$

Experiment shows that the pressure is actually 183 atm under these conditions, so the assumption that the gas is perfect leads to a 10 per cent error.

Self-test 1.3 What temperature would result in the same sample exerting a pressure of 300 atm? [900 K]

The perfect gas equation is of the greatest importance in physical chemistry because it is used to derive a wide range of relations that are used throughout thermodynamics. However, it is also of considerable practical utility for calculating the properties of a gas under a variety of conditions. For instance, the molar volume, $V_m = V/n$, of a perfect gas under the conditions called **standard ambient temperature and pressure** (SATP), which means 298.15 K and 1 bar (that is, exactly 10^5 Pa), is easily calculated from $V_m = RT/p$ to be 24.789 $\text{dm}^3\ \text{mol}^{-1}$. An earlier definition, **standard temperature and pressure** (STP), was 0°C and 1 atm; at STP, the molar volume of a perfect gas is 22.414 $\text{dm}^3\ \text{mol}^{-1}$. Among other applications, eqn 1.8 can be used to discuss processes in the atmosphere that give rise to the weather.

IMPACT ON ENVIRONMENTAL SCIENCE

I1.1 The gas laws and the weather

The biggest sample of gas readily accessible to us is the atmosphere, a mixture of gases with the composition summarized in Table 1.3. The composition is maintained moderately constant by diffusion and convection (winds, particularly the local turbulence called *eddies*) but the pressure and temperature vary with altitude and with the local conditions, particularly in the troposphere (the 'sphere of change'), the layer extending up to about 11 km.

Table 1.3 The composition of dry air at sea level

	Percentage	
Component	By volume	By mass
Nitrogen, N_2	78.08	75.53
Oxygen, O_2	20.95	23.14
Argon, Ar	0.93	1.28
Carbon dioxide, CO_2	0.031	0.047
Hydrogen, H_2	5.0×10^{-3}	2.0×10^{-4}
Neon, Ne	1.8×10^{-3}	1.3×10^{-3}
Helium, He	5.2×10^{-4}	7.2×10^{-5}
Methane, CH_4	2.0×10^{-4}	1.1×10^{-4}
Krypton, Kr	1.1×10^{-4}	3.2×10^{-4}
Nitric oxide, NO	5.0×10^{-5}	1.7×10^{-6}
Xenon, Xe	8.7×10^{-6}	1.2×10^{-5}
Ozone, O_3: summer	7.0×10^{-6}	1.2×10^{-5}
winter	2.0×10^{-6}	3.3×10^{-6}

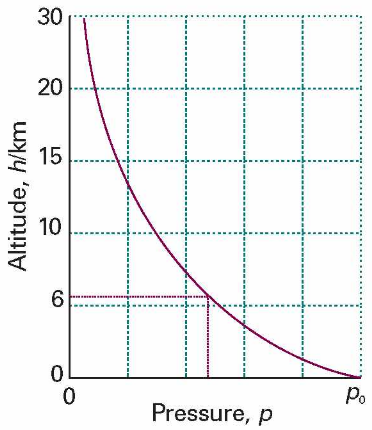

Fig. 1.10 The variation of atmospheric pressure with altitude, as predicted by the barometric formula and as suggested by the 'US Standard Atmosphere', which takes into account the variation of temperature with altitude.

Exploration How would the graph shown in the illustration change if the temperature variation with altitude were taken into account? Construct a graph allowing for a linear decrease in temperature with altitude.

In the troposphere the average temperature is 15°C at sea level, falling to −57°C at the bottom of the tropopause at 11 km. This variation is much less pronounced when expressed on the Kelvin scale, ranging from 288 K to 216 K, an average of 268 K. If we suppose that the temperature has its average value all the way up to the tropopause, then the pressure varies with altitude, h, according to the *barometric formula:*

$$p = p_0 e^{-h/H}$$

where p_0 is the pressure at sea level and H is a constant approximately equal to 8 km. More specifically, $H = RT/Mg$, where M is the average molar mass of air and T is the temperature. The barometric formula fits the observed pressure distribution quite well even for regions well above the troposphere (see Fig. 1.10). It implies that the pressure of the air and its density fall to half their sea-level value at $h = H \ln 2$, or 6 km.

Local variations of pressure, temperature, and composition in the troposphere are manifest as 'weather'. A small region of air is termed a *parcel*. First, we note that a parcel of warm air is less dense than the same parcel of cool air. As a parcel rises, it expands adiabatically (that is, without transfer of heat from its surroundings), so it cools. Cool air can absorb lower concentrations of water vapour than warm air, so the moisture forms clouds. Cloudy skies can therefore be associated with rising air and clear skies are often associated with descending air.

The motion of air in the upper altitudes may lead to an accumulation in some regions and a loss of molecules from other regions. The former result in the formation of regions of high pressure ('highs' or anticyclones) and the latter result in regions of low pressure ('lows', depressions, or cyclones). These regions are shown as H and L on the accompanying weather map (Fig. 1.11). The lines of constant pressure—differing by 4 mbar (400 Pa, about 3 Torr)—marked on it are called *isobars.* The elongated regions of high and low pressure are known, respectively, as *ridges* and *troughs.*

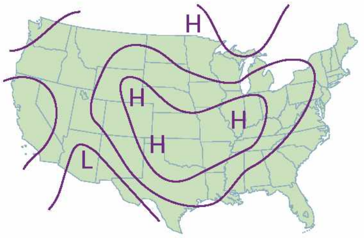

Fig. 1.11 A typical weather map; in this case, for the United States on 1 January 2000.

In meteorology, large-scale vertical movement is called *convection*. Horizontal pressure differentials result in the flow of air that we call *wind* (see Fig.1.12). Winds coming from the north in the Northern hemisphere and from the south in the Southern hemisphere are deflected towards the west as they migrate from a region where the Earth is rotating slowly (at the poles) to where it is rotating most rapidly (at the equator). Winds travel nearly parallel to the isobars, with low pressure to their left in the Northern hemisphere and to the right in the Southern hemisphere. At the surface, where wind speeds are lower, the winds tend to travel perpendicular to the isobars from high to low pressure. This differential motion results in a spiral outward flow of air clockwise in the Northern hemisphere around a high and an inward counter-clockwise flow around a low.

The air lost from regions of high pressure is restored as an influx of air converges into the region and descends. As we have seen, descending air is associated with clear skies. It also becomes warmer by compression as it descends, so regions of high pressure are associated with high surface temperatures. In winter, the cold surface air may prevent the complete fall of air, and result in a temperature *inversion*, with a layer of warm air over a layer of cold air. Geographical conditions may also trap cool air, as in Los Angeles, and the photochemical pollutants we know as *smog* may be trapped under the warm layer.

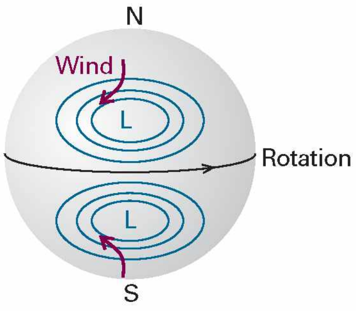

Fig. 1.12 The flow of air ('wind') around regions of high and low pressure in the Northern and Southern hemispheres.

(b) Mixtures of gases

When dealing with gaseous mixtures, we often need to know the contribution that each component makes to the total pressure of the sample. The **partial pressure**, p_J, of a gas J in a mixture (any gas, not just a perfect gas), is defined as

$$p_J = x_J p \qquad [1.13]$$

where x_J is the **mole fraction** of the component J, the amount of J expressed as a fraction of the total amount of molecules, n, in the sample:

$$x_J = \frac{n_J}{n} \qquad n = n_A + n_B + \cdots \qquad [1.14]$$

When no J molecules are present, $x_J = 0$; when only J molecules are present, $x_J = 1$. It follows from the definition of x_J that, whatever the composition of the mixture, $x_A + x_B + \cdots = 1$ and therefore that the sum of the partial pressures is equal to the total pressure:

$$p_A + p_B + \cdots = (x_A + x_B + \cdots)p = p \qquad (1.15)$$

This relation is true for both real and perfect gases.

When all the gases are perfect, the partial pressure as defined in eqn 1.13 is also the pressure that each gas would occupy if it occupied the same container alone at the same temperature. The latter is the original meaning of 'partial pressure'. That identification was the basis of the original formulation of **Dalton's law**:

> The pressure exerted by a mixture of gases is the sum of the pressures that each one would exist if it occupied the container alone.

Now, however, the relation between partial pressure (as defined in eqn 1.13) and total pressure (as given by eqn 1.15) is true for all gases and the identification of partial pressure with the pressure that the gas would exert on its own is valid only for a perfect gas.

Example 1.3 *Calculating partial pressures*

The mass percentage composition of dry air at sea level is approximately N_2: 75.5; O_2: 23.2; Ar: 1.3. What is the partial pressure of each component when the total pressure is 1.00 atm?

Method We expect species with a high mole fraction to have a proportionally high partial pressure. Partial pressures are defined by eqn 1.13. To use the equation, we need the mole fractions of the components. To calculate mole fractions, which are defined by eqn 1.14, we use the fact that the amount of molecules J of molar mass M_J in a sample of mass m_J is $n_J = m_J/M_J$. The mole fractions are independent of the total mass of the sample, so we can choose the latter to be 100 g (which makes the conversion from mass percentages very easy). Thus, the mass of N_2 present is 75.5 per cent of 100 g, which is 75.5 g.

Answer The amounts of each type of molecule present in 100 g of air, in which the masses of N_2, O_2, and Ar are 75.5 g, 23.2 g, and 1.3 g, respectively, are

$$n(N_2) = \frac{75.5\ \text{g}}{28.02\ \text{g mol}^{-1}} = \frac{75.5}{28.02}\ \text{mol}$$

$$n(O_2) = \frac{23.2\ \text{g}}{32.00\ \text{g mol}^{-1}} = \frac{23.2}{32.00}\ \text{mol}$$

$$n(\text{Ar}) = \frac{1.3\ \text{g}}{39.95\ \text{g mol}^{-1}} = \frac{1.3}{39.95}\ \text{mol}$$

These three amounts work out as 2.69 mol, 0.725 mol, and 0.033 mol, respectively, for a total of 3.45 mol. The mole fractions are obtained by dividing each of the above amounts by 3.45 mol and the partial pressures are then obtained by multiplying the mole fraction by the total pressure (1.00 atm):

	N_2	O_2	Ar
Mole fraction:	0.780	0.210	0.0096
Partial pressure/atm:	0.780	0.210	0.0096

We have not had to assume that the gases are perfect: partial pressures are defined as $p_J = x_J p$ for any kind of gas.

Self-test 1.4 When carbon dioxide is taken into account, the mass percentages are 75.52 (N_2), 23.15 (O_2), 1.28 (Ar), and 0.046 (CO_2). What are the partial pressures when the total pressure is 0.900 atm? [0.703, 0.189, 0.0084, 0.00027 atm]

Real gases

Real gases do not obey the perfect gas law exactly. Deviations from the law are particularly important at high pressures and low temperatures, especially when a gas is on the point of condensing to liquid.

1.3 Molecular interactions

Real gases show deviations from the perfect gas law because molecules interact with one another. Repulsive forces between molecules assist expansion and attractive forces assist compression.

Repulsive forces are significant only when molecules are almost in contact: they are short-range interactions, even on a scale measured in molecular diameters (Fig. 1.13). Because they are short-range interactions, repulsions can be expected to be important only when the average separation of the molecules is small. This is the case at high pressure, when many molecules occupy a small volume. On the other hand, attractive intermolecular forces have a relatively long range and are effective over several molecular diameters. They are important when the molecules are fairly close together but not necessarily touching (at the intermediate separations in Fig. 1.13). Attractive forces are ineffective when the molecules are far apart (well to the right in Fig. 1.13). Intermolecular forces are also important when the temperature is so low that the molecules travel with such low mean speeds that they can be captured by one another.

At low pressures, when the sample occupies a large volume, the molecules are so far apart for most of the time that the intermolecular forces play no significant role, and the gas behaves virtually perfectly. At moderate pressures, when the average separation of the molecules is only a few molecular diameters, the attractive forces dominate the repulsive forces. In this case, the gas can be expected to be more compressible than a perfect gas because the forces help to draw the molecules together. At high pressures, when the average separation of the molecules is small, the repulsive forces dominate and the gas can be expected to be less compressible because now the forces help to drive the molecules apart.

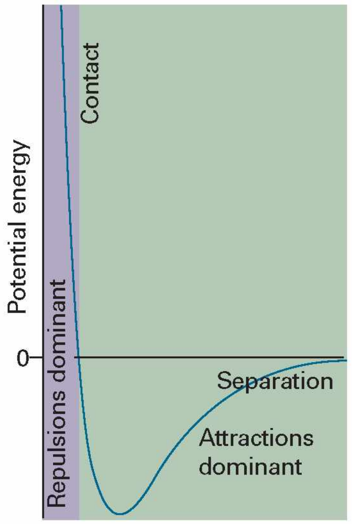

Fig. 1.13 The variation of the potential energy of two molecules on their separation. High positive potential energy (at very small separations) indicates that the interactions between them are strongly repulsive at these distances. At intermediate separations, where the potential energy is negative, the attractive interactions dominate. At large separations (on the right) the potential energy is zero and there is no interaction between the molecules.

(a) The compression factor

The **compression factor**, Z, of a gas is the ratio of its measured molar volume, $V_m = V/n$, to the molar volume of a perfect gas, V_m°, at the same pressure and temperature:

$$Z=\frac{V_{\mathrm{m}}}{V_{\mathrm{m}}^{\circ}} \qquad [1.16]$$

Because the molar volume of a perfect gas is equal to RT/p, an equivalent expression is $Z = RT/pV_{\mathrm{m}}^{\circ}$, which we can write as

$$pV_{\mathrm{m}} = RTZ \qquad (1.17)$$

Because for a perfect gas $Z = 1$ under all conditions, deviation of Z from 1 is a measure of departure from perfect behaviour.

Some experimental values of Z are plotted in Fig. 1.14. At very low pressures, all the gases shown have $Z \approx 1$ and behave nearly perfectly. At high pressures, all the gases have $Z > 1$, signifying that they have a larger molar volume than a perfect gas. Repulsive forces are now dominant. At intermediate pressures, most gases have $Z < 1$, indicating that the attractive forces are reducing the molar volume relative to that of a perfect gas.

(b) Virial coefficients

Figure 1.15 shows the experimental isotherms for carbon dioxide. At large molar volumes and high temperatures the real-gas isotherms do not differ greatly from perfect-gas isotherms. The small differences suggest that the perfect gas law is in fact the first term in an expression of the form

$$pV_{\mathrm{m}} = RT(1 + B'p + C'p^2 + \cdots) \qquad (1.18)$$

This expression is an example of a common procedure in physical chemistry, in which a simple law that is known to be a good first approximation (in this case $pV = nRT$) is

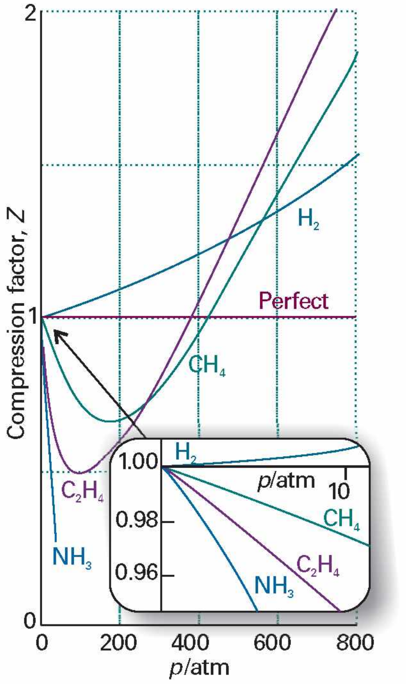

Fig. 1.14 The variation of the compression factor, Z, with pressure for several gases at 0°C. A perfect gas has $Z = 1$ at all pressures. Notice that, although the curves approach 1 as $p \to 0$, they do so with different slopes.

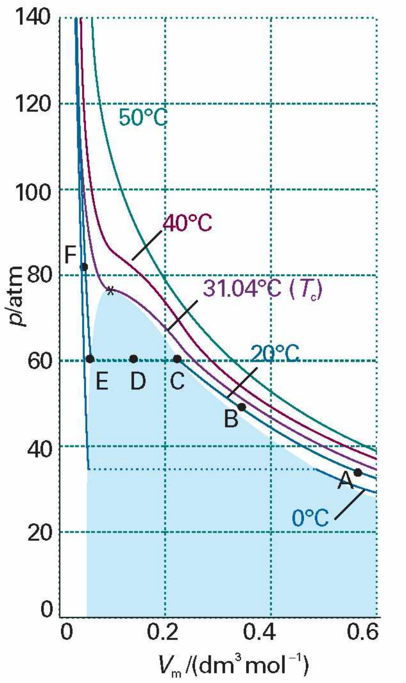

Fig. 1.15 Experimental isotherms of carbon dioxide at several temperatures. The 'critical isotherm', the isotherm at the critical temperature, is at 31.04°C. The critical point is marked with a star.

Comment 1.4

Series expansions are discussed in Appendix 2.

treated as the first term in a series in powers of a variable (in this case p). A more convenient expansion for many applications is

$$pV_\mathrm{m} = RT\left(1 + \frac{B}{V_\mathrm{m}} + \frac{C}{V_\mathrm{m}^2} + \cdots\right) \tag{1.19}$$

These two expressions are two versions of the **virial equation of state.**[4] By comparing the expression with eqn 1.17 we see that the term in parentheses can be identified with the compression factor, Z.

The coefficients B, C, . . . , which depend on the temperature, are the second, third, . . . **virial coefficients** (Table 1.4); the first virial coefficient is 1. The third virial coefficient, C, is usually less important than the second coefficient, B, in the sense that at typical molar volumes $C/V_\mathrm{m}^2 \ll B/V_\mathrm{m}$.

We can use the virial equation to demonstrate the important point that, although the equation of state of a real gas may coincide with the perfect gas law as $p \to 0$, not all its properties necessarily coincide with those of a perfect gas in that limit. Consider, for example, the value of $\mathrm{d}Z/\mathrm{d}p$, the slope of the graph of compression factor against pressure. For a perfect gas $\mathrm{d}Z/\mathrm{d}p = 0$ (because $Z = 1$ at all pressures), but for a real gas from eqn 1.18 we obtain

$$\frac{\mathrm{d}Z}{\mathrm{d}p} = B' + 2pC' + \cdots \to B' \qquad \text{as} \qquad p \to 0 \tag{1.20a}$$

However, B' is not necessarily zero, so the slope of Z with respect to p does not necessarily approach 0 (the perfect gas value), as we can see in Fig. 1.14. Because several physical properties of gases depend on derivatives, the properties of real gases do not always coincide with the perfect gas values at low pressures. By a similar argument,

$$\frac{\mathrm{d}Z}{\mathrm{d}(1/V_\mathrm{m})} \to B \text{ as } V_\mathrm{m} \to \infty, \qquad \text{corresponding to} \quad p \to 0 \tag{1.20b}$$

Because the virial coefficients depend on the temperature, there may be a temperature at which $Z \to 1$ with zero slope at low pressure or high molar volume (Fig. 1.16). At this temperature, which is called the **Boyle temperature**, T_B, the properties of the real gas do coincide with those of a perfect gas as $p \to 0$. According to eqn 1.20b, Z has zero slope as $p \to 0$ if $B = 0$, so we can conclude that $B = 0$ at the Boyle temperature. It then follows from eqn 1.19 that $pV_\mathrm{m} \approx RT_\mathrm{B}$ over a more extended range of pressures than at other temperatures because the first term after 1 (that is, B/V_m) in the virial equation is zero and C/V_m^2 and higher terms are negligibly small. For helium $T_\mathrm{B} = 22.64$ K; for air $T_\mathrm{B} = 346.8$ K; more values are given in Table 1.5.

Synoptic Table 1.4* Second virial coefficients, B/(cm^3 mol^{-1})

	Temperature	
	273 K	600 K
Ar	−21.7	11.9
CO_2	−149.7	−12.4
N_2	−10.5	21.7
Xe	−153.7	−19.6

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

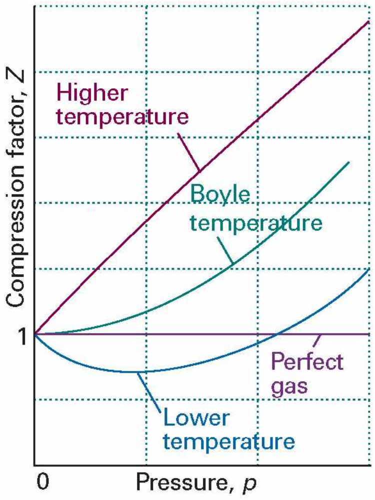

Fig. 1.16 The compression factor, Z, approaches 1 at low pressures, but does so with different slopes. For a perfect gas, the slope is zero, but real gases may have either positive or negative slopes, and the slope may vary with temperature. At the Boyle temperature, the slope is zero and the gas behaves perfectly over a wider range of conditions than at other temperatures.

Synoptic Table 1.5* Critical constants of gases

	p_c/atm	V_c/(cm^3 mol^{-1})	T_c/K	Z_c	T_B/K
Ar	48.0	75.3	150.7	0.292	411.5
CO_2	72.9	94.0	304.2	0.274	714.8
He	2.26	57.8	5.2	0.305	22.64
O_2	50.14	78.0	154.8	0.308	405.9

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

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[4] The name comes from the Latin word for force. The coefficients are sometimes denoted B_2, B_3, ...

(c) Condensation

Now consider what happens when we compress a sample of gas initially in the state marked A in Fig. 1.15 at constant temperature (by pushing in a piston). Near A, the pressure of the gas rises in approximate agreement with Boyle's law. Serious deviations from that law begin to appear when the volume has been reduced to B.

At C (which corresponds to about 60 atm for carbon dioxide), all similarity to perfect behaviour is lost, for suddenly the piston slides in without any further rise in pressure: this stage is represented by the horizontal line CDE. Examination of the contents of the vessel shows that just to the left of C a liquid appears, and there are two phases separated by a sharply defined surface. As the volume is decreased from C through D to E, the amount of liquid increases. There is no additional resistance to the piston because the gas can respond by condensing. The pressure corresponding to the line CDE, when both liquid and vapour are present in equilibrium, is called the **vapour pressure** of the liquid at the temperature of the experiment.

At E, the sample is entirely liquid and the piston rests on its surface. Any further reduction of volume requires the exertion of considerable pressure, as is indicated by the sharply rising line to the left of E. Even a small reduction of volume from E to F requires a great increase in pressure.

(d) Critical constants

The isotherm at the temperature T_c (304.19 K, or 31.04°C for CO_2) plays a special role in the theory of the states of matter. An isotherm slightly below T_c behaves as we have already described: at a certain pressure, a liquid condenses from the gas and is distinguishable from it by the presence of a visible surface. If, however, the compression takes place at T_c itself, then a surface separating two phases does not appear and the volumes at each end of the horizontal part of the isotherm have merged to a single point, the **critical point** of the gas. The temperature, pressure, and molar volume at the critical point are called the **critical temperature**, T_c, **critical pressure**, p_c, and **critical molar volume**, V_c, of the substance. Collectively, p_c, V_c, and T_c are the **critical constants** of a substance (Table 1.5).

Comment 1.5

The web site contains links to online databases of properties of gases.

At and above T_c, the sample has a single phase that occupies the entire volume of the container. Such a phase is, by definition, a gas. Hence, the liquid phase of a substance does not form above the critical temperature. The critical temperature of oxygen, for instance, signifies that it is impossible to produce liquid oxygen by compression alone if its temperature is greater than 155 K: to liquefy oxygen—to obtain a fluid phase that does not occupy the entire volume—the temperature must first be lowered to below 155 K, and then the gas compressed isothermally. The single phase that fills the entire volume when $T > T_c$ may be much denser than we normally consider typical of gases, and the name **supercritical fluid** is preferred.

1.4 The van der Waals equation

We can draw conclusions from the virial equations of state only by inserting specific values of the coefficients. It is often useful to have a broader, if less precise, view of all gases. Therefore, we introduce the approximate equation of state suggested by J.D. van der Waals in 1873. This equation is an excellent example of an expression that can be obtained by thinking scientifically about a mathematically complicated but physically simple problem, that is, it is a good example of 'model building'.

The **van der Waals equation** is

$$p = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2 \qquad (1.21a)$$

and a derivation is given in *Justification 1.1*. The equation is often written in terms of the molar volume $V_m = V/n$ as

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \tag{1.21b}$$

The constants a and b are called the **van der Waals coefficients**. They are characteristic of each gas but independent of the temperature (Table 1.6).

Synoptic Table 1.6* van der Waals coefficients

	$a/(\text{atm dm}^6\ \text{mol}^{-2})$	$b/(10^{-2}\ \text{dm}^3\ \text{mol}^{-1})$
Ar	1.337	3.20
CO_2	3.610	4.29
He	0.0341	2.38
Xe	4.137	5.16

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

Justification 1.1 *The van der Waals equation of state*

The repulsive interactions between molecules are taken into account by supposing that they cause the molecules to behave as small but impenetrable spheres. The non-zero volume of the molecules implies that instead of moving in a volume V they are restricted to a smaller volume $V - nb$, where nb is approximately the total volume taken up by the molecules themselves. This argument suggests that the perfect gas law $p = nRT/V$ should be replaced by

$$p = \frac{nRT}{V - nb}$$

when repulsions are significant. The closest distance of two hard-sphere molecules of radius r, and volume $V_{\text{molecule}} = \frac{4}{3}\pi r^3$, is $2r$, so the volume excluded is $\frac{4}{3}\pi(2r)^3$, or $8V_{\text{molecule}}$. The volume excluded per molecule is one-half this volume, or $4V_{\text{molecule}}$, so $b \approx 4V_{\text{molecule}}N_A$.

The pressure depends on both the frequency of collisions with the walls and the force of each collision. Both the frequency of the collisions and their force are reduced by the attractive forces, which act with a strength proportional to the molar concentration, n/V, of molecules in the sample. Therefore, because both the frequency and the force of the collisions are reduced by the attractive forces, the pressure is reduced in proportion to the square of this concentration. If the reduction of pressure is written as $-a(n/V)^2$, where a is a positive constant characteristic of each gas, the combined effect of the repulsive and attractive forces is the van der Waals equation of state as expressed in eqn 1.21.

In this *Justification* we have built the van der Waals equation using vague arguments about the volumes of molecules and the effects of forces. The equation can be derived in other ways, but the present method has the advantage that it shows how to derive the form of an equation out of general ideas. The derivation also has the advantage of keeping imprecise the significance of the coefficients a and b: they are much better regarded as empirical parameters than as precisely defined molecular properties.

Example 1.4 *Using the van der Waals equation to estimate a molar volume*

Estimate the molar volume of CO_2 at 500 K and 100 atm by treating it as a van der Waals gas.

Method To express eqn 1.21b as an equation for the molar volume, we multiply both sides by $(V_m - b)V_m^2$, to obtain

$$(V_m - b)V_m^2 p = RTV_m^2 - (V_m - b)a$$

and, after division by p, collect powers of V_m to obtain

$$V_m^3 - \left(b + \frac{RT}{p}\right)V_m^2 + \left(\frac{a}{p}\right)V_m - \frac{ab}{p} = 0$$

Although closed expressions for the roots of a cubic equation can be given, they are very complicated. Unless analytical solutions are essential, it is usually more expedient to solve such equations with commercial software.

Answer According to Table 1.6, $a = 3.592\ \mathrm{dm^6\ atm\ mol^{-2}}$ and $b = 4.267 \times 10^{-2}\ \mathrm{dm^3\ mol^{-1}}$. Under the stated conditions, $RT/p = 0.410\ \mathrm{dm^3\ mol^{-1}}$. The coefficients in the equation for V_m are therefore

$$b + RT/p = 0.453\ \mathrm{dm^3\ mol^{-1}}$$

$$a/p = 3.61 \times 10^{-2}\ (\mathrm{dm^3\ mol^{-1}})^2$$

$$ab/p = 1.55 \times 10^{-3}\ (\mathrm{dm^3\ mol^{-1}})^3$$

Therefore, on writing $x = V_\mathrm{m}/(\mathrm{dm^3\ mol^{-1}})$, the equation to solve is

$$x^3 - 0.453x^2 + (3.61 \times 10^{-2})x - (1.55 \times 10^{-3}) = 0$$

The acceptable root is $x = 0.366$, which implies that $V_\mathrm{m} = 0.366\ \mathrm{dm^3\ mol^{-1}}$. For a perfect gas under these conditions, the molar volume is $0.410\ \mathrm{dm^3\ mol^{-1}}$.

Self-test 1.5 Calculate the molar volume of argon at 100°C and 100 atm on the assumption that it is a van der Waals gas. [$0.298\ \mathrm{dm^3\ mol^{-1}}$]

(a) The reliability of the equation

We now examine to what extent the van der Waals equation predicts the behaviour of real gases. It is too optimistic to expect a single, simple expression to be the true equation of state of all substances, and accurate work on gases must resort to the virial equation, use tabulated values of the coefficients at various temperatures, and analyse the systems numerically. The advantage of the van der Waals equation, however, is that it is analytical (that is, expressed symbolically) and allows us to draw some general conclusions about real gases. When the equation fails we must use one of the other equations of state that have been proposed (some are listed in Table 1.7), invent a new one, or go back to the virial equation.

That having been said, we can begin to judge the reliability of the equation by comparing the isotherms it predicts with the experimental isotherms in Fig. 1.15. Some

Table 1.7 Selected equations of state

	Equation	Reduced form*	Critical constants		
			p_c	V_c	T_c
Perfect gas	$p = \dfrac{RT}{V_\mathrm{m}}$				
van der Waals	$p = \dfrac{RT}{V_\mathrm{m} - b} - \dfrac{a}{V_\mathrm{m}^2}$	$p = \dfrac{8T_\mathrm{r}}{3V_\mathrm{r} - 1} - \dfrac{3}{V_\mathrm{r}^2}$	$\dfrac{a}{27b^2}$	$3b$	$\dfrac{8a}{27bR}$
Berthelot	$p = \dfrac{RT}{V_\mathrm{m} - b} - \dfrac{a}{TV_\mathrm{m}^2}$	$p = \dfrac{8T_\mathrm{r}}{3V_\mathrm{r} - 1} - \dfrac{3}{T_\mathrm{r}V_\mathrm{r}^2}$	$\dfrac{1}{12}\left(\dfrac{2aR}{3b^3}\right)^{1/2}$	$3b$	$\dfrac{2}{3}\left(\dfrac{2a}{3bR}\right)^{1/2}$
Dieterici	$p = \dfrac{RT\mathrm{e}^{-a/RTV_\mathrm{m}}}{V_\mathrm{m} - b}$	$p = \dfrac{\mathrm{e}^2T_\mathrm{r}\mathrm{e}^{-2/T_\mathrm{r}V_\mathrm{r}}}{2V_\mathrm{r} - 1}$	$\dfrac{a}{4\mathrm{e}^2b^2}$	$2b$	$\dfrac{a}{4bR}$
Virial	$p = \dfrac{RT}{V_\mathrm{m}}\left\{1 + \dfrac{B(T)}{V_\mathrm{m}} + \dfrac{C(T)}{V_\mathrm{m}^2} + \cdots\right\}$				

* Reduced variables are defined in Section 1.5.

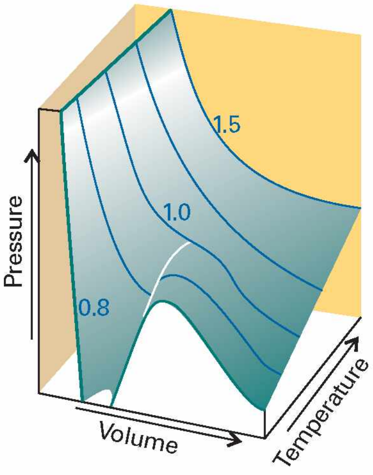


Fig. 1.17 The surface of possible states allowed by the van der Waals equation. Compare this surface with that shown in Fig. 1.8.

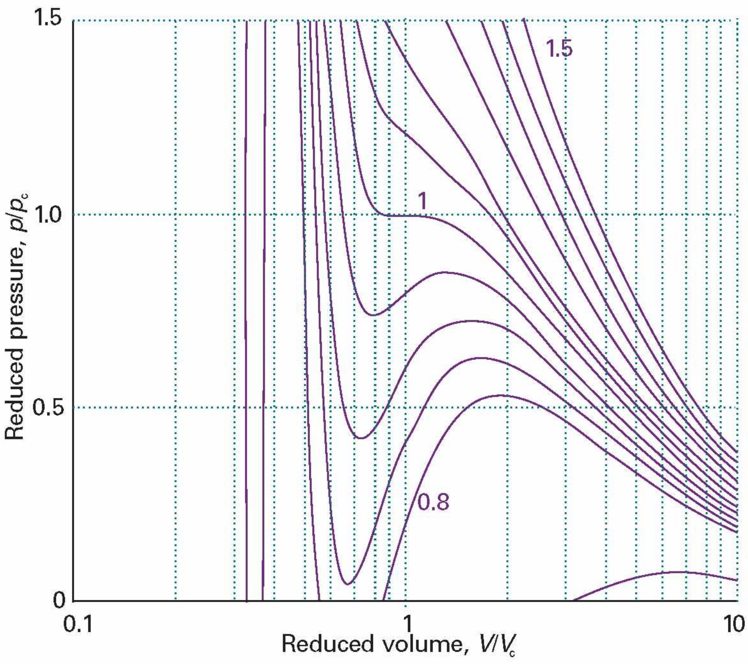
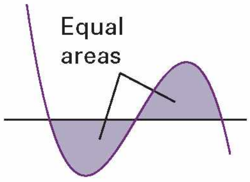


Fig. 1.18 Van der Waals isotherms at several values of T/T_c. Compare these curves with those in Fig. 1.15. The van der Waals loops are normally replaced by horizontal straight lines. The critical isotherm is the isotherm for $T/T_c = 1$.

Exploration Calculate the molar volume of chlorine gas on the basis of the van der Waals equation of state at 250 K and 150 kPa and calculate the percentage difference from the value predicted by the perfect gas equation.

calculated isotherms are shown in Figs. 1.17 and 1.18. Apart from the oscillations below the critical temperature, they do resemble experimental isotherms quite well. The oscillations, the **van der Waals loops**, are unrealistic because they suggest that under some conditions an increase of pressure results in an increase of volume. Therefore they are replaced by horizontal lines drawn so the loops define equal areas above and below the lines: this procedure is called the **Maxwell construction** (**3**). The van der Waals coefficients, such as those in Table 1.7, are found by fitting the calculated curves to the experimental curves.



3

(b) The features of the equation

The principal features of the van der Waals equation can be summarized as follows.

(1) Perfect gas isotherms are obtained at high temperatures and large molar volumes.

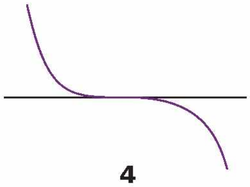
When the temperature is high, RT may be so large that the first term in eqn 1.21b greatly exceeds the second. Furthermore, if the molar volume is large in the sense $V_m \gg b$, then the denominator $V_m - b \approx V_m$. Under these conditions, the equation reduces to $p = RT/V_m$, the perfect gas equation.

(2) Liquids and gases coexist when cohesive and dispersing effects are in balance.

The van der Waals loops occur when both terms in eqn 1.21b have similar magnitudes. The first term arises from the kinetic energy of the molecules and their repulsive interactions; the second represents the effect of the attractive interactions.

(3) The critical constants are related to the van der Waals coefficients.

For $T < T_c$, the calculated isotherms oscillate, and each one passes through a minimum followed by a maximum. These extrema converge as $T \rightarrow T_c$ and coincide at $T = T_c$; at the critical point the curve has a flat inflexion (**4**). From the properties of curves, we know that an inflexion of this type occurs when both the first and second derivatives are zero. Hence, we can find the critical constants by calculating these derivatives and setting them equal to zero:



4

$$\frac{\mathrm{d}p}{\mathrm{d}V_\mathrm{m}} = -\frac{RT}{(V_\mathrm{m} - b)^2} + \frac{2a}{V_\mathrm{m}^3} = 0$$

$$\frac{\mathrm{d}^2p}{\mathrm{d}V_\mathrm{m}^2} = \frac{2RT}{(V_\mathrm{m} - b)^3} - \frac{6a}{V_\mathrm{m}^4} = 0$$

at the critical point. The solutions of these two equations (and using eqn 1.21b to calculate p_c from V_c and T_c) are

$$V_c = 3b \qquad p_c = \frac{a}{27b^2} \qquad T_c = \frac{8a}{27Rb} \tag{1.22}$$

These relations provide an alternative route to the determination of a and b from the values of the critical constants. They can be tested by noting that the **critical compression factor**, Z_c, is predicted to be equal to

$$Z_c = \frac{p_cV_c}{RT_c} = \frac{3}{8} \tag{1.23}$$

for all gases. We see from Table 1.5 that, although $Z_c < \frac{3}{8} = 0.375$, it is approximately constant (at 0.3) and the discrepancy is reasonably small.

1.5 The principle of corresponding states

An important general technique in science for comparing the properties of objects is to choose a related fundamental property of the same kind and to set up a relative scale on that basis. We have seen that the critical constants are characteristic properties of gases, so it may be that a scale can be set up by using them as yardsticks. We therefore introduce the dimensionless **reduced variables** of a gas by dividing the actual variable by the corresponding critical constant:

$$p_r = \frac{p}{p_c} \qquad V_r = \frac{V_\mathrm{m}}{V_c} \qquad T_r = \frac{T}{T_c} \qquad [1.24]$$

If the reduced pressure of a gas is given, we can easily calculate its actual pressure by using $p = p_rp_c$, and likewise for the volume and temperature. Van der Waals, who first tried this procedure, hoped that gases confined to the same reduced volume, V_r, at the same reduced temperature, T_r, would exert the same reduced pressure, p_r. The hope was largely fulfilled (Fig. 1.19). The illustration shows the dependence of the compression factor on the reduced pressure for a variety of gases at various reduced temperatures. The success of the procedure is strikingly clear: compare this graph with Fig. 1.14, where similar data are plotted without using reduced variables. The observation that real gases at the same reduced volume and reduced temperature exert the same reduced pressure is called the **principle of corresponding states**. The principle is only an approximation. It works best for gases composed of spherical molecules; it fails, sometimes badly, when the molecules are non-spherical or polar.

The van der Waals equation sheds some light on the principle. First, we express eqn 1.21b in terms of the reduced variables, which gives

$$p_rp_c = \frac{RT_rT_c}{V_rV_c - b} - \frac{a}{V_r^2V_c^2}$$

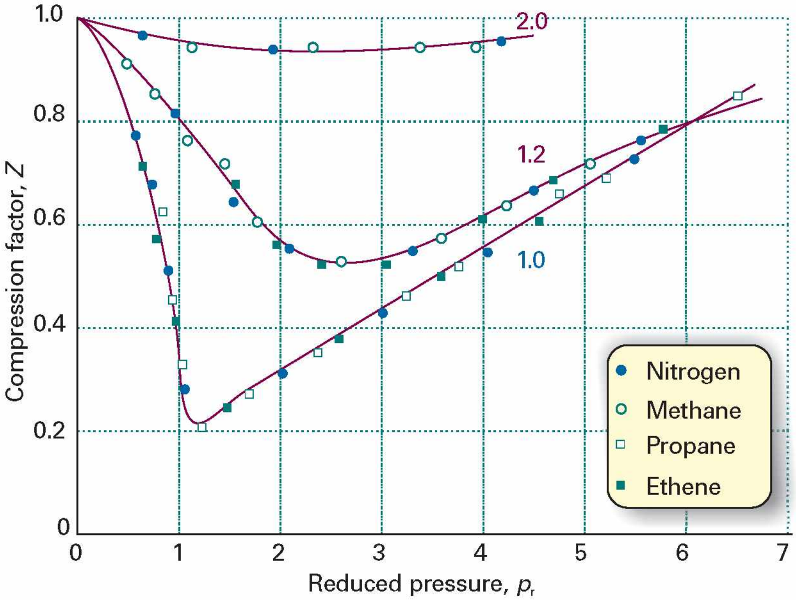


Fig. 1.19 The compression factors of four of the gases shown in Fig. 1.14 plotted using reduced variables. The curves are labelled with the reduced temperature $T_r = T/T_c$. The use of reduced variables organizes the data on to single curves.

Exploration Is there a set of conditions at which the compression factor of a van der Waals gas passes through a minimum? If so, how does the location and value of the minimum value of *Z* depend on the coefficients *a* and *b*?

Then we express the critical constants in terms of *a* and *b* by using eqn 1.22:

$$\frac{ap_r}{27b^2} = \frac{8aT_r}{27b(3bV_r - b)} - \frac{a}{9b^2V_r^2}$$

which can be reorganized into

$$p_r = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2} \qquad (1.25)$$

This equation has the same form as the original, but the coefficients *a* and *b*, which differ from gas to gas, have disappeared. It follows that if the isotherms are plotted in terms of the reduced variables (as we did in fact in Fig. 1.18 without drawing attention to the fact), then the same curves are obtained whatever the gas. This is precisely the content of the principle of corresponding states, so the van der Waals equation is compatible with it.

Looking for too much significance in this apparent triumph is mistaken, because other equations of state also accommodate the principle (Table 1.7). In fact, all we need are two parameters playing the roles of *a* and *b*, for then the equation can always be manipulated into reduced form. The observation that real gases obey the principle approximately amounts to saying that the effects of the attractive and repulsive interactions can each be approximated in terms of a single parameter. The importance of the principle is then not so much its theoretical interpretation but the way that it enables the properties of a range of gases to be coordinated on to a single diagram (for example, Fig. 1.19 instead of Fig. 1.14).

Checklist of key ideas

☐ 1. A gas is a form of matter that fills any container it occupies.

☐ 2. An equation of state interrelates pressure, volume, temperature, and amount of substance: $p = f(T,V,n)$.

☐ 3. The pressure is the force divided by the area to which the force is applied. The standard pressure is $p^\ominus = 1$ bar (10^5 Pa).

☐ 4. Mechanical equilibrium is the condition of equality of pressure on either side of a movable wall.

☐ 5. Temperature is the property that indicates the direction of the flow of energy through a thermally conducting, rigid wall.

☐ 6. A diathermic boundary is a boundary that permits the passage of energy as heat. An adiabatic boundary is a boundary that prevents the passage of energy as heat.

☐ 7. Thermal equilibrium is a condition in which no change of state occurs when two objects A and B are in contact through a diathermic boundary.

☐ 8. The Zeroth Law of thermodynamics states that, if A is in thermal equilibrium with B, and B is in thermal equilibrium with C, then C is also in thermal equilibrium with A.

☐ 9. The Celsius and thermodynamic temperature scales are related by $T/\mathrm{K} = \theta/{}^\circ\mathrm{C} + 273.15$.

☐ 10. A perfect gas obeys the perfect gas equation, $pV = nRT$, exactly under all conditions.

☐ 11. Dalton's law states that the pressure exerted by a mixture of gases is the sum of the partial pressures of the gases.

☐ 12. The partial pressure of any gas is defined as $p_J = x_J p$, where $x_J = n_J/n$ is its mole fraction in a mixture and p is the total pressure.

☐ 13. In real gases, molecular interactions affect the equation of state; the true equation of state is expressed in terms of virial coefficients $B, C, \ldots$: $pV_m = RT(1 + B/V_m + C/V_m^2 + \cdots)$.

☐ 14. The vapour pressure is the pressure of a vapour in equilibrium with its condensed phase.

☐ 15. The critical point is the point at which the volumes at each end of the horizontal part of the isotherm have merged to a single point. The critical constants p_c, V_c, and T_c are the pressure, molar volume, and temperature, respectively, at the critical point.

☐ 16. A supercritical fluid is a dense fluid phase above its critical temperature and pressure.

☐ 17. The van der Waals equation of state is an approximation to the true equation of state in which attractions are represented by a parameter a and repulsions are represented by a parameter b: $p = nRT/(V - nb) - a(n/V)^2$.

☐ 18. A reduced variable is the actual variable divided by the corresponding critical constant.

☐ 19. According to the principle of corresponding states, real gases at the same reduced volume and reduced temperature exert the same reduced pressure.

Further reading

Articles and texts

J.L. Pauley and E.H. Davis, *P-V-T* isotherms of real gases: Experimental versus calculated values. *J. Chem. Educ.* **63**, 466 (1986).

M. Ross, Equations of state. In *Encyclopedia of applied physics* (ed. G.L. Trigg), **6**, 291. VCH, New York (1993).

A. J. Walton, *Three phases of matter*. Oxford University Press (1983).

R.P. Wayne, *Chemistry of atmospheres, an introduction to the chemistry of atmospheres of earth, the planets, and their satellites.* Oxford University Press (2000).

Sources of data and information

J.H. Dymond and E.B. Smith, *The virial coefficients of pure gases and mixtures*. Oxford University Press (1980).

A.D. McNaught and A. Wilkinson, *Compendium of chemical terminology*. Blackwell Scientific, Oxford (1997).

Discussion questions

1.1 Explain how the perfect gas equation of state arises by combination of Boyle's law, Charles's law, and Avogadro's principle.

1.2 Explain the term 'partial pressure' and explain why Dalton's law is a limiting law.

1.3 Explain how the compression factor varies with pressure and temperature and describe how it reveals information about intermolecular interactions in real gases.

1.4 What is the significance of the critical constants?

1.5 Describe the formulation of the van der Waals equation and suggest a rationale for one other equation of state in Table 1.7.

1.6 Explain how the van der Waals equation accounts for critical behaviour.

Exercises

1.1(a) (a) Could 131 g of xenon gas in a vessel of volume 1.0 dm^3 exert a pressure of 20 atm at 25°C if it behaved as a perfect gas? If not, what pressure would it exert? (b) What pressure would it exert if it behaved as a van der Waals gas?

1.1(b) (a) Could 25 g of argon gas in a vessel of volume 1.5 dm^3 exert a pressure of 2.0 bar at 30°C if it behaved as a perfect gas? If not, what pressure would it exert? (b) What pressure would it exert if it behaved as a van der Waals gas?

1.2(a) A perfect gas undergoes isothermal compression, which reduces its volume by 2.20 dm^3. The final pressure and volume of the gas are 5.04 bar and 4.65 dm^3, respectively. Calculate the original pressure of the gas in (a) bar, (b) atm.

1.2(b) A perfect gas undergoes isothermal compression, which reduces its volume by 1.80 dm^3. The final pressure and volume of the gas are 1.97 bar and 2.14 dm^3, respectively. Calculate the original pressure of the gas in (a) bar, (b) Torr.

1.3(a) A car tyre (i.e. an automobile tire) was inflated to a pressure of 24 lb in^{-2} (1.00 atm = 14.7 lb in^{-2}) on a winter's day when the temperature was –5°C. What pressure will be found, assuming no leaks have occurred and that the volume is constant, on a subsequent summer's day when the temperature is 35°C? What complications should be taken into account in practice?

1.3(b) A sample of hydrogen gas was found to have a pressure of 125 kPa when the temperature was 23°C. What can its pressure be expected to be when the temperature is 11°C?

1.4(a) A sample of 255 mg of neon occupies 3.00 dm^3 at 122 K. Use the perfect gas law to calculate the pressure of the gas.

1.4(b) A homeowner uses 4.00×10^3 m^3 of natural gas in a year to heat a home. Assume that natural gas is all methane, CH_4, and that methane is a perfect gas for the conditions of this problem, which are 1.00 atm and 20°C. What is the mass of gas used?

1.5(a) A diving bell has an air space of 3.0 m^3 when on the deck of a boat. What is the volume of the air space when the bell has been lowered to a depth of 50 m? Take the mean density of sea water to be 1.025 g cm^{-3} and assume that the temperature is the same as on the surface.

1.5(b) What pressure difference must be generated across the length of a 15 cm vertical drinking straw in order to drink a water-like liquid of density 1.0 g cm^{-3}?

1.6(a) A manometer consists of a U-shaped tube containing a liquid. One side is connected to the apparatus and the other is open to the atmosphere. The pressure inside the apparatus is then determined from the difference in heights of the liquid. Suppose the liquid is water, the external pressure is 770 Torr, and the open side is 10.0 cm lower than the side connected to the apparatus. What is the pressure in the apparatus? (The density of water at 25°C is 0.997 07 g cm^{-3}.)

1.6(b) A manometer like that described in Exercise 1.6a contained mercury in place of water. Suppose the external pressure is 760 Torr, and the open side is 10.0 cm higher than the side connected to the apparatus. What is the pressure in the apparatus? (The density of mercury at 25°C is 13.55 g cm^{-3}.)

1.7(a) In an attempt to determine an accurate value of the gas constant, *R*, a student heated a container of volume 20.000 dm^3 filled with 0.251 32 g of helium gas to 500°C and measured the pressure as 206.402 cm of water in a manometer at 25°C. Calculate the value of *R* from these data. (The density of water at 25°C is 0.997 07 g cm^{-3}; the construction of a manometer is described in Exercise 1.6a.)

1.7(b) The following data have been obtained for oxygen gas at 273.15 K. Calculate the best value of the gas constant *R* from them and the best value of the molar mass of O_2.

p/atm	0.750 000	0.500 000	0.250 000
$V_m/(dm^3\ mol^{-1})$	29.9649	44.8090	89.6384
$\rho/(g\ dm^{-3})$	1.07144	0.714110	0.356975

1.8(a) At 500°C and 93.2 kPa, the mass density of sulfur vapour is 3.710 kg m^{-3}. What is the molecular formula of sulfur under these conditions?

1.8(b) At 100°C and 1.60 kPa, the mass density of phosphorus vapour is 0.6388 kg m^{-3}. What is the molecular formula of phosphorus under these conditions?

1.9(a) Calculate the mass of water vapour present in a room of volume 400 m^3 that contains air at 27°C on a day when the relative humidity is 60 per cent.

1.9(b) Calculate the mass of water vapour present in a room of volume 250 m^3 that contains air at 23°C on a day when the relative humidity is 53 per cent.

1.10(a) Given that the density of air at 0.987 bar and 27°C is 1.146 kg m^{-3}, calculate the mole fraction and partial pressure of nitrogen and oxygen assuming that (a) air consists only of these two gases, (b) air also contains 1.0 mole per cent Ar.

1.10(b) A gas mixture consists of 320 mg of methane, 175 mg of argon, and 225 mg of neon. The partial pressure of neon at 300 K is 8.87 kPa. Calculate (a) the volume and (b) the total pressure of the mixture.

1.11(a) The density of a gaseous compound was found to be 1.23 kg m^{-3} at 330 K and 20 kPa. What is the molar mass of the compound?

1.11(b) In an experiment to measure the molar mass of a gas, 250 cm^3 of the gas was confined in a glass vessel. The pressure was 152 Torr at 298 K and, after correcting for buoyancy effects, the mass of the gas was 33.5 mg. What is the molar mass of the gas?

1.12(a) The densities of air at –85°C, 0°C, and 100°C are 1.877 g dm^{-3}, 1.294 g dm^{-3}, and 0.946 g dm^{-3}, respectively. From these data, and assuming that air obeys Charles's law, determine a value for the absolute zero of temperature in degrees Celsius.

1.12(b) A certain sample of a gas has a volume of 20.00 dm^3 at 0°C and 1.000 atm. A plot of the experimental data of its volume against the Celsius temperature, θ, at constant p, gives a straight line of slope 0.0741 $dm^3\ (°C)^{-1}$. From these data alone (without making use of the perfect gas law), determine the absolute zero of temperature in degrees Celsius.

1.13(a) Calculate the pressure exerted by 1.0 mol C_2H_6 behaving as (a) a perfect gas, (b) a van der Waals gas when it is confined under the following conditions: (i) at 273.15 K in 22.414 dm^3, (ii) at 1000 K in 100 cm^3. Use the data in Table 1.6.

1.13(b) Calculate the pressure exerted by 1.0 mol H_2S behaving as (a) a perfect gas, (b) a van der Waals gas when it is confined under the following conditions: (i) at 273.15 K in 22.414 dm^3, (ii) at 500 K in 150 cm^3. Use the data in Table 1.6.

1.14(a) Express the van der Waals parameters $a = 0.751$ atm dm^6 mol^{-2} and $b = 0.0226$ dm^3 mol^{-1} in SI base units.

1.14(b) Express the van der Waals parameters $a = 1.32$ atm dm^6 mol^{-2} and $b = 0.0436$ dm^3 mol^{-1} in SI base units.

1.15(a) A gas at 250 K and 15 atm has a molar volume 12 per cent smaller than that calculated from the perfect gas law. Calculate (a) the compression factor under these conditions and (b) the molar volume of the gas. Which are dominating in the sample, the attractive or the repulsive forces?

1.15(b) A gas at 350 K and 12 atm has a molar volume 12 per cent larger than that calculated from the perfect gas law. Calculate (a) the compression factor under these conditions and (b) the molar volume of the gas. Which are dominating in the sample, the attractive or the repulsive forces?

1.16(a) In an industrial process, nitrogen is heated to 500 K at a constant volume of 1.000 m^3. The gas enters the container at 300 K and 100 atm. The mass of the gas is 92.4 kg. Use the van der Waals equation to determine the approximate pressure of the gas at its working temperature of 500 K. For nitrogen, $a = 1.352\ dm^6\ atm\ mol^{-2}$, $b = 0.0387\ dm^3\ mol^{-1}$.

1.16(b) Cylinders of compressed gas are typically filled to a pressure of 200 bar. For oxygen, what would be the molar volume at this pressure and 25°C based on (a) the perfect gas equation, (b) the van der Waals equation. For oxygen, $a = 1.364\ dm^6\ atm\ mol^{-2}$, $b = 3.19 \times 10^{-2}\ dm^3\ mol^{-1}$.

1.17(a) Suppose that 10.0 mol $C_2H_6(g)$ is confined to 4.860 dm^3 at 27°C. Predict the pressure exerted by the ethane from (a) the perfect gas and (b) the van der Waals equations of state. Calculate the compression factor based on these calculations. For ethane, $a = 5.507\ dm^6\ atm\ mol^{-2}$, $b = 0.0651\ dm^3\ mol^{-1}$.

1.17(b) At 300 K and 20 atm, the compression factor of a gas is 0.86. Calculate (a) the volume occupied by 8.2 mmol of the gas under these conditions and (b) an approximate value of the second virial coefficient B at 300 K.

1.18(a) A vessel of volume 22.4 dm^3 contains 2.0 mol H_2 and 1.0 mol N_2 at 273.15 K. Calculate (a) the mole fractions of each component, (b) their partial pressures, and (c) their total pressure.

1.18(b) A vessel of volume 22.4 dm^3 contains 1.5 mol H_2 and 2.5 mol N_2 at 273.15 K. Calculate (a) the mole fractions of each component, (b) their partial pressures, and (c) their total pressure.

1.19(a) The critical constants of methane are $p_c = 45.6$ atm, $V_c = 98.7\ cm^3\ mol^{-1}$, and $T_c = 190.6$ K. Calculate the van der Waals parameters of the gas and estimate the radius of the molecules.

1.19(b) The critical constants of ethane are $p_c = 48.20$ atm, $V_c = 148\ cm^3\ mol^{-1}$, and $T_c = 305.4$ K. Calculate the van der Waals parameters of the gas and estimate the radius of the molecules.

1.20(a) Use the van der Waals parameters for chlorine to calculate approximate values of (a) the Boyle temperature of chlorine and (b) the radius of a Cl_2 molecule regarded as a sphere.

1.20(b) Use the van der Waals parameters for hydrogen sulfide to calculate approximate values of (a) the Boyle temperature of the gas and (b) the radius of a H_2S molecule regarded as a sphere ($a = 4.484\ dm^6\ atm\ mol^{-2}$, $b = 0.0434\ dm^3\ mol^{-1}$).

1.21(a) Suggest the pressure and temperature at which 1.0 mol of (a) NH_3, (b) Xe, (c) He will be in states that correspond to 1.0 mol H_2 at 1.0 atm and 25°C.

1.21(b) Suggest the pressure and temperature at which 1.0 mol of (a) H_2S, (b) CO_2, (c) Ar will be in states that correspond to 1.0 mol N_2 at 1.0 atm and 25°C.

1.22(a) A certain gas obeys the van der Waals equation with $a = 0.50\ m^6\ Pa\ mol^{-2}$. Its volume is found to be $5.00 \times 10^{-4}\ m^3\ mol^{-1}$ at 273 K and 3.0 MPa. From this information calculate the van der Waals constant b. What is the compression factor for this gas at the prevailing temperature and pressure?

1.22(b) A certain gas obeys the van der Waals equation with $a = 0.76\ m^6\ Pa\ mol^{-2}$. Its volume is found to be $4.00 \times 10^{-4}\ m^3\ mol^{-1}$ at 288 K and 4.0 MPa. From this information calculate the van der Waals constant b. What is the compression factor for this gas at the prevailing temperature and pressure?

Problems*

Numerical problems

1.1 Recent communication with the inhabitants of Neptune have revealed that they have a Celsius-type temperature scale, but based on the melting point (0°N) and boiling point (100°N) of their most common substance, hydrogen. Further communications have revealed that the Neptunians know about perfect gas behaviour and they find that, in the limit of zero pressure, the value of pV is 28 dm^3 atm at 0°N and 40 dm^3 atm at 100°N. What is the value of the absolute zero of temperature on their temperature scale?

1.2 Deduce the relation between the pressure and mass density, ρ, of a perfect gas of molar mass M. Confirm graphically, using the following data on dimethyl ether at 25°C, that perfect behaviour is reached at low pressures and find the molar mass of the gas.

p/kPa	12.223	25.20	36.97	60.37	85.23	101.3
$\rho/(kg\ m^{-3})$	0.225	0.456	0.664	1.062	1.468	1.734

1.3 Charles's law is sometimes expressed in the form $V = V_0(1 + \alpha\theta)$, where θ is the Celsius temperature, α is a constant, and V_0 is the volume of the sample at 0°C. The following values for α have been reported for nitrogen at 0°C:

p/Torr	749.7	599.6	333.1	98.6
$10^3\alpha/(°C)^{-1}$	3.6717	3.6697	3.6665	3.6643

For these data calculate the best value for the absolute zero of temperature on the Celsius scale.

1.4 The molar mass of a newly synthesized fluorocarbon was measured in a gas microbalance. This device consists of a glass bulb forming one end of a beam, the whole surrounded by a closed container. The beam is pivoted, and the balance point is attained by raising the pressure of gas in the container, so increasing the buoyancy of the enclosed bulb. In one experiment, the balance point was reached when the fluorocarbon pressure was 327.10 Torr; for the same setting of the pivot, a balance was reached when CHF_3 ($M = 70.014\ g\ mol^{-1}$) was introduced at 423.22 Torr. A repeat of the experiment with a different setting of the pivot required a pressure of 293.22 Torr of the fluorocarbon and 427.22 Torr of the CHF_3. What is the molar mass of the fluorocarbon? Suggest a molecular formula.

1.5 A constant-volume perfect gas thermometer indicates a pressure of 6.69 kPa at the triple point temperature of water (273.16 K). (a) What change of pressure indicates a change of 1.00 K at this temperature? (b) What pressure indicates a temperature of 100.00°C? (c) What change of pressure indicates a change of 1.00 K at the latter temperature?

1.6 A vessel of volume 22.4 dm^3 contains 2.0 mol H_2 and 1.0 mol N_2 at 273.15 K initially. All the H_2 reacted with sufficient N_2 to form NH_3. Calculate the partial pressures and the total pressure of the final mixture.

1.7 Calculate the molar volume of chlorine gas at 350 K and 2.30 atm using (a) the perfect gas law and (b) the van der Waals equation. Use the answer to (a) to calculate a first approximation to the correction term for attraction and then use successive approximations to obtain a numerical answer for part (b).

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

1.8 At 273 K measurements on argon gave $B = -21.7\ \text{cm}^3\ \text{mol}^{-1}$ and $C = 1200\ \text{cm}^6\ \text{mol}^{-2}$, where B and C are the second and third virial coefficients in the expansion of Z in powers of $1/V_m$. Assuming that the perfect gas law holds sufficiently well for the estimation of the second and third terms of the expansion, calculate the compression factor of argon at 100 atm and 273 K. From your result, estimate the molar volume of argon under these conditions.

1.9 Calculate the volume occupied by 1.00 mol N_2 using the van der Waals equation in the form of a virial expansion at (a) its critical temperature, (b) its Boyle temperature, and (c) its inversion temperature. Assume that the pressure is 10 atm throughout. At what temperature is the gas most perfect? Use the following data: $T_c = 126.3$ K, $a = 1.352\ \text{dm}^6\ \text{atm}\ \text{mol}^{-2}$, $b = 0.0387\ \text{dm}^3\ \text{mol}^{-1}$.

1.10‡ The second virial coefficient of methane can be approximated by the empirical equation $B'(T) = a + be^{-c/T^2}$, where $a = -0.1993\ \text{bar}^{-1}$, $b = 0.2002\ \text{bar}^{-1}$, and $c = 1131\ \text{K}^2$ with $300\ \text{K} < T < 600\ \text{K}$. What is the Boyle temperature of methane?

1.11 The mass density of water vapour at 327.6 atm and 776.4 K is $133.2\ \text{kg m}^{-3}$. Given that for water $T_c = 647.4$ K, $p_c = 218.3$ atm, $a = 5.464\ \text{dm}^6\ \text{atm}\ \text{mol}^{-2}$, $b = 0.03049\ \text{dm}^3\ \text{mol}^{-1}$, and $M = 18.02\ \text{g mol}^{-1}$, calculate (a) the molar volume. Then calculate the compression factor (b) from the data, (c) from the virial expansion of the van der Waals equation.

1.12 The critical volume and critical pressure of a certain gas are $160\ \text{cm}^3\ \text{mol}^{-1}$ and 40 atm, respectively. Estimate the critical temperature by assuming that the gas obeys the Berthelot equation of state. Estimate the radii of the gas molecules on the assumption that they are spheres.

1.13 Estimate the coefficients a and b in the Dieterici equation of state from the critical constants of xenon. Calculate the pressure exerted by 1.0 mol Xe when it is confined to $1.0\ \text{dm}^3$ at 25°C.

Theoretical problems

1.14 Show that the van der Waals equation leads to values of $Z < 1$ and $Z > 1$, and identify the conditions for which these values are obtained.

1.15 Express the van der Waals equation of state as a virial expansion in powers of $1/V_m$ and obtain expressions for B and C in terms of the parameters a and b. The expansion you will need is $(1-x)^{-1} = 1 + x + x^2 + \cdots$. Measurements on argon gave $B = -21.7\ \text{cm}^3\ \text{mol}^{-1}$ and $C = 1200\ \text{cm}^6\ \text{mol}^{-2}$ for the virial coefficients at 273 K. What are the values of a and b in the corresponding van der Waals equation of state?

1.16‡ Derive the relation between the critical constants and the Dieterici equation parameters. Show that $Z_c = 2e^{-2}$ and derive the reduced form of the Dieterici equation of state. Compare the van der Waals and Dieterici predictions of the critical compression factor. Which is closer to typical experimental values?

1.17 A scientist proposed the following equation of state:

$$p = \frac{RT}{V_m} - \frac{B}{V_m^2} + \frac{C}{V_m^3}$$

Show that the equation leads to critical behaviour. Find the critical constants of the gas in terms of B and C and an expression for the critical compression factor.

1.18 Equations 1.18 and 1.19 are expansions in p and $1/V_m$, respectively. Find the relation between B, C and B', C'.

1.19 The second virial coefficient B' can be obtained from measurements of the density ρ of a gas at a series of pressures. Show that the graph of p/ρ against p should be a straight line with slope proportional to B'. Use the data on dimethyl ether in Problem 1.2 to find the values of B' and B at 25°C.

1.20 The equation of state of a certain gas is given by $p = RT/V_m + (a + bT)/V_m^2$, where a and b are constants. Find $(\partial V/\partial T)_p$.

1.21 The following equations of state are occasionally used for approximate calculations on gases: (gas A) $pV_m = RT(1 + b/V_m)$, (gas B) $p(V_m - b) = RT$. Assuming that there were gases that actually obeyed these equations of state, would it be possible to liquefy either gas A or B? Would they have a critical temperature? Explain your answer.

1.22 Derive an expression for the compression factor of a gas that obeys the equation of state $p(V - nb) = nRT$, where b and R are constants. If the pressure and temperature are such that $V_m = 10b$, what is the numerical value of the compression factor?

1.23‡ The discovery of the element argon by Lord Rayleigh and Sir William Ramsay had its origins in Rayleigh's measurements of the density of nitrogen with an eye toward accurate determination of its molar mass. Rayleigh prepared some samples of nitrogen by chemical reaction of nitrogen-containing compounds; under his standard conditions, a glass globe filled with this 'chemical nitrogen' had a mass of 2.2990 g. He prepared other samples by removing oxygen, carbon dioxide, and water vapour from atmospheric air; under the same conditions, this 'atmospheric nitrogen' had a mass of 2.3102 g (Lord Rayleigh, *Royal Institution Proceedings* **14**, 524 (1895)). With the hindsight of knowing accurate values for the molar masses of nitrogen and argon, compute the mole fraction of argon in the latter sample on the assumption that the former was pure nitrogen and the latter a mixture of nitrogen and argon.

1.24‡ A substance as elementary and well known as argon still receives research attention. Stewart and Jacobsen have published a review of thermodynamic properties of argon (R.B. Stewart and R.T. Jacobsen, *J. Phys. Chem. Ref. Data* **18**, 639 (1989)) that included the following 300 K isotherm.

p/MPa	0.4000	0.5000	0.6000	0.8000	1.000
$V_m/(\text{dm}^3\ \text{mol}^{-1})$	6.2208	4.9736	4.1423	3.1031	2.4795
p/MPa	1.500	2.000	2.500	3.000	4.000
$V_m/(\text{dm}^3\ \text{mol}^{-1})$	1.6483	1.2328	0.98357	0.81746	0.60998

(a) Compute the second virial coefficient, B, at this temperature. (b) Use non-linear curve-fitting software to compute the third virial coefficient, C, at this temperature.

Applications: to environmental science

1.25 Atmospheric pollution is a problem that has received much attention. Not all pollution, however, is from industrial sources. Volcanic eruptions can be a significant source of air pollution. The Kilauea volcano in Hawaii emits 200–300 t of SO_2 per day. If this gas is emitted at 800°C and 1.0 atm, what volume of gas is emitted?

1.26 Ozone is a trace atmospheric gas that plays an important role in screening the Earth from harmful ultraviolet radiation, and the abundance of ozone is commonly reported in *Dobson units*. One Dobson unit is the thickness, in thousandths of a centimetre, of a column of gas if it were collected as a pure gas at 1.00 atm and 0°C. What amount of O_3 (in moles) is found in a column of atmosphere with a cross-sectional area of $1.00\ \text{dm}^2$ if the abundance is 250 Dobson units (a typical mid-latitude value)? In the seasonal Antarctic ozone hole, the column abundance drops below 100 Dobson units; how many moles of ozone are found in such a column of air above a $1.00\ \text{dm}^2$ area? Most atmospheric ozone is found between 10 and 50 km above the surface of the earth. If that ozone is spread uniformly through this portion of the atmosphere, what is the average molar concentration corresponding to (a) 250 Dobson units, (b) 100 Dobson units?

1.27 The barometric formula relates the pressure of a gas of molar mass M at an altitude h to its pressure p_0 at sea level. Derive this relation by showing that the change in pressure dp for an infinitesimal change in altitude dh where the density is ρ is d$p = -\rho g$dh. Remember that ρ depends on the pressure. Evaluate (a) the pressure difference between the top and bottom of a laboratory vessel of height 15 cm, and (b) the external atmospheric pressure at a typical cruising altitude of an aircraft (11 km) when the pressure at ground level is 1.0 atm.

1.28 Balloons are still used to deploy sensors that monitor meteorological phenomena and the chemistry of the atmosphere. It is possible to investigate some of the technicalities of ballooning by using the perfect gas law. Suppose your balloon has a radius of 3.0 m and that it is spherical. (a) What amount of H_2 (in moles) is needed to inflate it to 1.0 atm in an ambient temperature of 25°C at sea level? (b) What mass can the balloon lift at sea level, where the density of air is 1.22 kg m^{-3}? (c) What would be the payload if He were used instead of H_2?

1.29‡ The preceding problem is most readily solved (see the *Solutions manual*) with the use of the Archimedes principle, which states that the lifting force is equal to the difference between the weight of the displaced air and the weight of the balloon. Prove the Archimedes principle for the atmosphere from the barometric formula. *Hint*. Assume a simple shape for the balloon, perhaps a right circular cylinder of cross–sectional area A and height h.

1.30 ‡ Chlorofluorocarbons such as CCl_3F and CCl_2F_2 have been linked to ozone depletion in Antarctica. As of 1994, these gases were found in quantities of 261 and 509 parts per trillion (10^{12}) by volume (World Resources Institute, *World resources* 1996–97). Compute the molar concentration of these gases under conditions typical of (a) the mid-latitude troposphere (10°C and 1.0 atm) and (b) the Antarctic stratosphere (200 K and 0.050 atm).

2

The First Law

This chapter introduces some of the basic concepts of thermodynamics. It concentrates on the conservation of energy—the experimental observation that energy can be neither created nor destroyed—and shows how the principle of the conservation of energy can be used to assess the energy changes that accompany physical and chemical processes. Much of this chapter examines the means by which a system can exchange energy with its surroundings in terms of the work it may do or the heat that it may produce. The target concept of the chapter is enthalpy, which is a very useful book-keeping property for keeping track of the heat output (or requirements) of physical processes and chemical reactions at constant pressure. We also begin to unfold some of the power of thermodynamics by showing how to establish relations between different properties of a system. We shall see that one very useful aspect of thermodynamics is that a property can be measured indirectly by measuring others and then combining their values. The relations we derive also enable us to discuss the liquefaction of gases and to establish the relation between the heat capacities of a substance under different conditions.

The release of energy can be used to provide heat when a fuel burns in a furnace, to produce mechanical work when a fuel burns in an engine, and to generate electrical work when a chemical reaction pumps electrons through a circuit. In chemistry, we encounter reactions that can be harnessed to provide heat and work, reactions that liberate energy which is squandered (often to the detriment of the environment) but which give products we require, and reactions that constitute the processes of life. **Thermodynamics**, the study of the transformations of energy, enables us to discuss all these matters quantitatively and to make useful predictions.

The basic concepts

For the purposes of physical chemistry, the universe is divided into two parts, the system and its surroundings. The **system** is the part of the world in which we have a special interest. It may be a reaction vessel, an engine, an electrochemical cell, a biological cell, and so on. The **surroundings** comprise the region outside the system and are where we make our measurements. The type of system depends on the characteristics of the boundary that divides it from the surroundings (Fig. 2.1). If matter can be transferred through the boundary between the system and its surroundings the system is classified as **open**. If matter cannot pass through the boundary the system is classified as **closed**. Both open and closed systems can exchange energy with their surroundings. For example, a closed system can expand and thereby raise a weight in the surroundings; it may also transfer energy to them if they are at a lower temperature.

An **isolated system** is a closed system that has neither mechanical nor thermal contact with its surroundings.

2.1 Work, heat, and energy

The fundamental physical property in thermodynamics is work: **work** is motion against an opposing force. Doing work is equivalent to raising a weight somewhere in the surroundings. An example of doing work is the expansion of a gas that pushes out a piston and raises a weight. A chemical reaction that drives an electric current through a resistance also does work, because the same current could be driven through a motor and used to raise a weight.

The **energy** of a system is its capacity to do work. When work is done on an otherwise isolated system (for instance, by compressing a gas or winding a spring), the capacity of the system to do work is increased; in other words, the energy of the system is increased. When the system does work (when the piston moves out or the spring unwinds), the energy of the system is reduced and it can do less work than before.

Experiments have shown that the energy of a system may be changed by means other than work itself. When the energy of a system changes as a result of a temperature difference between the system and its surroundings we say that energy has been transferred as **heat**. When a heater is immersed in a beaker of water (the system), the capacity of the system to do work increases because hot water can be used to do more work than the same amount of cold water. Not all boundaries permit the transfer of energy even though there is a temperature difference between the system and its surroundings.

An **exothermic process** is a process that releases energy as heat into its surroundings. All combustion reactions are exothermic. An **endothermic process** is a process in which energy is acquired from its surroundings as heat. An example of an endothermic process is the vaporization of water. To avoid a lot of awkward circumlocution, we say that in an exothermic process energy is transferred 'as heat' to the surroundings and in an endothermic process energy is transferred 'as heat' from the surroundings into the system. However, it must never be forgotten that heat is a process (the transfer of energy as a result of a temperature difference), not an entity. An endothermic process in a diathermic container results in energy flowing into the system as heat. An exothermic process in a similar diathermic container results in a release of energy as heat into the surroundings. When an endothermic process takes place in an adiabatic container, it results in a lowering of temperature of the system; an exothermic process results in a rise of temperature. These features are summarized in Fig. 2.2.

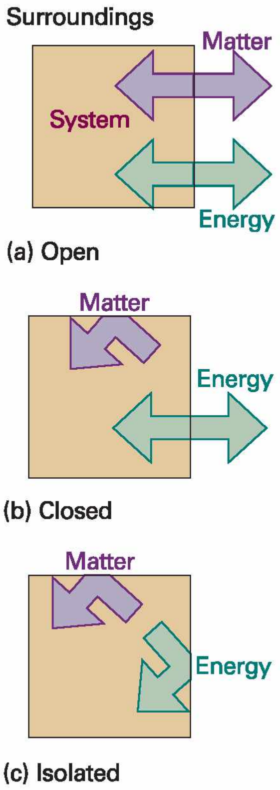


Fig. 2.1 (a) An open system can exchange matter and energy with its surroundings. (b) A closed system can exchange energy with its surroundings, but it cannot exchange matter. (c) An isolated system can exchange neither energy nor matter with its surroundings.

Molecular interpretation 2.1 *Heat and work*

In molecular terms, heating is the transfer of energy that makes use of *disorderly molecular motion*. The disorderly motion of molecules is called **thermal motion**. The thermal motion of the molecules in the hot surroundings stimulates the molecules in the cooler system to move more vigorously and, as a result, the energy of the system is increased. When a system heats its surroundings, molecules of the system stimulate the thermal motion of the molecules in the surroundings (Fig. 2.3).

In contrast, *work is the transfer of energy that makes use of organized motion* (Fig. 2.4). When a weight is raised or lowered, its atoms move in an organized way (up or down). The atoms in a spring move in an orderly way when it is wound; the

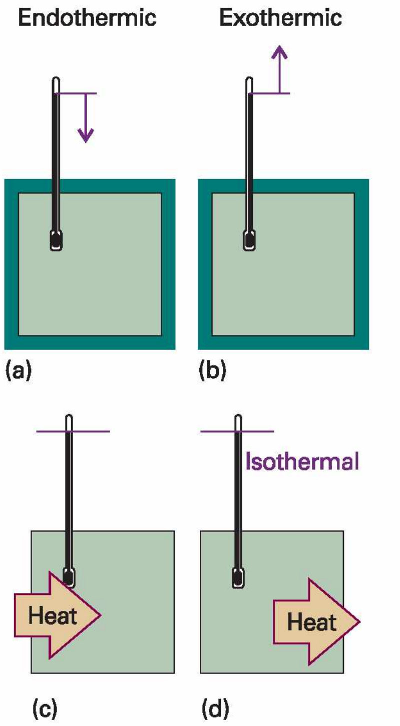


Fig. 2.2 (a) When an endothermic process occurs in an adiabatic system, the temperature falls; (b) if the process is exothermic, then the temperature rises. (c) When an endothermic process occurs in a diathermic container, energy enters as heat from the surroundings, and the system remains at the same temperature. (d) If the process is exothermic, then energy leaves as heat, and the process is isothermal.

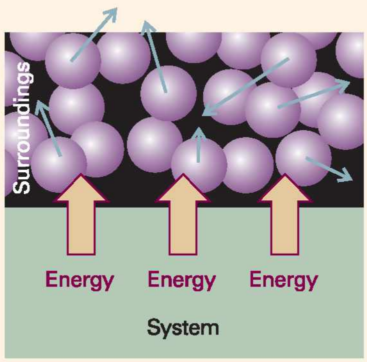


Fig. 2.3 When energy is transferred to the surroundings as heat, the transfer stimulates random motion of the atoms in the surroundings. Transfer of energy from the surroundings to the system makes use of random motion (thermal motion) in the surroundings.

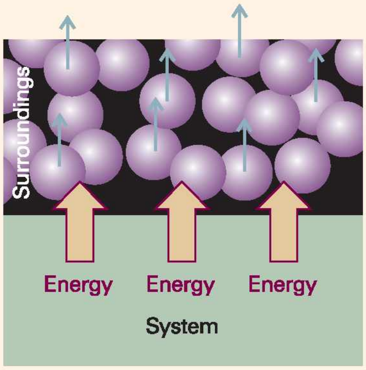


Fig. 2.4 When a system does work, it stimulates orderly motion in the surroundings. For instance, the atoms shown here may be part of a weight that is being raised. The ordered motion of the atoms in a falling weight does work on the system.

electrons in an electric current move in an orderly direction when it flows. When a system does work it causes atoms or electrons in its surroundings to move in an organized way. Likewise, when work is done on a system, molecules in the surroundings are used to transfer energy to it in an organized way, as the atoms in a weight are lowered or a current of electrons is passed.

The distinction between work and heat is made in the surroundings. The fact that a falling weight may stimulate thermal motion in the system is irrelevant to the distinction between heat and work: work is identified as energy transfer making use of the organized motion of atoms in the surroundings, and heat is identified as energy transfer making use of thermal motion in the surroundings. In the compression of a gas, for instance, work is done as the atoms of the compressing weight descend in an orderly way, but the effect of the incoming piston is to accelerate the gas molecules to higher average speeds. Because collisions between molecules quickly randomize their directions, the orderly motion of the atoms of the weight is in effect stimulating thermal motion in the gas. We observe the falling weight, the orderly descent of its atoms, and report that work is being done even though it is stimulating thermal motion.

2.2 The internal energy

In thermodynamics, the total energy of a system is called its **internal energy**, U. The internal energy is the total kinetic and potential energy of the molecules in the system (see *Comment 1.3* for the definitions of kinetic and potential energy).[1] We denote by ΔU the change in internal energy when a system changes from an initial state i with internal energy U_i to a final state f of internal energy U_f:

$$\Delta U = U_\mathrm{f} - U_\mathrm{i} \qquad [2.1]$$

---

[1] The internal energy does not include the kinetic energy arising from the motion of the system as a whole, such as its kinetic energy as it accompanies the Earth on its orbit round the Sun.

The internal energy is a **state function** in the sense that its value depends only on the current state of the system and is independent of how that state has been prepared. In other words, it is a function of the properties that determine the current state of the system. Changing any one of the state variables, such as the pressure, results in a change in internal energy. The internal energy is an extensive property. That the internal energy is a state function has consequences of the greatest importance, as we start to unfold in Section 2.10.

Comment 2.1

An extensive property is a property that depends on the amount of substance in the sample. An intensive property is a property that is independent of the amount of substance in the sample. Two examples of extensive properties are mass and volume. Examples of intensive properties are temperature, mass density (mass divided by volume), and pressure.

Internal energy, heat, and work are all measured in the same units, the joule (J). The joule, which is named after the nineteenth-century scientist J.P. Joule, is defined as

$$1\ \mathrm{J} = 1\ \mathrm{kg\ m^2\ s^{-2}}$$

A joule is quite a small unit of energy: for instance, each beat of the human heart consumes about 1 J. Changes in molar internal energy, ΔU_m, are typically expressed in kilojoules per mole (kJ $\mathrm{mol^{-1}}$). Certain other energy units are also used, but are more common in fields other than thermodynamics. Thus, 1 electronvolt (1 eV) is defined as the kinetic energy acquired when an electron is accelerated from rest through a potential difference of 1 V; the relation between electronvolts and joules is 1 eV ≈ 0.16 aJ (where 1 aJ = 10^{-18} J). Many processes in chemistry have an energy of several electronvolts. Thus, the energy to remove an electron from a sodium atom is close to 5 eV. Calories (cal) and kilocalories (kcal) are still encountered. The current definition of the calorie in terms of joules is

$$1\ \mathrm{cal} = 4.184\ \mathrm{J\ exactly}$$

An energy of 1 cal is enough to raise the temperature of 1 g of water by 1°C.

Molecular interpretation 2.2 *The internal energy of a gas*

A molecule has a certain number of degrees of freedom, such as the ability to translate (the motion of its centre of mass through space), rotate around its centre of mass, or vibrate (as its bond lengths and angles change). Many physical and chemical properties depend on the energy associated with each of these modes of motion. For example, a chemical bond might break if a lot of energy becomes concentrated in it.

The *equipartition theorem* of classical mechanics is a useful guide to the average energy associated with each degree of freedom when the sample is at a temperature T. First, we need to know that a 'quadratic contribution' to the energy means a contribution that can be expressed as the square of a variable, such as the position or the velocity. For example, the kinetic energy an atom of mass m as it moves through space is

$$E_K = \tfrac{1}{2}mv_x^2 + \tfrac{1}{2}mv_y^2 + \tfrac{1}{2}mv_z^2$$

and there are three quadratic contributions to its energy. The equipartition theorem then states that, for a collection of particles at thermal equilibrium at a temperature T, *the average value of each quadratic contribution to the energy is the same and equal to* $\tfrac{1}{2}kT$, where k is Boltzmann's constant ($k = 1.381 \times 10^{-23}\ \mathrm{J\ K^{-1}}$).

The equipartition theorem is a conclusion from classical mechanics and is applicable only when the effects of quantization can be ignored (see Chapters 16 and 17). In practice, it can be used for molecular translation and rotation but not vibration. At 25°C, $\tfrac{1}{2}kT = 2$ zJ (where 1 zJ = 10^{-21} J), or about 13 meV.

According to the equipartition theorem, the average energy of each term in the expression above is $\tfrac{1}{2}kT$. Therefore, the mean energy of the atoms is $\tfrac{3}{2}kT$ and the total energy of the gas (there being no potential energy contribution) is $\frac{3}{2}NkT$, or $\frac{3}{2}nRT$ (because $N = nN_A$ and $R = N_Ak$). We can therefore write

$$U_m = U_m(0) + \tfrac{3}{2}RT$$

where $U_m(0)$ is the molar internal energy at $T = 0$, when all translational motion has ceased and the sole contribution to the internal energy arises from the internal structure of the atoms. This equation shows that the internal energy of a perfect gas increases linearly with temperature. At 25°C, $\frac{3}{2}RT = 3.7\ \text{kJ mol}^{-1}$, so translational motion contributes about 4 kJ mol^{-1} to the molar internal energy of a gaseous sample of atoms or molecules (the remaining contribution arises from the internal structure of the atoms and molecules).

When the gas consists of polyatomic molecules, we need to take into account the effect of rotation and vibration. A linear molecule, such as N_2 and CO_2, can rotate around two axes perpendicular to the line of the atoms (Fig. 2.5), so it has two rotational modes of motion, each contributing a term $\frac{1}{2}kT$ to the internal energy. Therefore, the mean rotational energy is kT and the rotational contribution to the molar internal energy is RT. By adding the translational and rotational contributions, we obtain

$$U_m = U_m(0) + \tfrac{5}{2}RT \qquad \text{(linear molecule, translation and rotation only)}$$

A nonlinear molecule, such as CH_4 or water, can rotate around three axes and, again, each mode of motion contributes a term $\frac{1}{2}kT$ to the internal energy. Therefore, the mean rotational energy is $\frac{3}{2}kT$ and there is a rotational contribution of $\frac{3}{2}RT$ to the molar internal energy of the molecule. That is,

$$U_m = U_m(0) + 3RT \qquad \text{(nonlinear molecule, translation and rotation only)}$$

The internal energy now increases twice as rapidly with temperature compared with the monatomic gas.

The internal energy of interacting molecules in condensed phases also has a contribution from the potential energy of their interaction. However, no simple expressions can be written down in general. Nevertheless, the crucial molecular point is that, as the temperature of a system is raised, the internal energy increases as the various modes of motion become more highly excited.

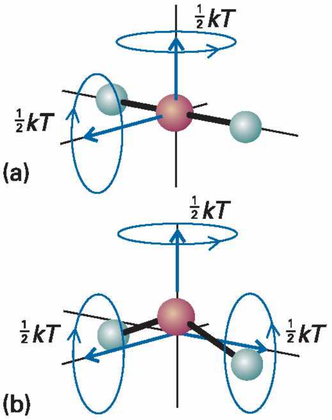


Fig. 2.5 The rotational modes of molecules and the corresponding average energies at a temperature T. (a) A linear molecule can rotate about two axes perpendicular to the line of the atoms. (b) A nonlinear molecule can rotate about three perpendicular axes.

It has been found experimentally that the internal energy of a system may be changed either by doing work on the system or by heating it. Whereas we may know how the energy transfer has occurred (because we can see if a weight has been raised or lowered in the surroundings, indicating transfer of energy by doing work, or if ice has melted in the surroundings, indicating transfer of energy as heat), the system is blind to the mode employed. *Heat and work are equivalent ways of changing a system's internal energy*. A system is like a bank: it accepts deposits in either currency, but stores its reserves as internal energy. It is also found experimentally that, if a system is isolated from its surroundings, then no change in internal energy takes place. This summary of observations is now known as the **First Law of thermodynamics** and expressed as follows:

The internal energy of an isolated system is constant.

We cannot use a system to do work, leave it isolated for a month, and then come back expecting to find it restored to its original state and ready to do the same work again. The evidence for this property is that no 'perpetual motion machine' (a machine that does work without consuming fuel or some other source of energy) has ever been built.

These remarks may be summarized as follows. If we write w for the work done on a system, q for the energy transferred as heat to a system, and ΔU for the resulting change in internal energy, then it follows that

$$\Delta U = q + w \tag{2.2}$$

Equation 2.2 is the mathematical statement of the First Law, for it summarizes the equivalence of heat and work and the fact that the internal energy is constant in an isolated system (for which $q = 0$ and $w = 0$). The equation states that the change in internal energy of a closed system is equal to the energy that passes through its boundary as heat or work. It employs the 'acquisitive convention', in which $w > 0$ or $q > 0$ if energy is transferred to the system as work or heat and $w < 0$ or $q < 0$ if energy is lost from the system as work or heat. In other words, we view the flow of energy as work or heat from the system's perspective.

Illustration 2.1 *The sign convention in thermodynamics*

If an electric motor produced 15 kJ of energy each second as mechanical work and lost 2 kJ as heat to the surroundings, then the change in the internal energy of the motor each second is

$$\Delta U = -2\ \text{kJ} - 15\ \text{kJ} = -17\ \text{kJ}$$

Suppose that, when a spring was wound, 100 J of work was done on it but 15 J escaped to the surroundings as heat. The change in internal energy of the spring is

$$\Delta U = +100\ \text{kJ} - 15\ \text{kJ} = +85\ \text{kJ}$$

2.3 Expansion work

The way can now be opened to powerful methods of calculation by switching attention to infinitesimal changes of state (such as infinitesimal change in temperature) and infinitesimal changes in the internal energy $\text{d}U$. Then, if the work done on a system is $\text{d}w$ and the energy supplied to it as heat is $\text{d}q$, in place of eqn 2.2 we have

$$\text{d}U = \text{d}q + \text{d}w \tag{2.3}$$

To use this expression we must be able to relate $\text{d}q$ and $\text{d}w$ to events taking place in the surroundings.

We begin by discussing **expansion work**, the work arising from a change in volume. This type of work includes the work done by a gas as it expands and drives back the atmosphere. Many chemical reactions result in the generation or consumption of gases (for instance, the thermal decomposition of calcium carbonate or the combustion of octane), and the thermodynamic characteristics of a reaction depend on the work it can do. The term 'expansion work' also includes work associated with negative changes of volume, that is, compression.

(a) The general expression for work

The calculation of expansion work starts from the definition used in physics, which states that the work required to move an object a distance $\text{d}z$ against an opposing force of magnitude F is

$$\text{d}w = -F\text{d}z \qquad [2.4]$$

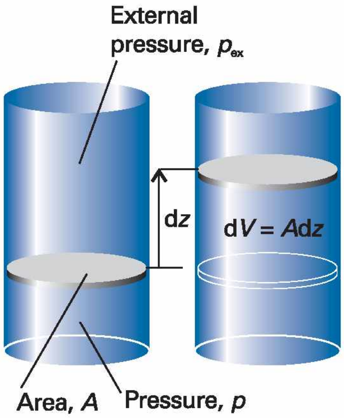


Fig. 2.6 When a piston of area A moves out through a distance dz, it sweeps out a volume d$V = A$dz. The external pressure p_{ex} is equivalent to a weight pressing on the piston, and the force opposing expansion is $F = p_{ex}A$.

The negative sign tells us that, when the system moves an object against an opposing force, the internal energy of the system doing the work will decrease. Now consider the arrangement shown in Fig. 2.6, in which one wall of a system is a massless, frictionless, rigid, perfectly fitting piston of area A. If the external pressure is p_{ex}, the magnitude of the force acting on the outer face of the piston is $F = p_{ex}A$. When the system expands through a distance dz against an external pressure p_{ex}, it follows that the work done is d$w = -p_{ex}A$dz. But Adz is the change in volume, dV, in the course of the expansion. Therefore, the work done when the system expands by dV against a pressure p_{ex} is

$$\mathrm{d}w = -p_{ex}\mathrm{d}V \tag{2.5}$$

To obtain the total work done when the volume changes from V_i to V_f we integrate this expression between the initial and final volumes:

$$w = -\int_{V_i}^{V_f} p_{ex}\mathrm{d}V \tag{2.6}$$

The force acting on the piston, $p_{ex}A$, is equivalent to a weight that is raised as the system expands.

If the system is compressed instead, then the same weight is lowered in the surroundings and eqn 2.6 can still be used, but now $V_f < V_i$. It is important to note that it is still the external pressure that determines the magnitude of the work. This somewhat perplexing conclusion seems to be inconsistent with the fact that the gas *inside* the container is opposing the compression. However, when a gas is compressed, the ability of the *surroundings* to do work is diminished by an amount determined by the weight that is lowered, and it is this energy that is transferred into the system.

Other types of work (for example, electrical work), which we shall call either **non-expansion work** or **additional work**, have analogous expressions, with each one the product of an intensive factor (the pressure, for instance) and an extensive factor (the change in volume). Some are collected in Table 2.1. For the present we continue with the work associated with changing the volume, the expansion work, and see what we can extract from eqns 2.5 and 2.6.

(b) Free expansion

By **free expansion** we mean expansion against zero opposing force. It occurs when $p_{ex} = 0$. According to eqn 2.5, d$w = 0$ for each stage of the expansion. Hence, overall:

Free expansion: $w = 0$ (2.7)

Table 2.1 Varieties of work*

Type of work	dw	Comments	Units†
Expansion	$-p_{ex}\mathrm{d}V$	p_{ex} is the external pressure dV is the change in volume	Pa m^3
Surface expansion	$\gamma\mathrm{d}\sigma$	γ is the surface tension dσ is the change in area	$\mathrm{N\,m^{-1}}$ m^2
Extension	$f\mathrm{d}l$	f is the tension dl is the change in length	N m
Electrical	$\phi\mathrm{d}Q$	ϕ is the electric potential dQ is the change in charge	V C

* In general, the work done on a system can be expressed in the form d$w = -F$dz, where F is a 'generalized force' and dz is a 'generalized displacement'.

† For work in joules (J). Note that 1 N m = 1 J and 1 V C = 1 J.

That is, no work is done when a system expands freely. Expansion of this kind occurs when a system expands into a vacuum.

(c) Expansion against constant pressure

Now suppose that the external pressure is constant throughout the expansion. For example, the piston may be pressed on by the atmosphere, which exerts the same pressure throughout the expansion. A chemical example of this condition is the expansion of a gas formed in a chemical reaction. We can evaluate eqn 2.6 by taking the constant p_{ex} outside the integral:

$$w = -p_{\mathrm{ex}}\int_{V_{\mathrm{i}}}^{V_{\mathrm{f}}} \mathrm{d}V = -p_{\mathrm{ex}}(V_{\mathrm{f}} - V_{\mathrm{i}})$$

Therefore, if we write the change in volume as $\Delta V = V_{\mathrm{f}} - V_{\mathrm{i}}$,

$$w = -p_{\mathrm{ex}}\Delta V \tag{2.8}$$

This result is illustrated graphically in Fig. 2.7, which makes use of the fact that an integral can be interpreted as an area. The magnitude of w, denoted $|w|$, is equal to the area beneath the horizontal line at $p = p_{\mathrm{ex}}$ lying between the initial and final volumes. A p,V-graph used to compute expansion work is called an **indicator diagram**; James Watt first used one to indicate aspects of the operation of his steam engine.

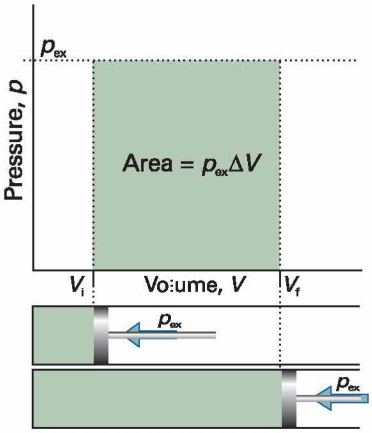


Fig. 2.7 The work done by a gas when it expands against a constant external pressure, p_{ex}, is equal to the shaded area in this example of an indicator diagram.

(d) Reversible expansion

A **reversible change** in thermodynamics is a change that can be reversed by an infinitesimal modification of a variable. The key word 'infinitesimal' sharpens the everyday meaning of the word 'reversible' as something that can change direction. We say that a system is in **equilibrium** with its surroundings if an infinitesimal change in the conditions in opposite directions results in opposite changes in its state. One example of reversibility that we have encountered already is the thermal equilibrium of two systems with the same temperature. The transfer of energy as heat between the two is reversible because, if the temperature of either system is lowered infinitesimally, then energy flows into the system with the lower temperature. If the temperature of either system at thermal equilibrium is raised infinitesimally, then energy flows out of the hotter system.

Suppose a gas is confined by a piston and that the external pressure, p_{ex}, is set equal to the pressure, p, of the confined gas. Such a system is in mechanical equilibrium with its surroundings (as illustrated in Section 1.1) because an infinitesimal change in the external pressure in either direction causes changes in volume in opposite directions. If the external pressure is reduced infinitesimally, then the gas expands slightly. If the external pressure is increased infinitesimally, then the gas contracts slightly. In either case the change is reversible in the thermodynamic sense. If, on the other hand, the external pressure differs measurably from the internal pressure, then changing p_{ex} infinitesimally will not decrease it below the pressure of the gas, so will not change the direction of the process. Such a system is not in mechanical equilibrium with its surroundings and the expansion is thermodynamically irreversible.

To achieve reversible expansion we set p_{ex} equal to p at each stage of the expansion. In practice, this equalization could be achieved by gradually removing weights from the piston so that the downward force due to the weights always matched the changing upward force due to the pressure of the gas. When we set $p_{\mathrm{ex}} = p$, eqn 2.5 becomes

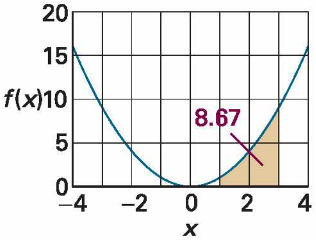
$$\mathrm{d}w = -p_{\mathrm{ex}}\mathrm{d}V = -p\mathrm{d}V \tag*{(2.9)$_{\mathrm{rev}}$}$$

(Equations valid only for reversible processes are labelled with a subscript rev.) Although the pressure inside the system appears in this expression for the work, it

Comment 2.2

The value of the integral $\int_a^b f(x)\mathrm{d}x$ is equal to the area under the graph of $f(x)$ between $x = a$ and $x = b$. For instance, the area under the curve $f(x) = x^2$ shown in the illustration that lies between $x = 1$ and 3 is

$$\int_1^3 x^2\mathrm{d}x = \left(\tfrac{1}{3}x^3 + \text{constant}\right)\Big|_1^3$$
$$= \tfrac{1}{3}(3^3 - 1^3) = \tfrac{26}{3} \approx 8.67$$



does so only because p_{ex} has been set equal to p to ensure reversibility. The total work of reversible expansion is therefore

$$w = -\int_{V_i}^{V_f} p\mathrm{d}V \qquad (2.10)_{\text{rev}}$$

We can evaluate the integral once we know how the pressure of the confined gas depends on its volume. Equation 2.10 is the link with the material covered in Chapter 1 for, if we know the equation of state of the gas, then we can express p in terms of V and evaluate the integral.

(e) Isothermal reversible expansion

Consider the isothermal, reversible expansion of a perfect gas. The expansion is made isothermal by keeping the system in thermal contact with its surroundings (which may be a constant-temperature bath). Because the equation of state is $pV = nRT$, we know that at each stage $p = nRT/V$, with V the volume at that stage of the expansion. The temperature T is constant in an isothermal expansion, so (together with n and R) it may be taken outside the integral. It follows that the work of reversible isothermal expansion of a perfect gas from V_i to V_f at a temperature T is

$$w = -nRT\int_{V_i}^{V_f}\frac{\mathrm{d}V}{V} = -nRT\ln\frac{V_f}{V_i} \qquad (2.11)^{\circ}_{\text{rev}}$$

When the final volume is greater than the initial volume, as in an expansion, the logarithm in eqn 2.11 is positive and hence $w < 0$. In this case, the system has done work on the surroundings and the internal energy of the system has decreased as a result.[2] The equations also show that more work is done for a given change of volume when the temperature is increased. The greater pressure of the confined gas then needs a higher opposing pressure to ensure reversibility.

We can express the result of the calculation as an indicator diagram, for the magnitude of the work done is equal to the area under the isotherm $p = nRT/V$ (Fig. 2.8). Superimposed on the diagram is the rectangular area obtained for irreversible expansion against constant external pressure fixed at the same final value as that reached in the reversible expansion. More work is obtained when the expansion is reversible (the area is greater) because matching the external pressure to the internal pressure at each stage of the process ensures that none of the system's pushing power is wasted. We cannot obtain more work than for the reversible process because increasing the external pressure even infinitesimally at any stage results in compression. We may infer from this discussion that, because some pushing power is wasted when $p > p_{ex}$, the maximum work available from a system operating between specified initial and final states and passing along a specified path is obtained when the change takes place reversibly.

We have introduced the connection between reversibility and maximum work for the special case of a perfect gas undergoing expansion. Later (in Section 3.5) we shall see that it applies to all substances and to all kinds of work.

Example 2.1 *Calculating the work of gas production*

Calculate the work done when 50 g of iron reacts with hydrochloric acid in (a) a closed vessel of fixed volume, (b) an open beaker at 25°C.

Comment 2.3

An integral that occurs throughout thermodynamics is

$$\int_a^b \frac{1}{x}\mathrm{d}x = (\ln x + \text{constant})\Big|_a^b = \ln\frac{b}{a}$$

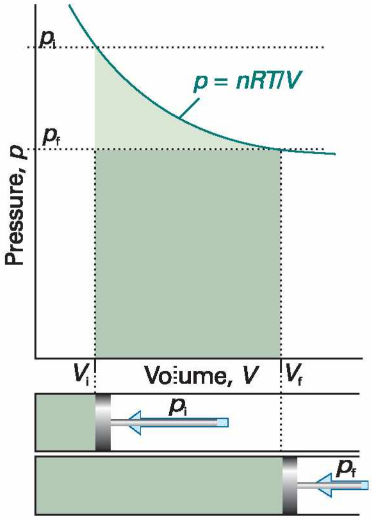


Fig. 2.8 The work done by a perfect gas when it expands reversibly and isothermally is equal to the area under the isotherm $p = nRT/V$. The work done during the irreversible expansion against the same final pressure is equal to the rectangular area shown slightly darker. Note that the reversible work is greater than the irreversible work.

Exploration Calculate the work of isothermal reversible expansion of 1.0 mol $CO_2(g)$ at 298 K from 1.0 m^3 to 3.0 m^3 on the basis that it obeys the van der Waals equation of state.

---

[2] We shall see later that there is a compensating influx of energy as heat, so overall the internal energy is constant for the isothermal expansion of a perfect gas.

Method We need to judge the magnitude of the volume change and then to decide how the process occurs. If there is no change in volume, there is no expansion work however the process takes place. If the system expands against a constant external pressure, the work can be calculated from eqn 2.8. A general feature of processes in which a condensed phase changes into a gas is that the volume of the former may usually be neglected relative to that of the gas it forms.

Answer In (a) the volume cannot change, so no expansion work is done and $w = 0$. In (b) the gas drives back the atmosphere and therefore $w = -p_{ex}\Delta V$. We can neglect the initial volume because the final volume (after the production of gas) is so much larger and $\Delta V = V_f - V_i \approx V_f = nRT/p_{ex}$, where n is the amount of H_2 produced. Therefore,

$$w = -p_{ex}\Delta V \approx -p_{ex} \times \frac{nRT}{p_{ex}} = -nRT$$

Because the reaction is $Fe(s) + 2\,HCl(aq) \rightarrow FeCl_2(aq) + H_2(g)$, we know that 1 mol H_2 is generated when 1 mol Fe is consumed, and n can be taken as the amount of Fe atoms that react. Because the molar mass of Fe is 55.85 g mol^{-1}, it follows that

$$\begin{aligned} w &\approx -\frac{50\text{ g}}{55.85\text{ g mol}^{-1}} \times (8.3145\text{ J K}^{-1}\text{ mol}^{-1}) \times (298\text{ K}) \\ &\approx -2.2\text{ kJ} \end{aligned}$$

The system (the reaction mixture) does 2.2 kJ of work driving back the atmosphere. Note that (for this perfect gas system) the magnitude of the external pressure does not affect the final result: the lower the pressure, the larger the volume occupied by the gas, so the effects cancel.

Self-test 2.1 Calculate the expansion work done when 50 g of water is electrolysed under constant pressure at 25°C. [−10 kJ]

2.4 Heat transactions

In general, the change in internal energy of a system is

$$dU = dq + dw_{exp} + dw_e \tag{2.12}$$

where dw_e is work in addition (e for 'extra') to the expansion work, dw_{exp}. For instance, dw_e might be the electrical work of driving a current through a circuit. A system kept at constant volume can do no expansion work, so $dw_{exp} = 0$. If the system is also incapable of doing any other kind of work (if it is not, for instance, an electrochemical cell connected to an electric motor), then $dw_e = 0$ too. Under these circumstances:

$$dU = dq \qquad \text{(at constant volume, no additional work)} \tag{2.13a}$$

We express this relation by writing $dU = dq_V$, where the subscript implies a change at constant volume. For a measurable change,

$$\Delta U = q_V \tag{2.13b}$$

It follows that, by measuring the energy supplied to a constant-volume system as heat ($q > 0$) or obtained from it as heat ($q < 0$) when it undergoes a change of state, we are in fact measuring the change in its internal energy.

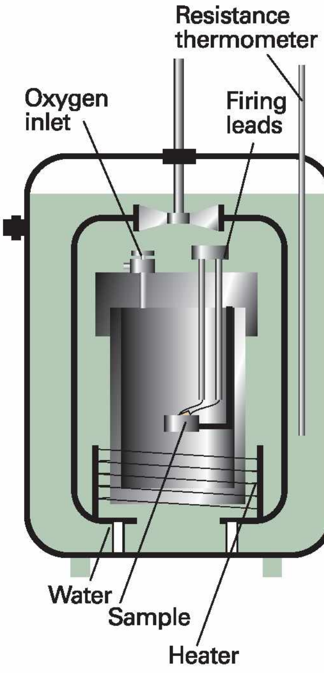


Fig. 2.9 A constant-volume bomb calorimeter. The 'bomb' is the central vessel, which is strong enough to withstand high pressures. The calorimeter (for which the heat capacity must be known) is the entire assembly shown here. To ensure adiabaticity, the calorimeter is immersed in a water bath with a temperature continuously readjusted to that of the calorimeter at each stage of the combustion.

(a) Calorimetry

Calorimetry is the study of heat transfer during physical and chemical processes. A **calorimeter** is a device for measuring energy transferred as heat. The most common device for measuring ΔU is an **adiabatic bomb calorimeter** (Fig. 2.9). The process we wish to study—which may be a chemical reaction—is initiated inside a constant-volume container, the 'bomb'. The bomb is immersed in a stirred water bath, and the whole device is the calorimeter. The calorimeter is also immersed in an outer water bath. The water in the calorimeter and of the outer bath are both monitored and adjusted to the same temperature. This arrangement ensures that there is no net loss of heat from the calorimeter to the surroundings (the bath) and hence that the calorimeter is adiabatic.

The change in temperature, ΔT, of the calorimeter is proportional to the heat that the reaction releases or absorbs. Therefore, by measuring ΔT we can determine q_V and hence find ΔU. The conversion of ΔT to q_V is best achieved by calibrating the calorimeter using a process of known energy output and determining the **calorimeter constant**, the constant C in the relation

$$q = C\Delta T \tag{2.14a}$$

The calorimeter constant may be measured electrically by passing a constant current, I, from a source of known potential difference, $\mathcal{V}$, through a heater for a known period of time, t, for then

$$q = I\mathcal{V}t \tag{2.14b}$$

Alternatively, C may be determined by burning a known mass of substance (benzoic acid is often used) that has a known heat output. With C known, it is simple to interpret an observed temperature rise as a release of heat.

Illustration 2.2 *The calibration of a calorimeter*

If we pass a current of 10.0 A from a 12 V supply for 300 s, then from eqn 2.14b the energy supplied as heat is

$$q = (10.0\ \text{A}) \times (12\ \text{V}) \times (300\ \text{s}) = 3.6 \times 10^4\ \text{A V s} = 36\ \text{kJ}$$

because 1 A V s = 1 J. If the observed rise in temperature is 5.5 K, then the calorimeter constant is $C = (36\ \text{kJ})/(5.5\ \text{K}) = 6.5\ \text{kJ K}^{-1}$.

Comment 2.4

Electrical charge is measured in *coulombs*, C. The motion of charge gives rise to an electric current, I, measured in coulombs per second, or *amperes*, A, where $1\ \text{A} = 1\ \text{C s}^{-1}$. If a constant current I flows through a potential difference $\mathcal{V}$ (measured in volts, V), the total energy supplied in an interval t is

$$\textit{Energy supplied} = I\mathcal{V}t$$

Because $1\ \text{A V s} = 1\ (\text{C s}^{-1})\ \text{V s} = 1\ \text{C V} = 1\ \text{J}$, the energy is obtained in joules with the current in amperes, the potential difference in volts, and the time in seconds. We write the electrical power, P, as

$$P = (\textit{energy supplied})/(\textit{time interval}) = I\mathcal{V}t/t = I\mathcal{V}$$

(b) Heat capacity

The internal energy of a substance increases when its temperature is raised. The increase depends on the conditions under which the heating takes place and for the present we suppose that the sample is confined to a constant volume. For example, the sample may be a gas in a container of fixed volume. If the internal energy is plotted against temperature, then a curve like that in Fig. 2.10 may be obtained. The slope of the tangent to the curve at any temperature is called the **heat capacity** of the system at that temperature. The **heat capacity at constant volume** is denoted C_V and is defined formally as[3]

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[3] If the system can change its composition, it is necessary to distinguish between equilibrium and fixed-composition values of C_V. All applications in this chapter refer to a single substance, so this complication can be ignored.

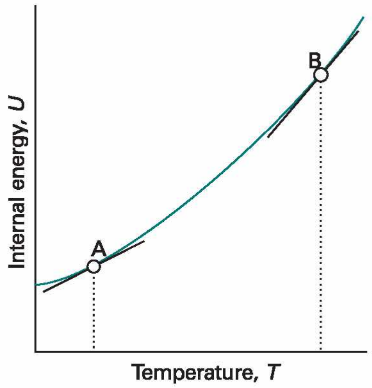


Fig. 2.10 The internal energy of a system increases as the temperature is raised; this graph shows its variation as the system is heated at constant volume. The slope of the tangent to the curve at any temperature is the heat capacity at constant volume at that temperature. Note that, for the system illustrated, the heat capacity is greater at B than at A.

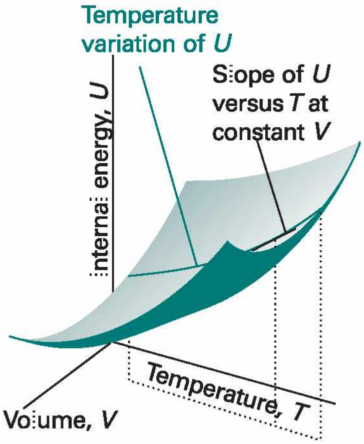


Fig. 2.11 The internal energy of a system varies with volume and temperature, perhaps as shown here by the surface. The variation of the internal energy with temperature at one particular constant volume is illustrated by the curve drawn parallel to T. The slope of this curve at any point is the partial derivative $(\partial U/\partial T)_V$.

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad [2.15]$$

In this case, the internal energy varies with the temperature and the volume of the sample, but we are interested only in its variation with the temperature, the volume being held constant (Fig. 2.11).

Comment 2.5

The partial-differential operation $(\partial z/\partial x)_y$ consists of taking the first derivative of $z(x,y)$ with respect to x, treating y as a constant. For example, if $z(x,y) = x^2y$, then

$$\left(\frac{\partial z}{\partial x}\right)_y = \left(\frac{\partial [x^2y]}{\partial x}\right)_y = y\frac{\mathrm{d}x^2}{\mathrm{d}x} = 2yx$$

Partial derivatives are reviewed in *Appendix 2*.

Illustration 2.3 *Estimating a constant-volume heat capacity*

The heat capacity of a monatomic perfect gas can be calculated by inserting the expression for the internal energy derived in *Molecular interpretation 2.2*. There we saw that $U_m = U_m(0) + \frac{3}{2}RT$, so from eqn 2.15

$$C_{V,m} = \frac{\partial}{\partial T}(U_m(0) + \tfrac{3}{2}RT) = \tfrac{3}{2}R$$

The numerical value is 12.47 J K^{-1} mol^{-1}.

Heat capacities are extensive properties: 100 g of water, for instance, has 100 times the heat capacity of 1 g of water (and therefore requires 100 times the energy as heat to bring about the same rise in temperature). The **molar heat capacity at constant volume**, $C_{V,m} = C_V/n$, is the heat capacity per mole of material, and is an intensive property (all molar quantities are intensive). Typical values of $C_{V,m}$ for polyatomic gases are close to 25 J K^{-1} mol^{-1}. For certain applications it is useful to know the **specific heat capacity** (more informally, the 'specific heat') of a substance, which is the heat capacity of the sample divided by the mass, usually in grams: $C_{V,s} = C_V/m$. The specific heat capacity of water at room temperature is close to 4 J K^{-1} g^{-1}. In general, heat capacities depend on the temperature and decrease at low temperatures. However, over small ranges of temperature at and above room temperature, the variation is quite small and for approximate calculations heat capacities can be treated as almost independent of temperature.

The heat capacity is used to relate a change in internal energy to a change in temperature of a constant-volume system. It follows from eqn 2.15 that

$$dU = C_V dT \qquad \text{(at constant volume)} \tag{2.16a}$$

That is, at constant volume, an infinitesimal change in temperature brings about an infinitesimal change in internal energy, and the constant of proportionality is C_V. If the heat capacity is independent of temperature over the range of temperatures of interest, a measurable change of temperature, ΔT, brings about a measurable increase in internal energy, ΔU, where

$$\Delta U = C_V \Delta T \qquad \text{(at constant volume)} \tag{2.16b}$$

Because a change in internal energy can be identified with the heat supplied at constant volume (eqn 2.13b), the last equation can be written

$$q_V = C_V \Delta T \tag{2.17}$$

This relation provides a simple way of measuring the heat capacity of a sample: a measured quantity of energy is transferred as heat to the sample (electrically, for example), and the resulting increase in temperature is monitored. The ratio of the energy transferred as heat to the temperature rise it causes ($q_V/\Delta T$) is the constant-volume heat capacity of the sample.

A large heat capacity implies that, for a given quantity of energy transferred as heat, there will be only a small increase in temperature (the sample has a large capacity for heat). An infinite heat capacity implies that there will be no increase in temperature however much energy is supplied as heat. At a phase transition, such as at the boiling point of water, the temperature of a substance does not rise as energy is supplied as heat: the energy is used to drive the endothermic transition, in this case to vaporize the water, rather than to increase its temperature. Therefore, at the temperature of a phase transition, the heat capacity of a sample is infinite. The properties of heat capacities close to phase transitions are treated more fully in Section 4.7.

2.5 Enthalpy

The change in internal energy is not equal to the energy transferred as heat when the system is free to change its volume. Under these circumstances some of the energy supplied as heat to the system is returned to the surroundings as expansion work (Fig. 2.12), so dU is less than dq. However, we shall now show that in this case the energy supplied as heat at constant pressure is equal to the change in another thermodynamic property of the system, the enthalpy.

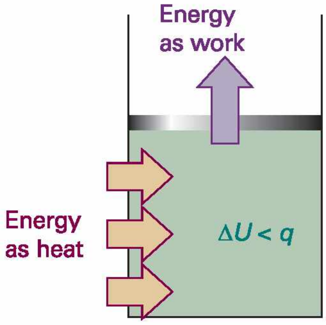


Fig. 2.12 When a system is subjected to constant pressure and is free to change its volume, some of the energy supplied as heat may escape back into the surroundings as work. In such a case, the change in internal energy is smaller than the energy supplied as heat.

(a) The definition of enthalpy

The **enthalpy**, H, is defined as

$$H = U + pV \tag*{[2.18]}$$

where p is the pressure of the system and V is its volume. Because U, p, and V are all state functions, the enthalpy is a state function too. As is true of any state function, the change in enthalpy, ΔH, between any pair of initial and final states is independent of the path between them.

Although the definition of enthalpy may appear arbitrary, it has important implications for thermochemisty. For instance, we show in the following *Justification* that eqn 2.18 implies that *the change in enthalpy is equal to the energy supplied as heat at constant pressure* (provided the system does no additional work):

$$\mathrm{d}H = \mathrm{d}q \qquad \text{(at constant pressure, no additional work)} \qquad (2.19a)$$

For a measurable change,

$$\Delta H = q_p \qquad (2.19b)$$

Justification 2.1 *The relation $\Delta H = q_p$*

For a general infinitesimal change in the state of the system, U changes to $U + \mathrm{d}U$, p changes to $p + \mathrm{d}p$, and V changes to $V + \mathrm{d}V$, so from the definition in eqn 2.18, H changes from $U + pV$ to

$$\begin{aligned} H + \mathrm{d}H &= (U + \mathrm{d}U) + (p + \mathrm{d}p)(V + \mathrm{d}V) \\ &= U + \mathrm{d}U + pV + p\mathrm{d}V + V\mathrm{d}p + \mathrm{d}p\mathrm{d}V \end{aligned}$$

The last term is the product of two infinitesimally small quantities and can therefore be neglected. As a result, after recognizing $U + pV = H$ on the right, we find that H changes to

$$H + \mathrm{d}H = H + \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p$$

and hence that

$$\mathrm{d}H = \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p$$

If we now substitute $\mathrm{d}U = \mathrm{d}q + \mathrm{d}w$ into this expression, we get

$$\mathrm{d}H = \mathrm{d}q + \mathrm{d}w + p\mathrm{d}V + V\mathrm{d}p$$

If the system is in mechanical equilibrium with its surroundings at a pressure p and does only expansion work, we can write $\mathrm{d}w = -p\mathrm{d}V$ and obtain

$$\mathrm{d}H = \mathrm{d}q + V\mathrm{d}p$$

Now we impose the condition that the heating occurs at constant pressure by writing $\mathrm{d}p = 0$. Then

$$\mathrm{d}H = \mathrm{d}q \qquad \text{(at constant pressure, no additional work)}$$

as in eqn 2.19a.

The result expressed in eqn 2.19 states that, when a system is subjected to a constant pressure, and only expansion work can occur, the change in enthalpy is equal to the energy supplied as heat. For example, if we supply 36 kJ of energy through an electric heater immersed in an open beaker of water, then the enthalpy of the water increases by 36 kJ and we write $\Delta H = +36$ kJ.

(b) The measurement of an enthalpy change

An enthalpy change can be measured calorimetrically by monitoring the temperature change that accompanies a physical or chemical change occurring at constant pressure. A calorimeter for studying processes at constant pressure is called an **isobaric calorimeter**. A simple example is a thermally insulated vessel open to the atmosphere: the heat released in the reaction is monitored by measuring the change in temperature of the contents. For a combustion reaction an **adiabatic flame calorimeter** may be used to measure ΔT when a given amount of substance burns in a supply of oxygen (Fig. 2.13). Another route to ΔH is to measure the internal energy change by using a bomb calorimeter, and then to convert ΔU to ΔH. Because solids and liquids have small molar volumes, for them pV_m is so small that the molar enthalpy and molar internal energy are almost identical ($H_m = U_m + pV_m \approx U_m$). Consequently, if a process involves only solids or liquids, the values of ΔH and ΔU are almost identical. Physically, such processes are accompanied by a very small change in volume, the system does negligible work on the surroundings when the process occurs, so the energy supplied as heat stays entirely within the system. The most sophisticated way to measure enthalpy changes, however, is to use a **differential scanning calorimeter** (DSC). Changes in enthalpy and internal energy may also be measured by noncalorimetric methods (see Chapter 7).

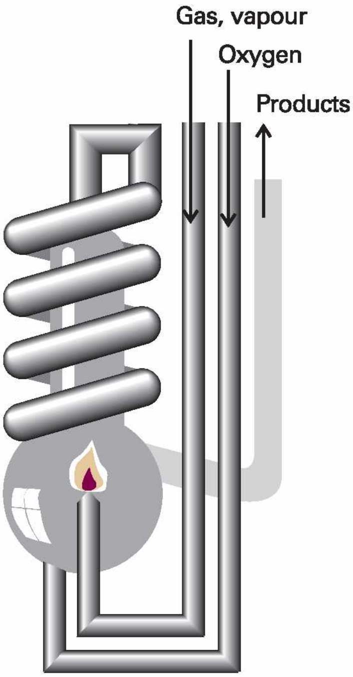


Fig. 2.13 A constant-pressure flame calorimeter consists of this component immersed in a stirred water bath. Combustion occurs as a known amount of reactant is passed through to fuel the flame, and the rise of temperature is monitored.

Example 2.2 *Relating ΔH and ΔU*

The internal energy change when 1.0 mol $CaCO_3$ in the form of calcite converts to aragonite is +0.21 kJ. Calculate the difference between the enthalpy change and the change in internal energy when the pressure is 1.0 bar given that the densities of the solids are 2.71 g cm^{-3} and 2.93 g cm^{-3}, respectively.

Method The starting point for the calculation is the relation between the enthalpy of a substance and its internal energy (eqn 2.18). The difference between the two quantities can be expressed in terms of the pressure and the difference of their molar volumes, and the latter can be calculated from their molar masses, M, and their mass densities, ρ, by using $\rho = M/V_m$.

Answer The change in enthalpy when the transition occurs is

$$\begin{aligned}\Delta H &= H(\text{aragonite}) - H(\text{calcite})\\ &= \{U(\text{a}) + pV(\text{a})\} - \{U(\text{c}) + pV(\text{c})\}\\ &= \Delta U + p\{V(\text{a}) - V(\text{c})\} = \Delta U + p\Delta V\end{aligned}$$

The volume of 1.0 mol $CaCO_3$ (100 g) as aragonite is 34 cm^3, and that of 1.0 mol $CaCO_3$ as calcite is 37 cm^3. Therefore,

$$p\Delta V = (1.0 \times 10^5\ \text{Pa}) \times (34 - 37) \times 10^{-6}\ \text{m}^3 = -0.3\ \text{J}$$

(because 1 Pa m^3 = 1 J). Hence,

$$\Delta H - \Delta U = -0.3\ \text{J}$$

which is only 0.1 per cent of the value of ΔU. We see that it is usually justifiable to ignore the difference between the enthalpy and internal energy of condensed phases, except at very high pressures, when pV is no longer negligible.

Self-test 2.2 Calculate the difference between ΔH and ΔU when 1.0 mol Sn(s, grey) of density 5.75 g cm^{-3} changes to Sn(s, white) of density 7.31 g cm^{-3} at 10.0 bar. At 298 K, $\Delta H = +2.1$ kJ. [$\Delta H - \Delta U = -4.4$ J]

The enthalpy of a perfect gas is related to its internal energy by using $pV = nRT$ in the definition of H:

$$H = U + pV = U + nRT \qquad (2.20)°$$

This relation implies that the change of enthalpy in a reaction that produces or consumes gas is

$$\Delta H = \Delta U + \Delta n_g RT \tag{2.21°}$$

where Δn_g is the change in the amount of gas molecules in the reaction.

Illustration 2.4 *The relation between ΔH and ΔU for gas-phase reactions*

In the reaction $2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(l)$, 3 mol of gas-phase molecules is replaced by 2 mol of liquid-phase molecules, so $\Delta n_g = -3$ mol. Therefore, at 298 K, when $RT = 2.5$ kJ mol^{-1}, the enthalpy and internal energy changes taking place in the system are related by

$$\Delta H - \Delta U = (-3\text{ mol}) \times RT \approx -7.4\text{ kJ}$$

Note that the difference is expressed in kilojoules, not joules as in Example 2.2. The enthalpy change is smaller (in this case, less negative) than the change in internal energy because, although heat escapes from the system when the reaction occurs, the system contracts when the liquid is formed, so energy is restored to it from the surroundings.

Example 2.3 *Calculating a change in enthalpy*

Water is heated to boiling under a pressure of 1.0 atm. When an electric current of 0.50 A from a 12 V supply is passed for 300 s through a resistance in thermal contact with it, it is found that 0.798 g of water is vaporized. Calculate the molar internal energy and enthalpy changes at the boiling point (373.15 K).

Method Because the vaporization occurs at constant pressure, the enthalpy change is equal to the heat supplied by the heater. Therefore, the strategy is to calculate the energy supplied as heat (from $q = I\mathcal{V}t$), express that as an enthalpy change, and then convert the result to a molar enthalpy change by division by the amount of H_2O molecules vaporized. To convert from enthalpy change to internal energy change, we assume that the vapour is a perfect gas and use eqn 2.21.

Answer The enthalpy change is

$$\Delta H = q_p = (0.50\text{ A}) \times (12\text{ V}) \times (300\text{ s}) = +(0.50 \times 12 \times 300)\text{ J}$$

Here we have used 1 A V s = 1 J (see *Comment 2.4*). Because 0.798 g of water is $(0.798\text{ g})/(18.02\text{ g mol}^{-1}) = (0.798/18.02)$ mol H_2O, the enthalpy of vaporization per mole of H_2O is

$$\Delta H_m = +\frac{0.50 \times 12 \times 300\text{ J}}{(0.798/18.02)\text{ mol}} = +41\text{ kJ mol}^{-1}$$

In the process $H_2O(l) \rightarrow H_2O(g)$ the change in the amount of gas molecules is $\Delta n_g = +1$ mol, so

$$\Delta U_m = \Delta H_m - RT = +38\text{ kJ mol}^{-1}$$

The plus sign is added to positive quantities to emphasize that they represent an increase in internal energy or enthalpy. Notice that the internal energy change is smaller than the enthalpy change because energy has been used to drive back the surrounding atmosphere to make room for the vapour.

Self-test 2.3 The molar enthalpy of vaporization of benzene at its boiling point (353.25 K) is 30.8 kJ mol^{-1}. What is the molar internal energy change? For how long would the same 12 V source need to supply a 0.50 A current in order to vaporize a 10 g sample? [+27.9 kJ mol^{-1}, 660 s]

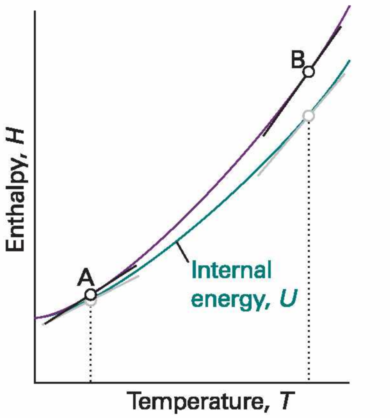


Fig. 2.14 The slope of the tangent to a curve of the enthalpy of a system subjected to a constant pressure plotted against temperature is the constant-pressure heat capacity. The slope may change with temperature, in which case the heat capacity varies with temperature. Thus, the heat capacities at A and B are different. For gases, at a given temperature the slope of enthalpy versus temperature is steeper than that of internal energy versus temperature, and $C_{p,\mathrm{m}}$ is larger than $C_{V,\mathrm{m}}$.

(c) The variation of enthalpy with temperature

The enthalpy of a substance increases as its temperature is raised. The relation between the increase in enthalpy and the increase in temperature depends on the conditions (for example, constant pressure or constant volume). The most important condition is constant pressure, and the slope of the tangent to a plot of enthalpy against temperature at constant pressure is called the **heat capacity at constant pressure**, C_p, at a given temperature (Fig. 2.14). More formally:

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \qquad [2.22]$$

The heat capacity at constant pressure is the analogue of the heat capacity at constant volume, and is an extensive property.[4] The **molar heat capacity at constant pressure**, $C_{p,\mathrm{m}}$, is the heat capacity per mole of material; it is an intensive property.

The heat capacity at constant pressure is used to relate the change in enthalpy to a change in temperature. For infinitesimal changes of temperature,

$$\mathrm{d}H = C_p\mathrm{d}T \qquad \text{(at constant pressure)} \qquad (2.23a)$$

If the heat capacity is constant over the range of temperatures of interest, then for a measurable increase in temperature

$$\Delta H = C_p\Delta T \qquad \text{(at constant pressure)} \qquad (2.23b)$$

Because an increase in enthalpy can be equated with the energy supplied as heat at constant pressure, the practical form of the latter equation is

$$q_p = C_p\Delta T \qquad (2.24)$$

This expression shows us how to measure the heat capacity of a sample: a measured quantity of energy is supplied as heat under conditions of constant pressure (as in a sample exposed to the atmosphere and free to expand), and the temperature rise is monitored.

The variation of heat capacity with temperature can sometimes be ignored if the temperature range is small; this approximation is highly accurate for a monatomic perfect gas (for instance, one of the noble gases at low pressure). However, when it is necessary to take the variation into account, a convenient approximate empirical expression is

$$C_{p,\mathrm{m}} = a + bT + \frac{c}{T^2} \qquad (2.25)$$

The empirical parameters *a*, *b*, and *c* are independent of temperature (Table 2.2).

---

[4] As in the case of C_V, if the system can change its composition it is necessary to distinguish between equilibrium and fixed-composition values. All applications in this chapter refer to pure substances, so this complication can be ignored.

Synoptic Table 2.2* Temperature variation of molar heat capacities, $C_{p,\mathrm{m}}/(\mathrm{J\,K^{-1}\,mol^{-1}}) = a + bT + c/T^2$

	a	$b/(10^{-3}\ \mathrm{K})$	$c/(10^{5}\ \mathrm{K}^2)$
C(s, graphite)	16.86	4.77	−8.54
CO_2(g)	44.22	8.79	−8.62
H_2O(l)	75.29	0	0
N_2(g)	28.58	3.77	−0.50

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

Example 2.4 *Evaluating an increase in enthalpy with temperature*

What is the change in molar enthalpy of N_2 when it is heated from 25°C to 100°C? Use the heat capacity information in Table 2.2.

Method The heat capacity of N_2 changes with temperature, so we cannot use eqn 2.23b (which assumes that the heat capacity of the substance is constant). Therefore, we must use eqn 2.23a, substitute eqn 2.25 for the temperature dependence of the heat capacity, and integrate the resulting expression from 25°C to 100°C.

Answer For convenience, we denote the two temperatures T_1 (298 K) and T_2 (373 K). The integrals we require are

$$\int_{H(T_1)}^{H(T_2)} \mathrm{d}H = \int_{T_1}^{T_2} \left(a + bT + \frac{c}{T^2} \right) \mathrm{d}T$$

Notice how the limits of integration correspond on each side of the equation: the integration over H on the left ranges from $H(T_1)$, the value of H at T_1, up to $H(T_2)$, the value of H at T_2, while on the right the integration over the temperature ranges from T_1 to T_2. Now we use the integrals

$$\int \mathrm{d}x = x + \text{constant} \qquad \int x\,\mathrm{d}x = \tfrac{1}{2}x^2 + \text{constant} \qquad \int \frac{\mathrm{d}x}{x^2} = -\frac{1}{x} + \text{constant}$$

to obtain

$$H(T_2) - H(T_1) = a(T_2 - T_1) + \tfrac{1}{2}b(T_2^2 - T_1^2) - c\left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Substitution of the numerical data results in

$$H(373\ \mathrm{K}) = H(298\ \mathrm{K}) + 2.20\ \mathrm{kJ\,mol^{-1}}$$

If we had assumed a constant heat capacity of 29.14 $\mathrm{J\,K^{-1}\,mol^{-1}}$ (the value given by eqn 2.25 at 25°C), we would have found that the two enthalpies differed by 2.19 $\mathrm{kJ\,mol^{-1}}$.

Comment 2.6

Integrals commonly encountered in physical chemistry are listed inside the front cover.

Self-test 2.4 At very low temperatures the heat capacity of a solid is proportional to T^3, and we can write $C_p = aT^3$. What is the change in enthalpy of such a substance when it is heated from 0 to a temperature T (with T close to 0)? [$\Delta H = \tfrac{1}{4}aT^4$]

Most systems expand when heated at constant pressure. Such systems do work on the surroundings and therefore some of the energy supplied to them as heat escapes back to the surroundings. As a result, the temperature of the system rises less than when the heating occurs at constant volume. A smaller increase in temperature implies a larger heat capacity, so we conclude that in most cases the heat capacity at constant pressure of a system is larger than its heat capacity at constant volume. We show later (Section 2.11) that there is a simple relation between the two heat capacities of a perfect gas:

$$C_p - C_V = nR \tag{2.26°}$$

It follows that the molar heat capacity of a perfect gas is about 8 J K^{-1} mol^{-1} larger at constant pressure than at constant volume. Because the heat capacity at constant volume of a monatomic gas is about 12 J K^{-1} mol^{-1}, the difference is highly significant and must be taken into account.

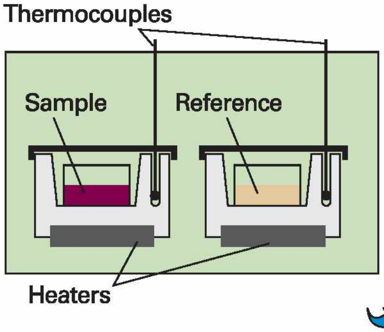


Fig. 2.15 A differential scanning calorimeter. The sample and a reference material are heated in separate but identical metal heat sinks. The output is the difference in power needed to maintain the heat sinks at equal temperatures as the temperature rises.

IMPACT ON BIOCHEMISTRY AND MATERIALS SCIENCE

I2.1 Differential scanning calorimetry

A *differential scanning calorimeter* (DSC) measures the energy transferred as heat to or from a sample at constant pressure during a physical or chemical change. The term 'differential' refers to the fact that the behaviour of the sample is compared to that of a reference material which does not undergo a physical or chemical change during the analysis. The term 'scanning' refers to the fact that the temperatures of the sample and reference material are increased, or scanned, during the analysis.

A DSC consists of two small compartments that are heated electrically at a constant rate. The temperature, T, at time t during a linear scan is $T = T_0 + \alpha t$, where T_0 is the initial temperature and α is the temperature scan rate (in kelvin per second, K s^{-1}). A computer controls the electrical power output in order to maintain the same temperature in the sample and reference compartments throughout the analysis (see Fig. 2.15).

The temperature of the sample changes significantly relative to that of the reference material if a chemical or physical process involving the transfer of energy as heat occurs in the sample during the scan. To maintain the same temperature in both compartments, excess energy is transferred as heat to or from the sample during the process. For example, an endothermic process lowers the temperature of the sample relative to that of the reference and, as a result, the sample must be heated more strongly than the reference in order to maintain equal temperatures.

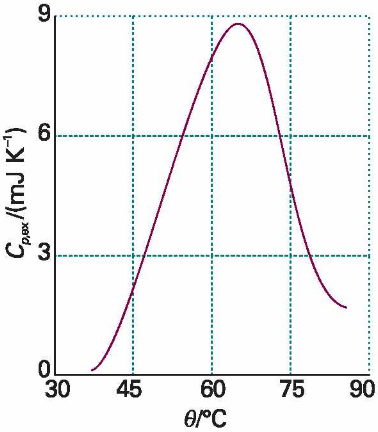


Fig. 2.16 A thermogram for the protein ubiquitin at pH = 2.45. The protein retains its native structure up to about 45°C and then undergoes an endothermic conformational change. (Adapted from B. Chowdhry and S. LeHarne, *J. Chem. Educ.* **74**, 236 (1997).)

If no physical or chemical change occurs in the sample at temperature T, we write the heat transferred to the sample as $q_p = C_p\Delta T$, where $\Delta T = T - T_0$ and we have assumed that C_p is independent of temperature. The chemical or physical process requires the transfer of $q_p + q_{p,\mathrm{ex}}$, where $q_{p,\mathrm{ex}}$ is excess energy transferred as heat, to attain the same change in temperature of the sample. We interpret $q_{p,\mathrm{ex}}$ in terms of an apparent change in the heat capacity at constant pressure of the sample, C_p, during the temperature scan. Then we write the heat capacity of the sample as $C_p + C_{p,\mathrm{ex}}$, and

$$q_p + q_{p,\mathrm{ex}} = (C_p + C_{p,\mathrm{ex}})\Delta T$$

It follows that

$$C_{p,\mathrm{ex}} = \frac{q_{p,\mathrm{ex}}}{\Delta T} = \frac{q_{p,\mathrm{ex}}}{\alpha t} = \frac{P_{\mathrm{ex}}}{\alpha}$$

where $P_{\mathrm{ex}} = q_{p,\mathrm{ex}}/t$ is the excess electrical power necessary to equalize the temperature of the sample and reference compartments.

A DSC trace, also called a *thermogram*, consists of a plot of P_{ex} or $C_{p,\mathrm{ex}}$ against T (see Fig. 2.16). Broad peaks in the thermogram indicate processes requiring transfer of energy as heat. From eqn 2.23a, the enthalpy change associated with the process is

$$\Delta H = \int_{T_1}^{T_2} C_{p,\mathrm{ex}} \mathrm{d}T$$

where T_1 and T_2 are, respectively, the temperatures at which the process begins and ends. This relation shows that the enthalpy change is then the area under the curve of $C_{p,\mathrm{ex}}$ against T. With a DSC, enthalpy changes may be determined in samples of masses as low as 0.5 mg, which is a significant advantage over bomb or flame calorimeters, which require several grams of material.

Differential scanning calorimetry is used in the chemical industry to characterize polymers and in the biochemistry laboratory to assess the stability of proteins, nucleic acids, and membranes. Large molecules, such as synthetic or biological polymers, attain complex three-dimensional structures due to intra- and intermolecular interactions, such as hydrogen bonding and hydrophobic interactions (Chapter 18). Disruption of these interactions is an endothermic process that can be studied with a DSC. For example, the thermogram shown in the illustration indicated that the protein ubiquitin retains its native structure up to about 45°C. At higher temperatures, the protein undergoes an endothermic conformational change that results in the loss of its three-dimensional structure. The same principles also apply to the study of structural integrity and stability of synthetic polymers, such as plastics.

2.6 Adiabatic changes

We are now equipped to deal with the changes that occur when a perfect gas expands adiabatically. A decrease in temperature should be expected: because work is done but no heat enters the system, the internal energy falls, and therefore the temperature of the working gas also falls. In molecular terms, the kinetic energy of the molecules falls as work is done, so their average speed decreases, and hence the temperature falls.

The change in internal energy of a perfect gas when the temperature is changed from T_i to T_f and the volume is changed from V_i to V_f can be expressed as the sum of two steps (Fig. 2.17). In the first step, only the volume changes and the temperature is held constant at its initial value. However, because the internal energy of a perfect gas is independent of the volume the molecules occupy, the overall change in internal energy arises solely from the second step, the change in temperature at constant volume. Provided the heat capacity is independent of temperature, this change is

$$\Delta U = C_V(T_\mathrm{f} - T_\mathrm{i}) = C_V\Delta T$$

Because the expansion is adiabatic, we know that $q = 0$; because $\Delta U = q + w$, it then follows that $\Delta U = w_\mathrm{ad}$. The subscript 'ad' denotes an adiabatic process. Therefore, by equating the two values we have obtained for ΔU, we obtain

$$w_\mathrm{ad} = C_V\Delta T \qquad (2.27)$$

That is, the work done during an adiabatic expansion of a perfect gas is proportional to the temperature difference between the initial and final states. That is exactly what we expect on molecular grounds, because the mean kinetic energy is proportional to T, so a change in internal energy arising from temperature alone is also expected to be proportional to ΔT. In *Further information 2.1* we show that the initial and final temperatures of a perfect gas that undergoes reversible adiabatic expansion (reversible expansion in a thermally insulated container) can be calculated from

$$T_\mathrm{f} = T_\mathrm{i}\left(\frac{V_\mathrm{i}}{V_\mathrm{f}}\right)^{1/c} \qquad (2.28\mathrm{a})^{\circ}_{\mathrm{rev}}$$

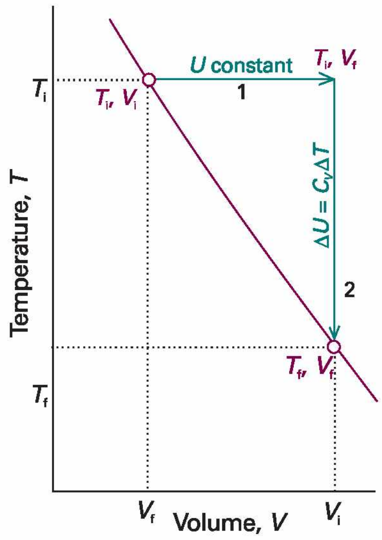


Fig. 2.17 To achieve a change of state from one temperature and volume to another temperature and volume, we may consider the overall change as composed of two steps. In the first step, the system expands at constant temperature; there is no change in internal energy if the system consists of a perfect gas. In the second step, the temperature of the system is reduced at constant volume. The overall change in internal energy is the sum of the changes for the two steps.

where $c = C_{V,\mathrm{m}}/R$, or equivalently

$$V_\mathrm{i}T_\mathrm{i}^c = V_\mathrm{f}T_\mathrm{f}^c \qquad (2.28\mathrm{b})^\circ_{\mathrm{rev}}$$

This result is often summarized in the form $VT^c = \text{constant}$.

Illustration 2.5 *Work of adiabatic expansion*

Consider the adiabatic, reversible expansion of 0.020 mol Ar, initially at 25°C, from 0.50 dm^3 to 1.00 dm^3. The molar heat capacity of argon at constant volume is 12.48 J K^{-1} mol^{-1}, so $c = 1.501$. Therefore, from eqn 2.28a,

$$T_\mathrm{f} = (298\ \mathrm{K}) \times \left(\frac{0.50\ \mathrm{dm}^3}{1.00\ \mathrm{dm}^3}\right)^{1/1.501} = 188\ \mathrm{K}$$

It follows that $\Delta T = -110$ K, and therefore, from eqn 2.27, that

$$w = \{(0.020\ \mathrm{mol}) \times (12.48\ \mathrm{J\ K^{-1}\ mol^{-1}})\} \times (-110\ \mathrm{K}) = -27\ \mathrm{J}$$

Note that temperature change is independent of the amount of gas but the work is not.

Self-test 2.5 Calculate the final temperature, the work done, and the change of internal energy when ammonia is used in a reversible adiabatic expansion from 0.50 dm^3 to 2.00 dm^3, the other initial conditions being the same.

[195 K, −56 J, −56 J]

We also show in *Further information 2.1* that the pressure of a perfect gas that undergoes reversible adiabatic expansion from a volume V_i to a volume V_f is related to its initial pressure by

$$p_\mathrm{f}V_\mathrm{f}^\gamma = p_\mathrm{i}V_\mathrm{i}^\gamma \qquad (2.29)^\circ_{\mathrm{rev}}$$

where $\gamma = C_{p,\mathrm{m}}/C_{V,\mathrm{m}}$. This result is summarized in the form $pV^\gamma = \text{constant}$. For a monatomic perfect gas, $C_{V,\mathrm{m}} = \frac{3}{2}R$ (see *Illustration 2.3*), and from eqn 2.26 $C_{p,\mathrm{m}} = \frac{5}{2}R$; so $\gamma = \frac{5}{3}$. For a gas of nonlinear polyatomic molecules (which can rotate as well as translate), $C_{V,\mathrm{m}} = 3R$, so $\gamma = \frac{4}{3}$. The curves of pressure versus volume for adiabatic change are known as **adiabats**, and one for a reversible path is illustrated in Fig. 2.18. Because $\gamma > 1$, an adiabat falls more steeply ($p \propto 1/V^\gamma$) than the corresponding isotherm ($p \propto 1/V$). The physical reason for the difference is that, in an isothermal expansion, energy flows into the system as heat and maintains the temperature; as a result, the pressure does not fall as much as in an adiabatic expansion.

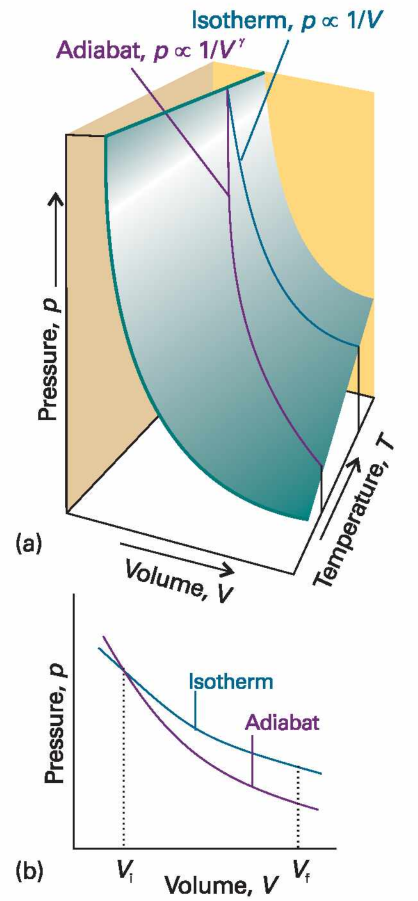


Fig. 2.18 An adiabat depicts the variation of pressure with volume when a gas expands adiabatically. (a) An adiabat for a perfect gas undergoing reversible expansion. (b) Note that the pressure declines more steeply for an adiabat than it does for an isotherm because the temperature decreases in the former.

Exploration Explore how the parameter γ affects the dependence of the pressure on the volume. Does the pressure–volume dependence become stronger or weaker with increasing volume?

Illustration 2.6 *The pressure change accompanying adiabatic expansion*

When a sample of argon (for which $\gamma = \frac{5}{3}$) at 100 kPa expands reversibly and adiabatically to twice its initial volume the final pressure will be

$$p_\mathrm{f} = \left(\frac{V_\mathrm{i}}{V_\mathrm{f}}\right)^\gamma p_\mathrm{i} = \left(\frac{1}{2}\right)^{5/3} \times (100\ \mathrm{kPa}) = 32\ \mathrm{kPa}$$

For an isothermal doubling of volume, the final pressure would be 50 kPa.

Thermochemistry

The study of the energy transferred as heat during the course of chemical reactions is called **thermochemistry**. Thermochemistry is a branch of thermodynamics because a reaction vessel and its contents form a system, and chemical reactions result in the exchange of energy between the system and the surroundings. Thus we can use calorimetry to measure the energy supplied or discarded as heat by a reaction, and can identify q with a change in internal energy (if the reaction occurs at constant volume) or a change in enthalpy (if the reaction occurs at constant pressure). Conversely, if we know ΔU or ΔH for a reaction, we can predict the energy (transferred as heat) the reaction can produce.

We have already remarked that a process that releases energy by heating the surroundings is classified as exothermic and one that absorbs energy by cooling the surroundings is classified as endothermic. Because the release of energy by heating the surroundings signifies a decrease in the enthalpy of a system (at constant pressure), we can now see that an exothermic process at constant pressure is one for which $\Delta H < 0$. Conversely, because the absorption of energy by cooling the surroundings results in an increase in enthalpy, an endothermic process at constant pressure has $\Delta H > 0$.

2.7 Standard enthalpy changes

Changes in enthalpy are normally reported for processes taking place under a set of standard conditions. In most of our discussions we shall consider the **standard enthalpy change**, $\Delta H^\ominus$, the change in enthalpy for a process in which the initial and final substances are in their standard states:

> The **standard state** of a substance at a specified temperature is its pure form at 1 bar.[5]

For example, the standard state of liquid ethanol at 298 K is pure liquid ethanol at 298 K and 1 bar; the standard state of solid iron at 500 K is pure iron at 500 K and 1 bar. The standard enthalpy change for a reaction or a physical process is the difference between the products in their standard states and the reactants in their standard states, all at the same specified temperature.

As an example of a standard enthalpy change, the *standard enthalpy of vaporization*, $\Delta_{\text{vap}}H^\ominus$, is the enthalpy change per mole when a pure liquid at 1 bar vaporizes to a gas at 1 bar, as in

$$H_2O(l) \rightarrow H_2O(g) \qquad \Delta_{\text{vap}}H^\ominus(373\ \text{K}) = +40.66\ \text{kJ mol}^{-1}$$

As implied by the examples, standard enthalpies may be reported for any temperature. However, the conventional temperature for reporting thermodynamic data is 298.15 K (corresponding to 25.00°C). Unless otherwise mentioned, all thermodynamic data in this text will refer to this conventional temperature.

A note on good practice The attachment of the name of the transition to the symbol Δ, as in $\Delta_{\text{vap}}H$, is the modern convention. However, the older convention, ΔH_{vap}, is still widely used. The new convention is more logical because the subscript identifies the type of change, not the physical observable related to the change.

---

[5] The definition of standard state is more sophisticated for a real gas (*Further information 3.2*) and for solutions (Sections 5.6 and 5.7).

Synoptic Table 2.3* Standard enthalpies of fusion and vaporization at the transition temperature, $\Delta_{trs}H^{\ominus}/(\text{kJ mol}^{-1})$

	T_f/K	Fusion	T_b/K	Vaporization
Ar	83.81	1.188	87.29	6.506
C_6H_6	278.61	10.59	353.2	30.8
H_2O	273.15	6.008	373.15	40.656 (44.016 at 298 K)
He	3.5	0.021	4.22	0.084

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

(a) Enthalpies of physical change

The standard enthalpy change that accompanies a change of physical state is called the **standard enthalpy of transition** and is denoted $\Delta_{trs}H^{\ominus}$ (Table 2.3). The **standard enthalpy of vaporization**, $\Delta_{vap}H^{\ominus}$, is one example. Another is the **standard enthalpy of fusion**, $\Delta_{fus}H^{\ominus}$, the standard enthalpy change accompanying the conversion of a solid to a liquid, as in

$$H_2O(s) \rightarrow H_2O(l) \qquad \Delta_{fus}H^{\ominus}(273\text{ K}) = +6.01\text{ kJ mol}^{-1}$$

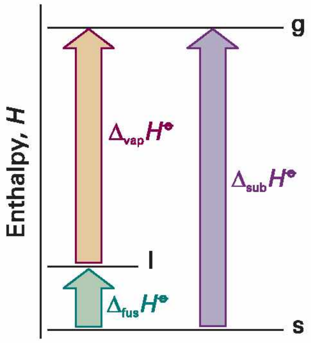
As in this case, it is sometimes convenient to know the standard enthalpy change at the transition temperature as well as at the conventional temperature.

Because enthalpy is a state function, a change in enthalpy is independent of the path between the two states. This feature is of great importance in thermochemistry, for it implies that the same value of $\Delta H^{\ominus}$ will be obtained however the change is brought about between the same initial and final states. For example, we can picture the conversion of a solid to a vapour either as occurring by sublimation (the direct conversion from solid to vapour),

$$H_2O(s) \rightarrow H_2O(g) \qquad \Delta_{sub}H^{\ominus}$$

or as occurring in two steps, first fusion (melting) and then vaporization of the resulting liquid:

$$\begin{aligned} &H_2O(s) \rightarrow H_2O(l) && \Delta_{fus}H^{\ominus} \\ &H_2O(l) \rightarrow H_2O(g) && \Delta_{vap}H^{\ominus} \\ \text{Overall: } &H_2O(s) \rightarrow H_2O(g) && \Delta_{fus}H^{\ominus} + \Delta_{vap}H^{\ominus} \end{aligned}$$



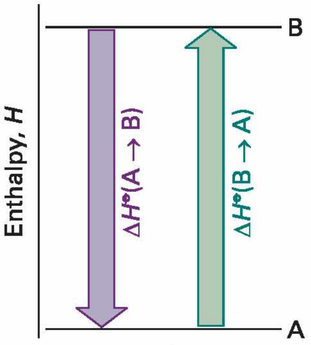
1

Because the overall result of the indirect path is the same as that of the direct path, the overall enthalpy change is the same in each case (**1**), and we can conclude that (for processes occurring at the same temperature)

$$\Delta_{sub}H^{\ominus} = \Delta_{fus}H^{\ominus} + \Delta_{vap}H^{\ominus} \tag{2.30}$$

An immediate conclusion is that, because all enthalpies of fusion are positive, the enthalpy of sublimation of a substance is greater than its enthalpy of vaporization (at a given temperature).

Another consequence of H being a state function is that the standard enthalpy changes of a forward process and its reverse differ in sign (**2**):



2

$$\Delta H^{\ominus}(A \rightarrow B) = -\Delta H^{\ominus}(B \rightarrow A) \tag{2.31}$$

For instance, because the enthalpy of vaporization of water is +44 kJ mol^{-1} at 298 K, its enthalpy of condensation at that temperature is –44 kJ mol^{-1}.

Table 2.4 Enthalpies of transition

Transition	Process	Symbol*
Transition	Phase α → phase β	$\Delta_{trs}H$
Fusion	s → l	$\Delta_{fus}H$
Vaporization	l → g	$\Delta_{vap}H$
Sublimation	s → g	$\Delta_{sub}H$
Mixing	Pure → mixture	$\Delta_{mix}H$
Solution	Solute → solution	$\Delta_{sol}H$
Hydration	$X^{\pm}(g) \rightarrow X^{\pm}(aq)$	$\Delta_{hyd}H$
Atomization	Species(s, l, g) → atoms(g)	$\Delta_{at}H$
Ionization	$X(g) \rightarrow X^{+}(g) + e^{-}(g)$	$\Delta_{ion}H$
Electron gain	$X(g) + e^{-}(g) \rightarrow X^{-}(g)$	$\Delta_{eg}H$
Reaction	Reactants → products	$\Delta_{r}H$
Combustion	Compounds(s, l, g) + $O_2(g) \rightarrow CO_2(g), H_2O(l, g)$	$\Delta_{c}H$
Formation	Elements → compound	$\Delta_{f}H$
Activation	Reactants → activated complex	$\Delta^{\ddagger}H$

* IUPAC recommendations. In common usage, the transition subscript is often attached to ΔH, as in ΔH_{trs}.

The different types of enthalpies encountered in thermochemistry are summarized in Table 2.4. We shall meet them again in various locations throughout the text.

(b) Enthalpies of chemical change

Now we consider enthalpy changes that accompany chemical reactions. There are two ways of reporting the change in enthalpy that accompanies a chemical reaction. One is to write the **thermochemical equation**, a combination of a chemical equation and the corresponding change in standard enthalpy:

$$CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(l) \qquad \Delta H^{\ominus} = -890\ \text{kJ}$$

$\Delta H^{\ominus}$ is the change in enthalpy when reactants in their standard states change to products in their standard states:

Pure, separate reactants in their standard states
→ pure, separate products in their standard states

Except in the case of ionic reactions in solution, the enthalpy changes accompanying mixing and separation are insignificant in comparison with the contribution from the reaction itself. For the combustion of methane, the standard value refers to the reaction in which 1 mol CH_4 in the form of pure methane gas at 1 bar reacts completely with 2 mol O_2 in the form of pure oxygen gas to produce 1 mol CO_2 as pure carbon dioxide at 1 bar and 2 mol H_2O as pure liquid water at 1 bar; the numerical value is for the reaction at 298 K.

Alternatively, we write the chemical equation and then report the **standard reaction enthalpy**, $\Delta_r H^{\ominus}$. Thus, for the combustion of reaction, we write

$$CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(l) \qquad \Delta_r H^{\ominus} = -890\ \text{kJ mol}^{-1}$$

For the reaction

$$2\,A + B \rightarrow 3\,C + D$$

Synoptic Table 2.5* Standard enthalpies of formation and combustion of organic compounds at 298 K

	$\Delta_f H^{\ominus}/(\text{kJ mol}^{-1})$	$\Delta_c H^{\ominus}/(\text{kJ mol}^{-1})$
Benzene, $C_6H_6(l)$	+49.0	−3268
Ethane, $C_2H_6(g)$	−84.7	−1560
Glucose, $C_6H_{12}O_6(s)$	−1274	−2808
Methane, $CH_4(g)$	−74.8	−890
Methanol, $CH_3OH(l)$	−238.7	−721

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

the standard reaction enthalpy is

$$\Delta_r H^{\ominus} = \{3H_m^{\ominus}(C) + H_m^{\ominus}(D)\} - \{2H_m^{\ominus}(A) + H_m^{\ominus}(B)\}$$

where $H_m^{\ominus}(J)$ is the standard molar enthalpy of species J at the temperature of interest. Note how the 'per mole' of $\Delta_r H^{\ominus}$ comes directly from the fact that molar enthalpies appear in this expression. We interpret the 'per mole' by noting the stoichiometic coefficients in the chemical equation. In this case 'per mole' in $\Delta_r H^{\ominus}$ means 'per 2 mol A', 'per mole B', 'per 3 mol C', or 'per mol D'. In general,

$$\Delta_r H^{\ominus} = \sum_{\text{Products}} \nu H_m^{\ominus} - \sum_{\text{Reactants}} \nu H_m^{\ominus} \tag{2.32}$$

where in each case the molar enthalpies of the species are multiplied by their stoichiometric coefficients, ν.[6]

Some standard reaction enthalpies have special names and a particular significance. For instance, the **standard enthalpy of combustion**, $\Delta_c H^{\ominus}$, is the standard reaction enthalpy for the complete oxidation of an organic compound to CO_2 gas and liquid H_2O if the compound contains C, H, and O, and to N_2 gas if N is also present. An example is the combustion of glucose:

$$C_6H_{12}O_6(s) + 6\,O_2(g) \rightarrow 6\,CO_2(g) + 6\,H_2O(l) \qquad \Delta_c H^{\ominus} = -2808\ \text{kJ mol}^{-1}$$

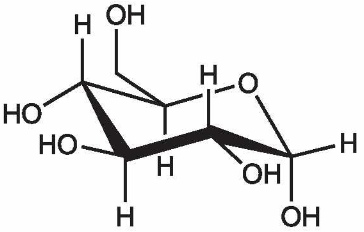
The value quoted shows that 2808 kJ of heat is released when 1 mol $C_6H_{12}O_6$ burns under standard conditions (at 298 K). Some further values are listed in Table 2.5.

IMPACT ON BIOLOGY

I2.2 Food and energy reserves

The thermochemical properties of fuels Table 2.6 and foods are commonly discussed in terms of their *specific enthalpy*, the enthalpy of combustion per gram of material. Thus, if the standard enthalpy of combustion is $\Delta_c H^{\ominus}$ and the molar mass of the compound is M, then the specific enthalpy is $\Delta_c H^{\ominus}/M$. Table 2.6 lists the specific enthalpies of several fuels.

A typical 18–20 year old man requires a daily input of about 12 MJ; a woman of the same age needs about 9 MJ. If the entire consumption were in the form of glucose (**3**; which has a specific enthalpy of 16 kJ g^{-1}), that would require the consumption of 750 g of glucose for a man and 560 g for a woman. In fact, digestible carbohydrates have a slightly higher specific enthalpy (17 kJ g^{-1}) than glucose itself, so a carbohydrate



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[6] In this and similar expressions, all stoichiometric coefficients are positive. For a more sophisticated way of writing eqn 2.32, see Section 7.2.

Table 2.6 Thermochemical properties of some fuels

Fuel	Combustion equation	$\Delta_c H^\ominus$/ (kJ mol^{-1})	Specific enthalpy/ (kJ g^{-1})	Enthalpy density/ (kJ dm^{-3})
Hydrogen	$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$	−286	142	13
Methane	$CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(l)$	−890	55	40
Octane	$C_8H_{18}(l) + \frac{25}{2} O_2(g) \rightarrow 8\,CO_2(g) + 9\,H_2O(l)$	−5471	48	3.8×10^4
Methanol	$CH_3OH(l) + \frac{3}{2} O_2(g) \rightarrow CO_2(g) + 2\,H_2O(l)$	−726	23	1.8×10^4

diet is slightly less daunting than a pure glucose diet, as well as being more appropriate in the form of fibre, the indigestible cellulose that helps move digestion products through the intestine.

The specific enthalpy of fats, which are long-chain esters like tristearin (beef fat), is much greater than that of carbohydrates, at around 38 kJ g^{-1}, slightly less than the value for the hydrocarbon oils used as fuel (48 kJ g^{-1}). Fats are commonly used as an energy store, to be used only when the more readily accessible carbohydrates have fallen into short supply. In Arctic species, the stored fat also acts as a layer of insulation; in desert species (such as the camel), the fat is also a source of water, one of its oxidation products.

Proteins are also used as a source of energy, but their components, the amino acids, are often too valuable to squander in this way, and are used to construct other proteins instead. When proteins are oxidized (to urea, $CO(NH_2)_2$), the equivalent enthalpy density is comparable to that of carbohydrates.

The heat released by the oxidation of foods needs to be discarded in order to maintain body temperature within its typical range of 35.6–37.8°C. A variety of mechanisms contribute to this aspect of homeostasis, the ability of an organism to counteract environmental changes with physiological responses. The general uniformity of temperature throughout the body is maintained largely by the flow of blood. When heat needs to be dissipated rapidly, warm blood is allowed to flow through the capillaries of the skin, so producing flushing. Radiation is one means of discarding heat; another is evaporation and the energy demands of the enthalpy of vaporization of water. Evaporation removes about 2.4 kJ per gram of water perspired. When vigorous exercise promotes sweating (through the influence of heat selectors on the hypothalamus), 1–2 dm^3 of perspired water can be produced per hour, corresponding to a heat loss of 2.4–5.0 MJ h^{-1}.

(c) Hess's law

Standard enthalpies of individual reactions can be combined to obtain the enthalpy of another reaction. This application of the First Law is called **Hess's law**:

> The standard enthalpy of an overall reaction is the sum of the standard enthalpies of the individual reactions into which a reaction may be divided.

The individual steps need not be realizable in practice: they may be hypothetical reactions, the only requirement being that their chemical equations should balance. The thermodynamic basis of the law is the path-independence of the value of $\Delta_r H^\ominus$ and the implication that we may take the specified reactants, pass through any (possibly hypothetical) set of reactions to the specified products, and overall obtain the same change of enthalpy. The importance of Hess's law is that information about a reaction of interest, which may be difficult to determine directly, can be assembled from information on other reactions.

Example 2.5 *Using Hess's law*

The standard reaction enthalpy for the hydrogenation of propene,

$$CH_2{=}CHCH_3(g) + H_2(g) \rightarrow CH_3CH_2CH_3(g)$$

is -124 kJ mol^{-1}. The standard reaction enthalpy for the combustion of propane,

$$CH_3CH_2CH_3(g) + 5\,O_2(g) \rightarrow 3\,CO_2(g) + 4\,H_2O(l)$$

is -2220 kJ mol^{-1}. Calculate the standard enthalpy of combustion of propene.

Method The skill to develop is the ability to assemble a given thermochemical equation from others. Add or subtract the reactions given, together with any others needed, so as to reproduce the reaction required. Then add or subtract the reaction enthalpies in the same way. Additional data are in Table 2.5.

Answer The combustion reaction we require is

$$C_3H_6(g) + \tfrac{9}{2}\,O_2(g) \rightarrow 3\,CO_2(g) + 3\,H_2O(l)$$

This reaction can be recreated from the following sum:

	$\Delta_r H^\ominus/(\text{kJ mol}^{-1})$
$C_3H_6(g) + H_2(g) \rightarrow C_3H_8(g)$	-124
$C_3H_8(g) + 5\,O_2(g) \rightarrow 3\,CO_2(g) + 4\,H_2O(l)$	-2220
$H_2O(l) \rightarrow H_2(g) + \tfrac{1}{2}\,O_2(g)$	$+286$
$C_3H_6(g) + \tfrac{9}{2}\,O_2(g) \rightarrow 3\,CO_2(g) + 3\,H_2O(l)$	-2058

Self-test 2.6 Calculate the enthalpy of hydrogenation of benzene from its enthalpy of combustion and the enthalpy of combustion of cyclohexane. [-205 kJ mol^{-1}]

Synoptic Table 2.7* Standard enthalpies of formation of inorganic compounds at 298 K

	$\Delta_f H^\ominus/(\text{kJ mol}^{-1})$
$H_2O(l)$	-285.83
$H_2O(g)$	-187.78
$NH_3(g)$	-46.11
$N_2H_4(l)$	$+50.63$
$NO_2(g)$	33.18
$N_2O_4(g)$	$+9.16$
$NaCl(s)$	-411.15
$KCl(s)$	-436.75

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

2.8 Standard enthalpies of formation

The **standard enthalpy of formation**, $\Delta_f H^\ominus$, of a substance is the standard reaction enthalpy for the formation of the compound from its elements in their reference states. The **reference state** of an element is its most stable state at the specified temperature and 1 bar. For example, at 298 K the reference state of nitrogen is a gas of N_2 molecules, that of mercury is liquid mercury, that of carbon is graphite, and that of tin is the white (metallic) form. There is one exception to this general prescription of reference states: the reference state of phosphorus is taken to be white phosphorus despite this allotrope not being the most stable form but simply the more reproducible form of the element. Standard enthalpies of formation are expressed as enthalpies per mole of molecules or (for ionic substances) formula units of the compound. The standard enthalpy of formation of liquid benzene at 298 K, for example, refers to the reaction

$$6\,C(s, \text{graphite}) + 3\,H_2(g) \rightarrow C_6H_6(l)$$

and is $+49.0$ kJ mol^{-1}. The standard enthalpies of formation of elements in their reference states are zero at all temperatures because they are the enthalpies of such 'null' reactions as $N_2(g) \rightarrow N_2(g)$. Some enthalpies of formation are listed in Tables 2.5 and 2.7.

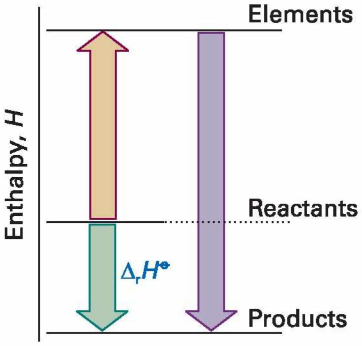
Comment 2.7

The NIST WebBook listed in the web site for this book links to online databases of thermochemical data.

The standard enthalpy of formation of ions in solution poses a special problem because it is impossible to prepare a solution of cations alone or of anions alone. This problem is solved by defining one ion, conventionally the hydrogen ion, to have zero standard enthalpy of formation at all temperatures:

$$\Delta_f H^\ominus(\mathrm{H^+}, \mathrm{aq}) = 0 \qquad [2.33]$$

Thus, if the enthalpy of formation of HBr(aq) is found to be −122 kJ mol^{-1}, then the whole of that value is ascribed to the formation of $\mathrm{Br^-}$(aq), and we write $\Delta_f H^\ominus(\mathrm{Br^-}, \mathrm{aq}) = -122$ kJ mol^{-1}. That value may then be combined with, for instance, the enthalpy formation of AgBr(aq) to determine the value of $\Delta_f H^\ominus(\mathrm{Ag^+}, \mathrm{aq})$, and so on. In essence, this definition adjusts the actual values of the enthalpies of formation of ions by a fixed amount, which is chosen so that the standard value for one of them, $\mathrm{H^+}$(aq), has the value zero.



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(a) The reaction enthalpy in terms of enthalpies of formation

Conceptually, we can regard a reaction as proceeding by decomposing the reactants into their elements and then forming those elements into the products. The value of $\Delta_r H^\ominus$ for the overall reaction is the sum of these 'unforming' and forming enthalpies. Because 'unforming' is the reverse of forming, the enthalpy of an unforming step is the negative of the enthalpy of formation (**4**). Hence, in the enthalpies of formation of substances, we have enough information to calculate the enthalpy of any reaction by using

$$\Delta_r H^\ominus = \sum_{\text{Products}} \nu \Delta_f H^\ominus - \sum_{\text{Reactants}} \nu \Delta_f H^\ominus \qquad (2.34)$$

where in each case the enthalpies of formation of the species that occur are multiplied by their stoichiometric coefficients.

Illustration 2.7 *Using standard enthalpies of formation*

The standard reaction enthalpy of $2\,\mathrm{HN_3(l)} + 2\,\mathrm{NO(g)} \rightarrow \mathrm{H_2O_2(l)} + 4\,\mathrm{N_2(g)}$ is calculated as follows:

$$\begin{aligned}\Delta_r H^\ominus &= \{\Delta_f H^\ominus(\mathrm{H_2O_2,l}) + 4\Delta_f H^\ominus(\mathrm{N_2,g})\} - \{2\Delta_f H^\ominus(\mathrm{HN_3,l}) + 2\Delta_f H^\ominus(\mathrm{NO,g})\} \\ &= \{-187.78 + 4(0)\}\ \mathrm{kJ\ mol^{-1}} - \{2(264.0) + 2(90.25)\}\ \mathrm{kJ\ mol^{-1}} \\ &= -896.3\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

(b) Enthalpies of formation and molecular modelling

We have seen how to construct standard reaction enthalpies by combining standard enthalpies of formation. The question that now arises is whether we can construct standard enthalpies of formation from a knowledge of the chemical constitution of the species. The short answer is that there is no thermodynamically exact way of expressing enthalpies of formation in terms of contributions from individual atoms and bonds. In the past, approximate procedures based on **mean bond enthalpies**, $\Delta H(\mathrm{A{-}B})$, the average enthalpy change associated with the breaking of a specific A—B bond,

$$\mathrm{A{-}B(g)} \rightarrow \mathrm{A(g)} + \mathrm{B(g)} \qquad \Delta H(\mathrm{A{-}B})$$

have been used. However, this procedure is notoriously unreliable, in part because the $\Delta H(\text{A—B})$ are average values for a series of related compounds. Nor does the approach distinguish between geometrical isomers, where the same atoms and bonds may be present but experimentally the enthalpies of formation might be significantly different.

Computer-aided molecular modelling has largely displaced this more primitive approach. Commercial software packages use the principles developed in Chapter 11 to calculate the standard enthalpy of formation of a molecule drawn on the computer screen. These techniques can be applied to different conformations of the same molecule. In the case of methylcyclohexane, for instance, the calculated conformational energy difference ranges from 5.9 to 7.9 kJ mol^{-1}, with the equatorial conformer having the lower standard enthalpy of formation. These estimates compare favourably with the experimental value of 7.5 kJ mol^{-1}. However, good agreement between calculated and experimental values is relatively rare. Computational methods almost always predict correctly which conformer is more stable but do not always predict the correct magnitude of the conformational energy difference.

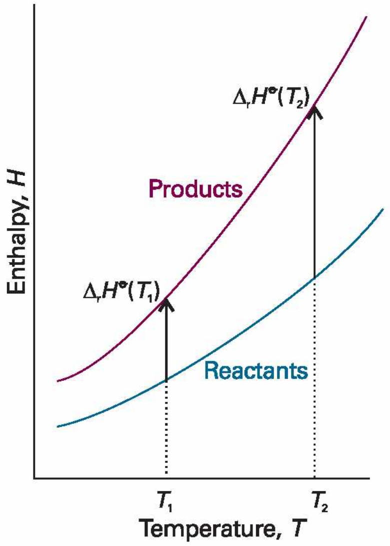

Fig. 2.19 An illustration of the content of Kirchhoff's law. When the temperature is increased, the enthalpy of the products and the reactants both increase, but may do so to different extents. In each case, the change in enthalpy depends on the heat capacities of the substances. The change in reaction enthalpy reflects the difference in the changes of the enthalpies.

2.9 The temperature-dependence of reaction enthalpies

The standard enthalpies of many important reactions have been measured at different temperatures. However, in the absence of this information, standard reaction enthalpies at different temperatures may be calculated from heat capacities and the reaction enthalpy at some other temperature (Fig. 2.19). In many cases heat capacity data are more accurate that reaction enthalpies so, providing the information is available, the procedure we are about to describe is more accurate that a direct measurement of a reaction enthalpy at an elevated temperature.

It follows from eqn 2.23a that, when a substance is heated from T_1 to T_2, its enthalpy changes from $H(T_1)$ to

$$H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_p \mathrm{d}T \tag{2.35}$$

(We have assumed that no phase transition takes place in the temperature range of interest.) Because this equation applies to each substance in the reaction, the standard reaction enthalpy changes from $\Delta_r H^\ominus(T_1)$ to

$$\Delta_r H^\ominus(T_2) = \Delta_r H^\ominus(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^\ominus \mathrm{d}T \tag{2.36}$$

where $\Delta_r C_p^\ominus$ is the difference of the molar heat capacities of products and reactants under standard conditions weighted by the stoichiometric coefficients that appear in the chemical equation:

$$\Delta_r C_p^\ominus = \sum_{\text{Products}} \nu C_{p,\mathrm{m}}^\ominus - \sum_{\text{Reactants}} \nu C_{p,\mathrm{m}}^\ominus \qquad [2.37]$$

Equation 2.36 is known as **Kirchhoff's law**. It is normally a good approximation to assume that $\Delta_r C_p$ is independent of the temperature, at least over reasonably limited ranges, as illustrated in the following example. Although the individual heat capacities may vary, their difference varies less significantly. In some cases the temperature dependence of heat capacities is taken into account by using eqn 2.25.

Example 2.6 *Using Kirchhoff's law*

The standard enthalpy of formation of gaseous H_2O at 298 K is -241.82 kJ mol^{-1}. Estimate its value at 100°C given the following values of the molar heat capacities at constant pressure: $H_2O(g)$: 33.58 J K^{-1} mol^{-1}; $H_2(g)$: 28.84 J K^{-1} mol^{-1}; $O_2(g)$: 29.37 J K^{-1} mol^{-1}. Assume that the heat capacities are independent of temperature.

Method When $\Delta C_p^{\ominus}$ is independent of temperature in the range T_1 to T_2, the integral in eqn 2.36 evaluates to $(T_2 - T_1)\Delta_r C_p^{\ominus}$. Therefore,

$$\Delta_r H^{\ominus}(T_2) = \Delta_r H^{\ominus}(T_1) + (T_2 - T_1)\Delta_r C_p^{\ominus}$$

To proceed, write the chemical equation, identify the stoichiometric coefficients, and calculate $\Delta_r C_p^{\ominus}$ from the data.

Answer The reaction is $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$, so

$$\Delta_r C_p^{\ominus} = C_{p,m}^{\ominus}(H_2O, g) - \{C_{p,m}^{\ominus}(H_2, g) + \tfrac{1}{2}C_{p,m}^{\ominus}(O_2, g)\} = -9.94 \text{ J K}^{-1} \text{ mol}^{-1}$$

It then follows that

$$\Delta_f H^{\ominus}(373 \text{ K}) = -241.82 \text{ kJ mol}^{-1} + (75 \text{ K}) \times (-9.94 \text{ J K}^{-1} \text{ mol}^{-1}) = -242.6 \text{ kJ mol}^{-1}$$

Self-test 2.7 Estimate the standard enthalpy of formation of cyclohexene at 400 K from the data in Table 2.5. [-163 kJ mol^{-1}]

State functions and exact differentials

We saw in Section 2.2 that a 'state function' is a property that is independent of how a sample is prepared. In general, such properties are functions of variables that define the current state of the system, such as pressure and temperature. The internal energy and enthalpy are examples of state functions, for they depend on the current state of the system and are independent of its previous history. Processes that describe the preparation of the state are called **path functions**. Examples of path functions are the work and heating that are done when preparing a state. We do not speak of a system in a particular state as possessing work or heat. In each case, the energy transferred as work or heat relates to the path being taken between states, not the current state itself.

We can use the mathematical properties of state functions to draw far-reaching conclusions about the relations between physical properties and establish connections that may be completely unexpected. The practical importance of these results is that we can combine measurements of different properties to obtain the value of a property we require.

2.10 Exact and inexact differentials

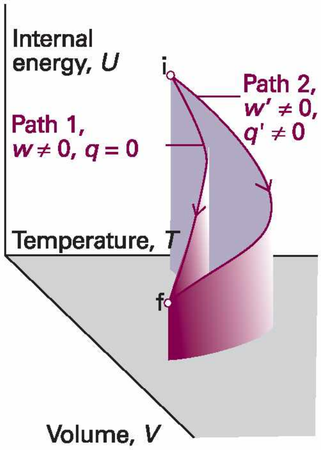

Fig. 2.20 As the volume and temperature of a system are changed, the internal energy changes. An adiabatic and a non-adiabatic path are shown as Path 1 and Path 2, respectively: they correspond to different values of q and w but to the same value of ΔU.

Consider a system undergoing the changes depicted in Fig. 2.20. The initial state of the system is i and in this state the internal energy is U_i. Work is done by the system as it expands adiabatically to a state f. In this state the system has an internal energy U_f and the work done on the system as it changes along Path 1 from i to f is w. Notice our use of language: U is a property of the state; w is a property of the path. Now consider another process, Path 2, in which the initial and final states are the same as those in Path 1 but in which the expansion is not adiabatic. The internal energy of both the initial and the final states are the same as before (because U is a state function). However, in the second path an energy q' enters the system as heat and the work w' is not the same as w. The work and the heat are path functions. In terms of the mountaineering analogy in Section 2.2, the change in altitude (a state function) is independent of the path, but the distance travelled (a path function) does depend on the path taken between the fixed endpoints.

If a system is taken along a path (for example, by heating it), U changes from U_i to U_f, and the overall change is the sum (integral) of all the infinitesimal changes along the path:

$$\Delta U = \int_\mathrm{i}^\mathrm{f} \mathrm{d}U \tag{2.38}$$

The value of ΔU depends on the initial and final states of the system but is independent of the path between them. This path-independence of the integral is expressed by saying that $\mathrm{d}U$ is an 'exact differential'. In general, an **exact differential** is an infinitesimal quantity that, when integrated, gives a result that is independent of the path between the initial and final states.

When a system is heated, the total energy transferred as heat is the sum of all individual contributions at each point of the path:

$$q = \int_{\mathrm{i,\,path}}^\mathrm{f} \mathrm{d}q \tag{2.39}$$

Notice the difference between this equation and eqn 2.38. First, we do not write Δq, because q is not a state function and the energy supplied as heat cannot be expressed as $q_\mathrm{f} - q_\mathrm{i}$. Secondly, we must specify the path of integration because q depends on the path selected (for example, an adiabatic path has $q = 0$, whereas a nonadiabatic path between the same two states would have $q \neq 0$). This path-dependence is expressed by saying that $\mathrm{d}q$ is an 'inexact differential'. In general, an **inexact differential** is an infinitesimal quantity that, when integrated, gives a result that depends on the path between the initial and final states. Often $\mathrm{d}q$ is written $đq$ to emphasize that it is inexact and requires the specification of a path.

The work done on a system to change it from one state to another depends on the path taken between the two specified states; for example, in general the work is different if the change takes place adiabatically and non-adiabatically. It follows that $\mathrm{d}w$ is an inexact differential. It is often written $đw$.

Example 2.7 *Calculating work, heat, and internal energy*

Consider a perfect gas inside a cylinder fitted with a piston. Let the initial state be T, V_i and the final state be T, V_f. The change of state can be brought about in many ways, of which the two simplest are the following: Path 1, in which there is free expansion against zero external pressure; Path 2, in which there is reversible, isothermal expansion. Calculate w, q, and ΔU for each process.

Method To find a starting point for a calculation in thermodynamics, it is often a good idea to go back to first principles, and to look for a way of expressing the quantity we are asked to calculate in terms of other quantities that are easier to calculate. We saw in *Molecular interpretation 2.2* that the internal energy of a perfect gas depends only on the temperature and is independent of the volume those molecules occupy, so for any isothermal change, $\Delta U = 0$. We also know that in general $\Delta U = q + w$. The question depends on being able to combine the two expressions. In this chapter, we derived a number of expressions for the work done in a variety of processes, and here we need to select the appropriate ones.

Answer Because $\Delta U = 0$ for both paths and $\Delta U = q + w$, in each case $q = -w$. The work of free expansion is zero (Section 2.3b); so in Path 1, $w = 0$ and $q = 0$. For Path 2, the work is given by eqn 2.11, so $w = -nRT\ln(V_f/V_i)$ and consequently $q = nRT\ln(V_f/V_i)$. These results are consequences of the path independence of U, a state function, and the path dependence of q and w, which are path functions.

Self-test 2.8 Calculate the values of q, w, and ΔU for an irreversible isothermal expansion of a perfect gas against a constant nonzero external pressure.

[$q = p_{ex}\Delta V$, $w = -p_{ex}\Delta V$, $\Delta U = 0$]

2.11 Changes in internal energy

We begin to unfold the consequences of dU being an exact differential by exploring a closed system of constant composition (the only type of system considered in the rest of this chapter). The internal energy U can be regarded as a function of V, T, and p, but, because there is an equation of state, stating the values of two of the variables fixes the value of the third. Therefore, it is possible to write U in terms of just two independent variables: V and T, p and T, or p and V. Expressing U as a function of volume and temperature fits the purpose of our discussion.

(a) General considerations

When V changes to $V + dV$ at constant temperature, U changes to

$$U' = U + \left(\frac{\partial U}{\partial V}\right)_T dV$$

The coefficient $(\partial U/\partial V)_T$, the slope of a plot of U against V at constant temperature, is the partial derivative of U with respect to V (Fig. 2.21). If, instead, T changes to $T + dT$ at constant volume (Fig. 2.22), then the internal energy changes to

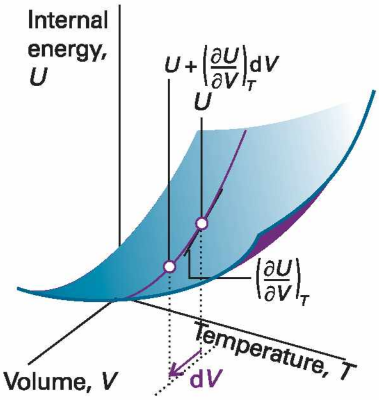

Fig. 2.21 The partial derivative $(\partial U/\partial V)_T$ is the slope of U with respect to V with the temperature T held constant.

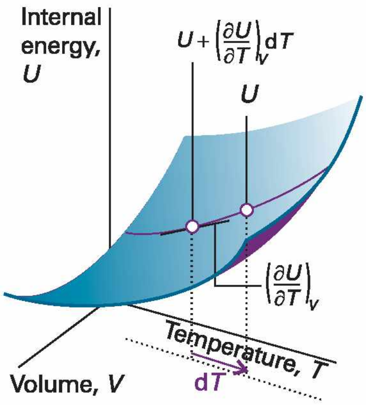

Fig. 2.22 The partial derivative $(\partial U/\partial T)_V$ is the slope of U with respect to T with the volume V held constant.

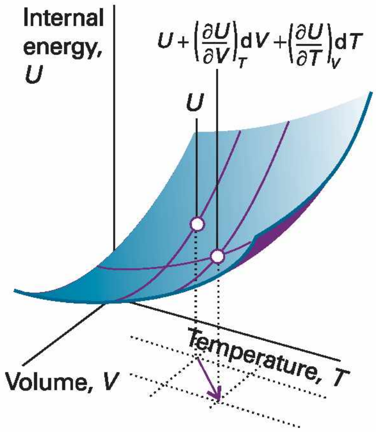

Fig. 2.23 An overall change in U, which is denoted $\mathrm{d}U$, arises when both V and T are allowed to change. If second-order infinitesimals are ignored, the overall change is the sum of changes for each variable separately.

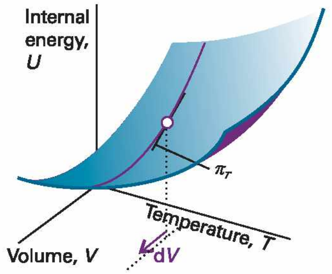

Fig. 2.24 The internal pressure, π_T, is the slope of U with respect to V with the temperature T held constant.

$$U' = U + \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T$$

Now suppose that V and T both change infinitesimally (Fig. 2.23). The new internal energy, neglecting second-order infinitesimals (those proportional to $\mathrm{d}V\mathrm{d}T$), is the sum of the changes arising from each increment:

$$U' = U + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V + \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T$$

As a result of the infinitesimal changes in conditions, the internal energy U' differs from U by the infinitesimal amount $\mathrm{d}U$, so we an write $U' = U + \mathrm{d}U$. Therefore, from the last equation we obtain the very important result that

$$\mathrm{d}U = \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V + \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T \qquad (2.40)$$

The interpretation of this equation is that, in a closed system of constant composition, any infinitesimal change in the internal energy is proportional to the infinitesimal changes of volume and temperature, the coefficients of proportionality being the two partial derivatives.

In many cases partial derivatives have a straightforward physical interpretation, and thermodynamics gets shapeless and difficult only when that interpretation is not kept in sight. In the present case, we have already met $(\partial U/\partial T)_V$ in eqn 2.15, where we saw that it is the constant-volume heat capacity, C_V. The other coefficient, $(\partial U/\partial V)_T$, plays a major role in thermodynamics because it is a measure of the variation of the internal energy of a substance as its volume is changed at constant temperature (Fig. 2.24). We shall denote it π_T and, because it has the same dimensions as pressure, call it the **internal pressure**:

$$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T \qquad [2.41]$$

In terms of the notation C_V and π_T, eqn 2.40 can now be written

$$\mathrm{d}U = \pi_T \mathrm{d}V + C_V \mathrm{d}T \qquad (2.42)$$

(b) The Joule experiment

When there are no interactions between the molecules, the internal energy is independent of their separation and hence independent of the volume of the sample (see *Molecular interpretation 2.2*). Therefore, for a perfect gas we can write $\pi_T = 0$. The statement $\pi_T = 0$ (that is, the internal energy is independent of the volume occupied by the sample) can be taken to be the definition of a perfect gas, for later we shall see that it implies the equation of state $pV = nRT$. If the internal energy increases ($\mathrm{d}U > 0$) as the volume of the sample expands isothermally ($\mathrm{d}V > 0$), which is the case when there are attractive forces between the particles, then a plot of internal energy against volume slopes upwards and $\pi_T > 0$ (Fig. 2.25).

James Joule thought that he could measure π_T by observing the change in temperature of a gas when it is allowed to expand into a vacuum. He used two metal vessels immersed in a water bath (Fig. 2.26). One was filled with air at about 22 atm and the other was evacuated. He then tried to measure the change in temperature of the water of the bath when a stopcock was opened and the air expanded into a vacuum. He observed no change in temperature.

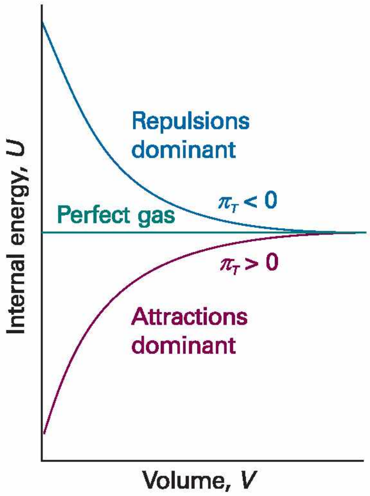

Fig. 2.25 For a perfect gas, the internal energy is independent of the volume (at constant temperature). If attractions are dominant in a real gas, the internal energy increases with volume because the molecules become farther apart on average. If repulsions are dominant, the internal energy decreases as the gas expands.

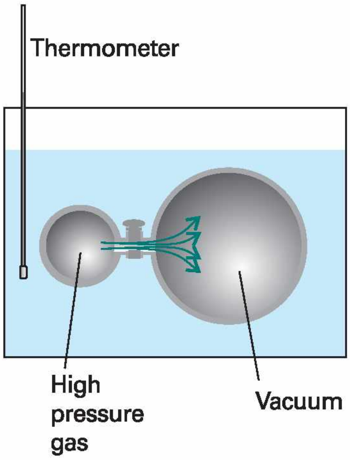

Fig. 2.26 A schematic diagram of the apparatus used by Joule in an attempt to measure the change in internal energy when a gas expands isothermally. The heat absorbed by the gas is proportional to the change in temperature of the bath.

The thermodynamic implications of the experiment are as follows. No work was done in the expansion into a vacuum, so $w = 0$. No energy entered or left the system (the gas) as heat because the temperature of the bath did not change, so $q = 0$. Consequently, within the accuracy of the experiment, $\Delta U = 0$. It follows that U does not change much when a gas expands isothermally and therefore that $\pi_T = 0$.

Joule's experiment was crude. In particular, the heat capacity of the apparatus was so large that the temperature change that gases do in fact cause was too small to measure. From his experiment Joule extracted an essential limiting property of a gas, a property of a perfect gas, without detecting the small deviations characteristic of real gases.

(c) Changes in internal energy at constant pressure

Partial derivatives have many useful properties and some that we shall draw on frequently are reviewed in *Appendix 2*. Skilful use of them can often turn some unfamiliar quantity into a quantity that can be recognized, interpreted, or measured.

As an example, suppose we want to find out how the internal energy varies with temperature when the pressure of the system is kept constant. If we divide both sides of eqn 2.42 by $\mathrm{d}T$ and impose the condition of constant pressure on the resulting differentials, so that $\mathrm{d}U/\mathrm{d}T$ on the left becomes $(\partial U/\partial T)_p$, we obtain

$$\left(\frac{\partial U}{\partial T}\right)_p = \pi_T\left(\frac{\partial V}{\partial T}\right)_p + C_V$$

It is usually sensible in thermodynamics to inspect the output of a manipulation like this to see if it contains any recognizable physical quantity. The partial derivative on the right in this expression is the slope of the plot of volume against temperature (at

Synoptic Table 2.8* Expansion coefficients (α) and isothermal compressibilities (κ_T) at 298 K

	$\alpha/(10^{-4}\,\mathrm{K}^{-1})$	$\kappa_T/(10^{-6}\,\mathrm{bar}^{-1})$
Benzene	12.4	90.9
Diamond	0.030	0.185
Lead	0.861	2.18
Water	2.1	49.0

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

constant pressure). This property is normally tabulated as the **expansion coefficient**, α, of a substance,[7] which is defined as

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \qquad [2.43]$$

and physically is the fractional change in volume that accompanies a rise in temperature. A large value of α means that the volume of the sample responds strongly to changes in temperature. Table 2.8 lists some experimental values of α and of the **isothermal compressibility**, κ_T (kappa), which is defined as

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \qquad [2.44]$$

The isothermal compressibility is a measure of the fractional change in volume when the pressure is increased by a small amount; the negative sign in the definition ensures that the compressibility is a positive quantity, because an increase of pressure, implying a positive $\mathrm{d}p$, brings about a reduction of volume, a negative $\mathrm{d}V$.

Example 2.8 *Calculating the expansion coefficient of a gas*

Derive an expression for the expansion coefficient of a perfect gas.

Method The expansion coefficient is defined in eqn 2.43. To use this expression, substitute the expression for V in terms of T obtained from the equation of state for the gas. As implied by the subscript in eqn 2.43, the pressure, p, is treated as a constant.

Answer Because $pV = nRT$, we can write

$$\alpha = \frac{1}{V}\left(\frac{\partial(nRT/p)}{\partial T}\right)_p = \frac{1}{V} \times \frac{nR}{p}\frac{\mathrm{d}T}{\mathrm{d}T} = \frac{nR}{pV} = \frac{1}{T}$$

The higher the temperature, the less responsive is the volume of a perfect gas to a change in temperature.

Self-test 2.9 Derive an expression for the isothermal compressibility of a perfect gas. [$\kappa_T. = 1/p$]

When we introduce the definition of α into the equation for $(\partial U/\partial T)_p$, we obtain

$$\left(\frac{\partial U}{\partial T}\right)_p = \alpha \pi_T V + C_V \qquad (2.45)$$

This equation is entirely general (provided the system is closed and its composition is constant). It expresses the dependence of the internal energy on the temperature at constant pressure in terms of C_V, which can be measured in one experiment, in terms of α, which can be measured in another, and in terms of the quantity π_T. For a perfect gas, $\pi_T = 0$, so then

$$\left(\frac{\partial U}{\partial T}\right)_p = C_V \qquad (2.46)^{\circ}$$

---

[7] As for heat capacities, the expansion coefficients of a mixture depends on whether or not the composition is allowed to change. Throughout this chapter, we deal only with pure substances, so this complication can be disregarded.

That is, although the constant-volume heat capacity of a perfect gas is defined as the slope of a plot of internal energy against temperature at constant volume, for a perfect gas C_V is also the slope at constant pressure.

Equation 2.46 provides an easy way to derive the relation between C_p and C_V for a perfect gas expressed in eqn 2.26. Thus, we can use it to express both heat capacities in terms of derivatives at constant pressure:

$$C_p - C_V = \left(\frac{\partial H}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_p \qquad (2.47)^\circ$$

Then we introduce $H = U + pV = U + nRT$ into the first term, which results in

$$C_p - C_V = \left(\frac{\partial U}{\partial T}\right)_p + nR - \left(\frac{\partial U}{\partial T}\right)_p = nR \qquad (2.48)^\circ$$

which is eqn 2.26. We show in *Further information 2.2* that in general

$$C_p - C_V = \frac{\alpha^2 TV}{\kappa_T} \qquad (2.49)$$

Equation 2.49 applies to any substance (that is, it is 'universally true'). It reduces to eqn 2.48 for a perfect gas when we set $\alpha = 1/T$ and $\kappa_T = 1/p$. Because expansion coefficients α of liquids and solids are small, it is tempting to deduce from eqn 2.49 that for them $C_p \approx C_V$. But this is not always so, because the compressibility κ_T might also be small, so α^2/κ_T might be large. That is, although only a little work need be done to push back the atmosphere, a great deal of work may have to be done to pull atoms apart from one another as the solid expands. As an illustration, for water at 25°C, eqn 2.49 gives $C_{p,\mathrm{m}} = 75.3\ \mathrm{J\ K^{-1}\ mol^{-1}}$ compared with $C_{V,\mathrm{m}} = 74.8\ \mathrm{J\ K^{-1}\ mol^{-1}}$. In some cases, the two heat capacities differ by as much as 30 per cent.

2.12 The Joule–Thomson effect

We can carry out a similar set of operations on the enthalpy, $H = U + pV$. The quantities U, p, and V are all state functions; therefore H is also a state function and $\mathrm{d}H$ is an exact differential. It turns out that H is a useful thermodynamic function when the pressure is under our control: we saw a sign of that in the relation $\Delta H = q_p$ (eqn 2.19). We shall therefore regard H as a function of p and T, and adapt the argument in Section 2.10 to find an expression for the variation of H with temperature at constant volume. As set out in *Justification 2.2*, we find that for a closed system of constant composition,

$$\mathrm{d}H = -\mu C_p \mathrm{d}p + C_p \mathrm{d}T \qquad (2.50)$$

where the **Joule–Thomson coefficient**, μ (mu), is defined as

$$\mu = \left(\frac{\partial T}{\partial p}\right)_H \qquad [2.51]$$

This relation will prove useful for relating the heat capacities at constant pressure and volume and for a discussion of the liquefaction of gases.

Justification 2.2 *The variation of enthalpy with pressure and temperature*

By the same argument that led to eqn 2.40 but with H regarded as a function of p and T we can write

$$\mathrm{d}H = \left(\frac{\partial H}{\partial p}\right)_T \mathrm{d}p + \left(\frac{\partial H}{\partial T}\right)_p \mathrm{d}T \qquad (2.52)$$

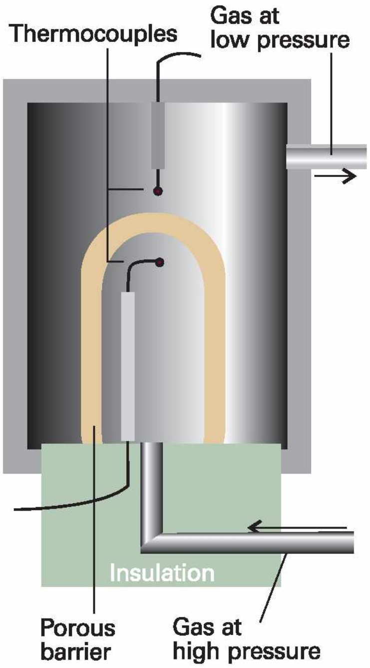

Fig. 2.27 The apparatus used for measuring the Joule–Thomson effect. The gas expands through the porous barrier, which acts as a throttle, and the whole apparatus is thermally insulated. As explained in the text, this arrangement corresponds to an isenthalpic expansion (expansion at constant enthalpy). Whether the expansion results in a heating or a cooling of the gas depends on the conditions.

The second partial derivative is C_p; our task here is to express $(\partial H/\partial p)_T$ in terms of recognizable quantities. The chain relation (see *Further information 2.2*) lets us write

$$\left(\frac{\partial H}{\partial p}\right)_T = -\frac{1}{(\partial p/\partial T)_H(\partial T/\partial H)_p}$$

and both partial derivatives can be brought into the numerator by using the reciprocal identity (see *Further information 2.2*) twice:

$$\left(\frac{\partial H}{\partial p}\right)_T = -\frac{(\partial T/\partial p)_H}{(\partial T/\partial H)_p} = \left(\frac{\partial T}{\partial p}\right)_H\left(\frac{\partial H}{\partial T}\right)_p = -\mu C_p \qquad (2.53)$$

We have used the definitions of the constant-pressure heat capacity, C_p, and the Joule–Thomson coefficient, μ (eqn 2.51). Equation 2.50 now follows directly.

The analysis of the Joule–Thomson coefficient is central to the technological problems associated with the liquefaction of gases. We need to be able to interpret it physically and to measure it. As shown in the *Justification* below, the cunning required to impose the constraint of constant enthalpy, so that the process is **isenthalpic**, was supplied by Joule and William Thomson (later Lord Kelvin). They let a gas expand through a porous barrier from one constant pressure to another, and monitored the difference of temperature that arose from the expansion (Fig. 2.27). The whole apparatus was insulated so that the process was adiabatic. They observed a lower temperature on the low pressure side, the difference in temperature being proportional to the pressure difference they maintained. This cooling by isenthalpic expansion is now called the **Joule–Thomson effect.**

Justification 2.3 *The Joule–Thomson effect*

Here we show that the experimental arrangement results in expansion at constant enthalpy. Because all changes to the gas occur adiabatically,

$q = 0$, which implies $\Delta U = w$

Consider the work done as the gas passes through the barrier. We focus on the passage of a fixed amount of gas from the high pressure side, where the pressure is p_i, the temperature T_i, and the gas occupies a volume V_i (Fig. 2.28). The gas emerges on the low pressure side, where the same amount of gas has a pressure p_f, a temperature T_f, and occupies a volume V_f. The gas on the left is compressed isothermally by the upstream gas acting as a piston. The relevant pressure is p_i and the volume changes from V_i to 0; therefore, the work done on the gas is

$$w_1 = -p_i(0 - V_i) = p_iV_i$$

The gas expands isothermally on the right of the barrier (but possibly at a different constant temperature) against the pressure p_f provided by the downstream gas acting as a piston to be driven out. The volume changes from 0 to V_f, so the work done on the gas in this stage is

$$w_2 = -p_f(V_f - 0) = -p_fV_f$$

The total work done on the gas is the sum of these two quantities, or

$$w = w_1 + w_2 = p_iV_i - p_fV_f$$

It follows that the change of internal energy of the gas as it moves adiabatically from one side of the barrier to the other is

$$U_\mathrm{f} - U_\mathrm{i} = w = p_\mathrm{i}V_\mathrm{i} - p_\mathrm{f}V_\mathrm{f}$$

Reorganization of this expression gives

$$U_\mathrm{f} + p_\mathrm{f}V_\mathrm{f} = U_\mathrm{i} + p_\mathrm{i}V_\mathrm{i}, \text{ or } H_\mathrm{f} = H_\mathrm{i}$$

Therefore, the expansion occurs without change of enthalpy.

The property measured in the experiment is the ratio of the temperature change to the change of pressure, $\Delta T/\Delta p$. Adding the constraint of constant enthalpy and taking the limit of small Δp implies that the thermodynamic quantity measured is $(\partial T/\partial p)_H$, which is the Joule–Thomson coefficient, μ. In other words, the physical interpretation of μ is that it is the ratio of the change in temperature to the change in pressure when a gas expands under conditions that ensure there is no change in enthalpy.

The modern method of measuring μ is indirect, and involves measuring the **isothermal Joule–Thomson coefficient**, the quantity

$$\mu_T = \left(\frac{\partial H}{\partial p}\right)_T \qquad [2.54]$$

which is the slope of a plot of enthalpy against pressure at constant temperature (Fig. 2.29). Comparing eqns 2.53 and 2.54, we see that the two coefficients are related by:

$$\mu_T = -C_p\mu \qquad (2.55)$$

To measure μ_T, the gas is pumped continuously at a steady pressure through a heat exchanger (which brings it to the required temperature), and then through a porous plug inside a thermally insulated container. The steep pressure drop is measured, and the cooling effect is exactly offset by an electric heater placed immediately after the plug (Fig. 2.30). The energy provided by the heater is monitored. Because the energy transferred as heat can be identified with the value of ΔH for the gas (because

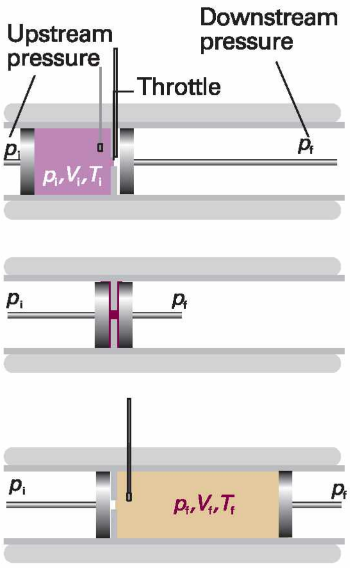

Fig. 2.28 The thermodynamic basis of Joule–Thomson expansion. The pistons represent the upstream and downstream gases, which maintain constant pressures either side of the throttle. The transition from the top diagram to the bottom diagram, which represents the passage of a given amount of gas through the throttle, occurs without change of enthalpy.

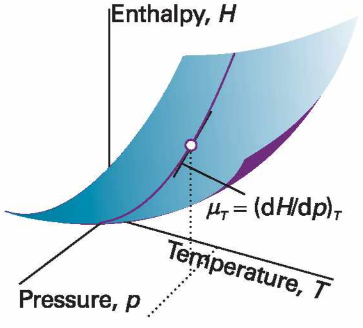

Fig. 2.29 The isothermal Joule–Thomson coefficient is the slope of the enthalpy with respect to changing pressure, the temperature being held constant.

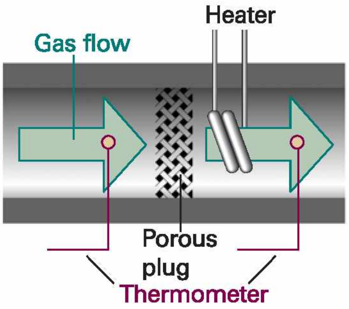

Fig. 2.30 A schematic diagram of the apparatus used for measuring the isothermal Joule–Thomson coefficient. The electrical heating required to offset the cooling arising from expansion is interpreted as ΔH and used to calculate $(\partial H/\partial p)_T$, which is then converted to μ as explained in the text.

$\Delta H = q_p$), and the pressure change Δp is known, we can find μ_T from the limiting value of $\Delta H/\Delta p$ as $\Delta p \to 0$, and then convert it to μ. Table 2.9 lists some values obtained in this way.

Real gases have nonzero Joule–Thomson coefficients. Depending on the identity of the gas, the pressure, the relative magnitudes of the attractive and repulsive intermolecular forces (see *Molecular interpretation 2.1*), and the temperature, the sign of the coefficient may be either positive or negative (Fig. 2.31). A positive sign implies that dT is negative when dp is negative, in which case the gas cools on expansion. Gases that show a heating effect ($\mu < 0$) at one temperature show a cooling effect ($\mu > 0$) when the temperature is below their upper **inversion temperature**, T_I (Table 2.9, Fig. 2.32). As indicated in Fig. 2.32, a gas typically has two inversion temperatures, one at high temperature and the other at low.

The 'Linde refrigerator' makes use of Joule–Thompson expansion to liquefy gases (Fig. 2.33). The gas at high pressure is allowed to expand through a throttle; it cools and is circulated past the incoming gas. That gas is cooled, and its subsequent expansion cools it still further. There comes a stage when the circulating gas becomes so cold that it condenses to a liquid.

For a perfect gas, $\mu = 0$; hence, the temperature of a perfect gas is unchanged by Joule–Thomson expansion.[8] This characteristic points clearly to the involvement of intermolecular forces in determining the size of the effect. However, the Joule–Thomson coefficient of a real gas does not necessarily approach zero as the pressure is reduced even though the equation of state of the gas approaches that of a perfect gas. The coefficient behaves like the properties discussed in Section 1.3b in the sense that it depends on derivatives and not on p, V, and T themselves.

Synoptic Table 2.9* Inversion temperatures (T_I), normal freezing (T_f) and boiling (T_b) points, and Joule–Thomson coefficient (μ) at 1 atm and 298 K

	T_I/K	T_f/K	T_b/K	μ/(K bar^{-1})
Ar	723	83.8	87.3	
CO_2	1500		194.7	+1.10
He	40		4.2	−0.060
N_2	621	63.3	77.4	+0.25

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

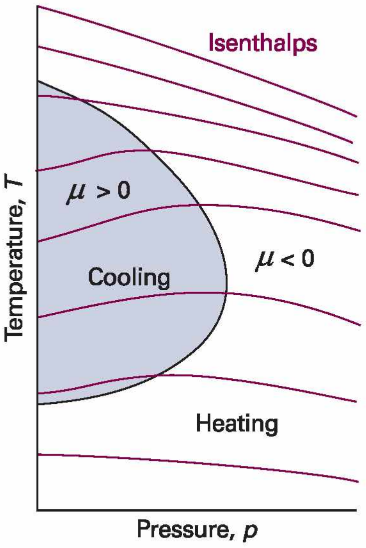

Fig. 2.31 The sign of the Joule–Thomson coefficient, μ, depends on the conditions. Inside the boundary, the shaded area, it is positive and outside it is negative. The temperature corresponding to the boundary at a given pressure is the 'inversion temperature' of the gas at that pressure. For a given pressure, the temperature must be below a certain value if cooling is required but, if it becomes too low, the boundary is crossed again and heating occurs. Reduction of pressure under adiabatic conditions moves the system along one of the isenthalps, or curves of constant enthalpy. The inversion temperature curve runs through the points of the isenthalps where their slope changes from negative to positive.

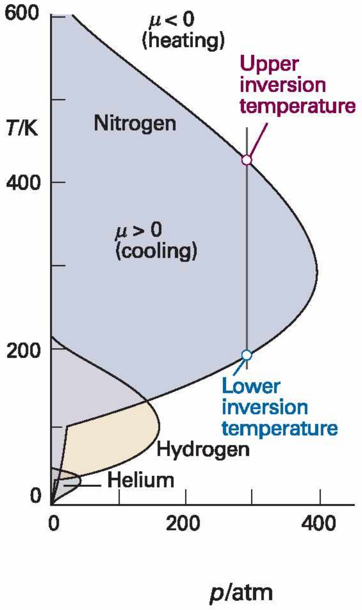

Fig. 2.32 The inversion temperatures for three real gases, nitrogen, hydrogen, and helium.

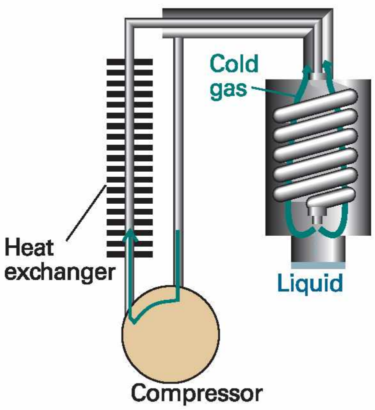

Fig. 2.33 The principle of the Linde refrigerator is shown in this diagram. The gas is recirculated, and so long as it is beneath its inversion temperature it cools on expansion through the throttle. The cooled gas cools the high-pressure gas, which cools still further as it expands. Eventually liquefied gas drips from the throttle.

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[8] Simple adiabatic expansion does cool a perfect gas, because the gas does work; recall Section 2.6.

Molecular interpretation 2.3 *Molecular interactions and the Joule–Thomson effect*

The kinetic model of gases (*Molecular interpretation 1.1*) and the equipartition theorem (*Molecular interpretation 2.2*) imply that the mean kinetic energy of molecules in a gas is proportional to the temperature. It follows that reducing the average speed of the molecules is equivalent to cooling the gas. If the speed of the molecules can be reduced to the point that neighbours can capture each other by their intermolecular attractions, then the cooled gas will condense to a liquid.

To slow the gas molecules, we make use of an effect similar to that seen when a ball is thrown into the air: as it rises it slows in response to the gravitational attraction of the Earth and its kinetic energy is converted into potential energy. We saw in Section 1.3 that molecules in a real gas attract each other (the attraction is not gravitational, but the effect is the same). It follows that, if we can cause the molecules to move apart from each other, like a ball rising from a planet, then they should slow. It is very easy to move molecules apart from each other: we simply allow the gas to expand, which increases the average separation of the molecules. To cool a gas, therefore, we allow it to expand without allowing any energy to enter from outside as heat. As the gas expands, the molecules move apart to fill the available volume, struggling as they do so against the attraction of their neighbours. Because some kinetic energy must be converted into potential energy to reach greater separations, the molecules travel more slowly as their separation increases. This sequence of molecular events explains the Joule–Thomson effect: the cooling of a real gas by adiabatic expansion. The cooling effect, which corresponds to $\mu > 0$, is observed under conditions when attractive interactions are dominant ($Z < 1$, eqn 1.17), because the molecules have to climb apart against the attractive force in order for them to travel more slowly. For molecules under conditions when repulsions are dominant ($Z > 1$), the Joule–Thomson effect results in the gas becoming warmer, or $\mu < 0$.

Checklist of key ideas

☐ 1. Thermodynamics is the study of the transformations of energy.

☐ 2. The system is the part of the world in which we have a special interest. The surroundings is the region outside the system where we make our measurements.

☐ 3. An open system has a boundary through which matter can be transferred. A closed system has a boundary through which matter cannot be transferred. An isolated system has a boundary through which neither matter nor energy can be transferred.

☐ 4. Energy is the capacity to do work. The internal energy is the total energy of a system.

☐ 5. Work is the transfer of energy by motion against an opposing force, $dw = -Fdz$. Heat is the transfer of energy as a result of a temperature difference between the system and the surroundings.

☐ 6. An exothermic process releases energy as heat to the surroundings. An endothermic process absorbs energy as heat from the surroundings.

☐ 7. A state function is a property that depends only on the current state of the system and is independent of how that state has been prepared.

☐ 8. The First Law of thermodynamics states that the internal energy of an isolated system is constant, $\Delta U = q + w$.

☐ 9. Expansion work is the work of expansion (or compression) of a system, $dw = -p_{ex}dV$. The work of free expansion is $w = 0$. The work of expansion against a constant external pressure is $w = -p_{ex}\Delta V$. The work of isothermal reversible expansion of a perfect gas is $w = -nRT\ln(V_f/V_i)$.

☐ 10. A reversible change is a change that can be reversed by an infinitesimal modification of a variable.

☐ 11. Maximum work is achieved in a reversible change.

☐ 12. Calorimetry is the study of heat transfers during physical and chemical processes.

☐ 13. The heat capacity at constant volume is defined as $C_V = (\partial U/\partial T)_V$. The heat capacity at constant pressure is $C_p = (\partial H/\partial T)_p$. For a perfect gas, the heat capacities are related by $C_p - C_V = nR$.

☐ 14. The enthalpy is defined as $H = U + pV$. The enthalpy change is the energy transferred as heat at constant pressure, $\Delta H = q_p$.

☐ 15. During a reversible adiabatic change, the temperature of a perfect gas varies according to $T_f = T_i(V_i/V_f)^{1/c}$, $c = C_{V,m}/R$. The pressure and volume are related by $pV^\gamma =$ constant, with $\gamma = C_{p,m}/C_{V,m}$.

☐ 16. The standard enthalpy change is the change in enthalpy for a process in which the initial and final substances are in their standard states. The standard state is the pure substance at 1 bar.

☐ 17. Enthalpy changes are additive, as in $\Delta_{sub}H^{\ominus} = \Delta_{fus}H^{\ominus} + \Delta_{vap}H^{\ominus}$.

☐ 18. The enthalpy change for a process and its reverse are related by $\Delta_{forward}H^{\ominus} = -\Delta_{reverse}H^{\ominus}$.

☐ 19. The standard enthalpy of combustion is the standard reaction enthalpy for the complete oxidation of an organic compound to CO_2 gas and liquid H_2O if the compound contains C, H, and O, and to N_2 gas if N is also present.

☐ 20. Hess's law states that the standard enthalpy of an overall reaction is the sum of the standard enthalpies of the individual reactions into which a reaction may be divided.

☐ 21. The standard enthalpy of formation ($\Delta_f H^{\ominus}$) is the standard reaction enthalpy for the formation of the compound from its elements in their reference states. The reference state is the most stable state of an element at the specified temperature and 1 bar.

☐ 22. The standard reaction enthalpy may be estimated by combining enthalpies of formation, $\Delta_r H^{\ominus} = \sum_{Products} \nu\Delta_f H^{\ominus} - \sum_{Reactants} \nu\Delta_f H^{\ominus}$.

☐ 23. The temperature dependence of the reaction enthalpy is given by Kirchhoff's law, $\Delta_r H^{\ominus}(T_2) = \Delta_r H^{\ominus}(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^{\ominus} dT$.

☐ 24. An exact differential is an infinitesimal quantity that, when integrated, gives a result that is independent of the path between the initial and final states. An inexact differential is an infinitesimal quantity that, when integrated, gives a result that depends on the path between the initial and final states.

☐ 25. The internal pressure is defined as $\pi_T = (\partial U/\partial V)_T$. For a perfect gas, $\pi_T = 0$.

☐ 26. The Joule–Thomson effect is the cooling of a gas by isenthalpic expansion.

☐ 27. The Joule–Thomson coefficient is defined as $\mu = (\partial T/\partial p)_H$. The isothermal Joule–Thomson coefficient is defined as $\mu_T = (\partial H/\partial p)_T = -C_p\mu$.

☐ 28. The inversion temperature is the temperature at which the Joule–Thomson coefficient changes sign.

Further reading

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Further information

Further information 2.1 *Adiabatic processes*

Consider a stage in a reversible adiabatic expansion when the pressure inside and out is p. The work done when the gas expands by $\mathrm{d}V$ is $\mathrm{d}w = -p\mathrm{d}V$; however, for a perfect gas, $\mathrm{d}U = C_V\mathrm{d}T$.

Therefore, because for an adiabatic change ($\mathrm{d}q = 0$) $\mathrm{d}U = \mathrm{d}w + \mathrm{d}q = \mathrm{d}w$, we can equate these two expressions for $\mathrm{d}U$ and write

$$C_V\mathrm{d}T = -p\mathrm{d}V$$

We are dealing with a perfect gas, so we can replace p by nRT/V and obtain

$$\frac{C_V\mathrm{d}T}{T} = -\frac{nR\mathrm{d}V}{V}$$

To integrate this expression we note that T is equal to T_i when V is equal to V_i, and is equal to T_f when V is equal to V_f at the end of the expansion. Therefore,

$$C_V\int_{T_\mathrm{i}}^{T_\mathrm{f}}\frac{\mathrm{d}T}{T} = -nR\int_{V_\mathrm{i}}^{V_\mathrm{f}}\frac{\mathrm{d}V}{V}$$

(We are taking C_V to be independent of temperature.) Then, because $\int\mathrm{d}x/x = \ln x + \text{constant}$, we obtain

$$C_V\ln\frac{T_\mathrm{f}}{T_\mathrm{i}} = -nR\ln\frac{V_\mathrm{f}}{V_\mathrm{i}}$$

Because $\ln(x/y) = -\ln(y/x)$, this expression rearranges to

$$\frac{C_V}{nR}\ln\frac{T_\mathrm{f}}{T_\mathrm{i}} = \ln\frac{V_\mathrm{i}}{V_\mathrm{f}}$$

With $c = C_V/nR$ we obtain (because $\ln x^a = a\ln x$)

$$\ln\left(\frac{T_\mathrm{f}}{T_\mathrm{i}}\right)^c = \ln\left(\frac{V_\mathrm{i}}{V_\mathrm{f}}\right)$$

which implies that $(T_\mathrm{f}/T_\mathrm{i})^c = (V_\mathrm{i}/V_\mathrm{f})$ and, upon rearrangement, eqn 2.28.

The initial and final states of a perfect gas satisfy the perfect gas law regardless of how the change of state takes place, so we can use $pV = nRT$ to write

$$\frac{p_\mathrm{i}V_\mathrm{i}}{p_\mathrm{f}V_\mathrm{f}} = \frac{T_\mathrm{i}}{T_\mathrm{f}}$$

However, we have just shown that

$$\frac{T_\mathrm{i}}{T_\mathrm{f}} = \left(\frac{V_\mathrm{f}}{V_\mathrm{i}}\right)^{1/c} = \left(\frac{V_\mathrm{f}}{V_\mathrm{i}}\right)^{\gamma-1}$$

where we use the definition of the heat capacity ratio where $\gamma = C_{p,\mathrm{m}}/C_{V,\mathrm{m}}$ and the fact that, for a perfect gas, $C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = R$ (the molar version of eqn 2.26). Then we combine the two expressions, to obtain

$$\frac{p_\mathrm{i}}{p_\mathrm{f}} = \frac{V_\mathrm{f}}{V_\mathrm{i}}\times\left(\frac{V_\mathrm{f}}{V_\mathrm{i}}\right)^{\gamma-1} = \left(\frac{V_\mathrm{f}}{V_\mathrm{i}}\right)^{\gamma}$$

which rearranges to $p_\mathrm{i}V_\mathrm{i}^\gamma = p_\mathrm{f}V_\mathrm{f}^\gamma$, which is eqn 2.29.

Further information 2.2 *The relation between heat capacities*

A useful rule when doing a problem in thermodynamics is to go back to first principles. In the present problem we do this twice, first by expressing C_p and C_V in terms of their definitions and then by inserting the definition $H = U + pV$:

$$\begin{aligned}C_p - C_V &= \left(\frac{\partial H}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V\\ &= \left(\frac{\partial U}{\partial T}\right)_p + \left(\frac{\partial(pV)}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V\end{aligned}$$

We have already calculated the difference of the first and third terms on the right, and eqn 2.45 lets us write this difference as $\alpha\pi_TV$. The factor αV gives the change in volume when the temperature is raised, and $\pi_T = (\partial U/\partial V)_T$ converts this change in volume into a change in internal energy. We can simplify the remaining term by noting that, because p is constant,

$$\left(\frac{\partial(pV)}{\partial T}\right)_p = p\left(\frac{\partial V}{\partial T}\right)_p = \alpha pV$$

The middle term of this expression identifies it as the contribution to the work of pushing back the atmosphere: $(\partial V/\partial T)_p$ is the change of volume caused by a change of temperature, and multiplication by p converts this expansion into work.

Collecting the two contributions gives

$$C_p - C_V = \alpha(p + \pi_T)V \tag{2.56}$$

As just remarked, the first term on the right, αpV, is a measure of the work needed to push back the atmosphere; the second term on the right, $\alpha\pi_TV$, is the work required to separate the molecules composing the system.

At this point we can go further by using the result we prove in Section 3.8 that

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

When this expression is inserted in the last equation we obtain

$$C_p - C_V = \alpha TV\left(\frac{\partial p}{\partial T}\right)_V \tag{2.57}$$

We now transform the remaining partial derivative. It follows from Euler's chain relation that

$$\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_p\left(\frac{\partial V}{\partial p}\right)_T = -1$$

Comment 2.8

The Euler chain relation states that, for a differentiable function $z = z(x,y)$,

$$\left(\frac{\partial y}{\partial x}\right)_z\left(\frac{\partial x}{\partial z}\right)_y\left(\frac{\partial z}{\partial y}\right)_x = -1$$

For instance, if $z(x,y) = x^2y$,

$$\left(\frac{\partial y}{\partial x}\right)_z = \left(\frac{\partial(z/x^2)}{\partial x}\right)_z = z\frac{\mathrm{d}(1/x^2)}{\mathrm{d}x} = -\frac{2z}{x^3}$$

$$\left(\frac{\partial x}{\partial z}\right)_y = \left(\frac{\partial(z/y)^{1/2}}{\partial z}\right)_y = \frac{1}{y^{1/2}}\frac{\mathrm{d}z^{1/2}}{\mathrm{d}z} = \frac{1}{2(yz)^{1/2}}$$

$$\left(\frac{\partial z}{\partial y}\right)_x = \left(\frac{\partial(x^2 y)}{\partial y}\right)_x = x^2\frac{\mathrm{d}y}{\mathrm{d}y} = x^2$$

Multiplication of the three terms together gives the result -1.

and therefore that

$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{1}{(\partial T/\partial V)_p(\partial V/\partial p)_T}$$

Unfortunately, $(\partial T/\partial V)_p$ occurs instead of $(\partial V/\partial T)_p$. However, the 'reciprocal identity' allows us to invert partial derivatives and to write

$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{(\partial V/\partial T)_p}{(\partial V/\partial p)_T} = \frac{\alpha}{\kappa_T}$$

Comment 2.9

The reciprocal identity states that

$$\left(\frac{\partial y}{\partial x}\right)_z = \frac{1}{(\partial x/\partial y)_z}$$

For example, for the function $z(x,y) = x^2 y$,

$$\left(\frac{\partial y}{\partial x}\right)_z = \left(\frac{\partial(z/x^2)}{\partial x}\right)_z = z\frac{\mathrm{d}(1/x^2)}{\mathrm{d}x} = -\frac{2z}{x^3}$$

We can also write $x = (z/y)^{1/2}$, in which case

$$\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial(z/y)^{1/2}}{\partial y}\right)_z = z^{1/2}\frac{\mathrm{d}(1/y^{1/2})}{\mathrm{d}y}$$

$$= -\frac{z^{1/2}}{2y^{3/2}} = -\frac{z^{1/2}}{2(z/x^2)^{3/2}} = -\frac{x^3}{2z}$$

which is the reciprocal of the coefficient derived above.

Insertion of this relation into eqn 2.57 produces eqn 2.49.

Discussion questions

2.1 Provide mechanical and molecular definitions of work and heat.

2.2 Consider the reversible expansion of a perfect gas. Provide a physical interpretation for the fact that pV^γ = constant for an adiabatic change, whereas pV = constant for an isothermal change.

2.3 Explain the difference between the change in internal energy and the change in enthalpy accompanying a chemical or physical process.

2.4 Explain the significance of a physical observable being a state function and compile a list of as many state functions as you can identify.

2.5 Explain the significance of the Joule and Joule–Thomson experiments. What would Joule observe in a more sensitive apparatus?

2.6 Suggest (with explanation) how the internal energy of a van der Waals gas should vary with volume at constant temperature.

2.7 In many experimental thermograms, such as that shown in Fig. 2.16, the baseline below T_1 is at a different level from that above T_2. Explain this observation.

Exercises

Assume all gases are perfect unless stated otherwise. Unless otherwise stated, thermochemical data are for 298.15 K.

2.1(a) Calculate the work needed for a 65 kg person to climb through 4.0 m on the surface of (a) the Earth and (b) the Moon (g = 1.60 m s^{-2}).

2.1(b) Calculate the work needed for a bird of mass 120 g to fly to a height of 50 m from the surface of the Earth.

2.2(a) A chemical reaction takes place in a container of cross-sectional area 100 cm^2. As a result of the reaction, a piston is pushed out through 10 cm against an external pressure of 1.0 atm. Calculate the work done by the system.

2.2(b) A chemical reaction takes place in a container of cross-sectional area 50.0 cm^2. As a result of the reaction, a piston is pushed out through 15 cm against an external pressure of 121 kPa. Calculate the work done by the system.

2.3(a) A sample consisting of 1.00 mol Ar is expanded isothermally at 0°C from 22.4 dm^3 to 44.8 dm^3 (a) reversibly, (b) against a constant external pressure equal to the final pressure of the gas, and (c) freely (against zero external pressure). For the three processes calculate q, w, ΔU, and ΔH.

2.3(b) A sample consisting of 2.00 mol He is expanded isothermally at 22°C from 22.8 dm^3 to 31.7 dm^3 (a) reversibly, (b) against a constant external pressure equal to the final pressure of the gas, and (c) freely (against zero external pressure). For the three processes calculate q, w, ΔU, and ΔH.

2.4(a) A sample consisting of 1.00 mol of perfect gas atoms, for which $C_{V,\mathrm{m}} = \frac{3}{2}R$, initially at p_1 = 1.00 atm and T_1 = 300 K, is heated reversibly to 400 K at constant volume. Calculate the final pressure, ΔU, q, and w.

2.4(b) A sample consisting of 2.00 mol of perfect gas molecules, for which $C_{V,\mathrm{m}} = \frac{5}{2}R$, initially at p_1 = 111 kPa and T_1 = 277 K, is heated reversibly to 356 K at constant volume. Calculate the final pressure, ΔU, q, and w.

2.5(a) A sample of 4.50 g of methane occupies 12.7 dm^3 at 310 K. (a) Calculate the work done when the gas expands isothermally against a constant external pressure of 200 Torr until its volume has increased by 3.3 dm^3. (b) Calculate the work that would be done if the same expansion occurred reversibly.

2.5(b) A sample of argon of mass 6.56 g occupies 18.5 dm^3 at 305 K. (a) Calculate the work done when the gas expands isothermally against a constant external pressure of 7.7 kPa until its volume has increased by 2.5 dm^3. (b) Calculate the work that would be done if the same expansion occurred reversibly.

2.6(a) A sample of 1.00 mol $H_2O(g)$ is condensed isothermally and reversibly to liquid water at 100°C. The standard enthalpy of vaporization of water at 100°C is 40.656 kJ mol^{-1}. Find w, q, ΔU, and ΔH for this process.

2.6(b) A sample of 2.00 mol $CH_3OH(g)$ is condensed isothermally and reversibly to liquid at 64°C. The standard enthalpy of vaporization of methanol at 64°C is 35.3 kJ mol^{-1}. Find w, q, ΔU, and ΔH for this process.

2.7(a) A strip of magnesium of mass 15 g is dropped into a beaker of dilute hydrochloric acid. Calculate the work done by the system as a result of the reaction. The atmospheric pressure is 1.0 atm and the temperature 25°C.

2.7(b) A piece of zinc of mass 5.0 g is dropped into a beaker of dilute hydrochloric acid. Calculate the work done by the system as a result of the reaction. The atmospheric pressure is 1.1 atm and the temperature 23°C.

2.8(a) The constant-pressure heat capacity of a sample of a perfect gas was found to vary with temperature according to the expression $C_p/(\mathrm{J\,K^{-1}}) = 20.17 + 0.3665(T/\mathrm{K})$. Calculate q, w, ΔU, and ΔH when the temperature is raised from 25°C to 200°C (a) at constant pressure, (b) at constant volume.

2.8(b) The constant-pressure heat capacity of a sample of a perfect gas was found to vary with temperature according to the expression $C_p/(\mathrm{J\,K^{-1}}) = 20.17 + 0.4001(T/\mathrm{K})$. Calculate q, w, ΔU, and ΔH when the temperature is raised from 0°C to 100°C (a) at constant pressure, (b) at constant volume.

2.9(a) Calculate the final temperature of a sample of argon of mass 12.0 g that is expanded reversibly and adiabatically from 1.0 dm^3 at 273.15 K to 3.0 dm^3.

2.9(b) Calculate the final temperature of a sample of carbon dioxide of mass 16.0 g that is expanded reversibly and adiabatically from 500 cm^3 at 298.15 K to 2.00 dm^3.

2.10(a) A sample of carbon dioxide of mass 2.45 g at 27.0°C is allowed to expand reversibly and adiabatically from 500 cm^3 to 3.00 dm^3. What is the work done by the gas?

2.10(b) A sample of nitrogen of mass 3.12 g at 23.0°C is allowed to expand reversibly and adiabatically from 400 cm^3 to 2.00 dm^3. What is the work done by the gas?

2.11(a) Calculate the final pressure of a sample of carbon dioxide that expands reversibly and adiabatically from 57.4 kPa and 1.0 dm^3 to a final volume of 2.0 dm^3. Take $\gamma = 1.4$.

2.11(b) Calculate the final pressure of a sample of water vapour that expands reversibly and adiabatically from 87.3 Torr and 500 cm^3 to a final volume of 3.0 dm^3. Take $\gamma = 1.3$.

2.12(a) When 229 J of energy is supplied as heat to 3.0 mol Ar(g), the temperature of the sample increases by 2.55 K. Calculate the molar heat capacities at constant volume and constant pressure of the gas.

2.12(b) When 178 J of energy is supplied as heat to 1.9 mol of gas molecules, the temperature of the sample increases by 1.78 K. Calculate the molar heat capacities at constant volume and constant pressure of the gas.

2.13(a) When 3.0 mol O_2 is heated at a constant pressure of 3.25 atm, its temperature increases from 260 K to 285 K. Given that the molar heat capacity of O_2 at constant pressure is 29.4 J K^{-1} mol^{-1}, calculate q, ΔH, and ΔU.

2.13(b) When 2.0 mol CO_2 is heated at a constant pressure of 1.25 atm, its temperature increases from 250 K to 277 K. Given that the molar heat capacity of CO_2 at constant pressure is 37.11 J K^{-1} mol^{-1}, calculate q, ΔH, and ΔU.

2.14(a) A sample of 4.0 mol O_2 is originally confined in 20 dm^3 at 270 K and then undergoes adiabatic expansion against a constant pressure of 600 Torr until the volume has increased by a factor of 3.0. Calculate q, w, ΔT, ΔU, and ΔH. (The final pressure of the gas is not necessarily 600 Torr.)

2.14(b) A sample of 5.0 mol CO_2 is originally confined in 15 dm^3 at 280 K and then undergoes adiabatic expansion against a constant pressure of 78.5 kPa until the volume has increased by a factor of 4.0. Calculate q, w, ΔT, ΔU, and ΔH. (The final pressure of the gas is not necessarily 78.5 kPa.)

2.15(a) A sample consisting of 1.0 mol of perfect gas molecules with $C_V = 20.8$ J K^{-1} is initially at 3.25 atm and 310 K. It undergoes reversible adiabatic expansion until its pressure reaches 2.50 atm. Calculate the final volume and temperature and the work done.

2.15(b) A sample consisting of 1.5 mol of perfect gas molecules with $C_{p,\mathrm{m}} = 20.8$ J K^{-1} mol^{-1} is initially at 230 kPa and 315 K. It undergoes reversible adiabatic expansion until its pressure reaches 170 kPa. Calculate the final volume and temperature and the work done.

2.16(a) A certain liquid has $\Delta_{\mathrm{vap}}H^\ominus = 26.0$ kJ mol^{-1}. Calculate q, w, ΔH, and ΔU when 0.50 mol is vaporized at 250 K and 750 Torr.

2.16(b) A certain liquid has $\Delta_{\mathrm{vap}}H^\ominus = 32.0$ kJ mol^{-1}. Calculate q, w, ΔH, and ΔU when 0.75 mol is vaporized at 260 K and 765 Torr.

2.17(a) The standard enthalpy of formation of ethylbenzene is −12.5 kJ mol^{-1}. Calculate its standard enthalpy of combustion.

2.17(b) The standard enthalpy of formation of phenol is −165.0 kJ mol^{-1}. Calculate its standard enthalpy of combustion.

2.18(a) The standard enthalpy of combustion of cyclopropane is −2091 kJ mol^{-1} at 25°C. From this information and enthalpy of formation data for $CO_2(g)$ and $H_2O(g)$, calculate the enthalpy of formation of cyclopropane. The enthalpy of formation of propene is +20.42 kJ mol^{-1}. Calculate the enthalpy of isomerization of cyclopropane to propene.

2.18(b) From the following data, determine $\Delta_f H^\ominus$ for diborane, $B_2H_6(g)$, at 298 K:

(1) $B_2H_6(g) + 3\,O_2(g) \rightarrow B_2O_3(s) + 3\,H_2O(g)$ $\Delta_r H^\ominus = -1941$ kJ mol^{-1}
(2) $2\,B(s) + \frac{3}{2}\,O_2(g) \rightarrow B_2O_3(s)$ $\Delta_r H^\ominus = -2368$ kJ mol^{-1}
(3) $H_2(g) + \frac{1}{2}\,O_2(g) \rightarrow H_2O(g)$ $\Delta_r H^\ominus = -241.8$ kJ mol^{-1}

2.19(a) When 120 mg of naphthalene, $C_{10}H_8(s)$, was burned in a bomb calorimeter the temperature rose by 3.05 K. Calculate the calorimeter constant. By how much will the temperature rise when 10 mg of phenol, $C_6H_5OH(s)$, is burned in the calorimeter under the same conditions?

2.19(b) When 2.25 mg of anthracene, $C_{14}H_{10}(s)$, was burned in a bomb calorimeter the temperature rose by 1.35 K. Calculate the calorimeter constant. By how much will the temperature rise when 135 mg of phenol, $C_6H_5OH(s)$, is burned in the calorimeter under the same conditions? ($\Delta_c H^\ominus(C_{14}H_{10}, s) = -7061$ kJ mol^{-1}.)

2.20(a) Calculate the standard enthalpy of solution of AgCl(s) in water from the enthalpies of formation of the solid and the aqueous ions.

2.20(b) Calculate the standard enthalpy of solution of AgBr(s) in water from the enthalpies of formation of the solid and the aqueous ions.

2.21(a) The standard enthalpy of decomposition of the yellow complex H_3NSO_2 into NH_3 and SO_2 is +40 kJ mol^{-1}. Calculate the standard enthalpy of formation of H_3NSO_2.

2.21(b) Given that the standard enthalpy of combustion of graphite is −393.51 kJ mol^{-1} and that of diamond is −395.41 kJ mol^{-1}, calculate the enthalpy of the graphite-to-diamond transition.

2.22(a) Given the reactions (1) and (2) below, determine (a) $\Delta_r H^\ominus$ and $\Delta_r U^\ominus$ for reaction (3), (b) $\Delta_f H^\ominus$ for both HCl(g) and $H_2O(g)$ all at 298 K.

(1) $H_2(g) + Cl_2(g) \rightarrow 2\,HCl(g)$ $\Delta_r H^\ominus = -184.62$ kJ mol^{-1}
(2) $2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(g)$ $\Delta_r H^\ominus = -483.64$ kJ mol^{-1}
(3) $4\,HCl(g) + O_2(g) \rightarrow Cl_2(g) + 2\,H_2O(g)$

2.22(b) Given the reactions (1) and (2) below, determine (a) $\Delta_r H^\ominus$ and $\Delta_r U^\ominus$ for reaction (3), (b) $\Delta_f H^\ominus$ for both HCl(g) and H_2O(g) all at 298 K.

(1) $H_2(g) + I_2(s) \rightarrow 2\,HI(g)$ $\Delta_r H^\ominus = +52.96\ \text{kJ mol}^{-1}$
(2) $2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(g)$ $\Delta_r H^\ominus = -483.64\ \text{kJ mol}^{-1}$
(3) $4\,HI(g) + O_2(g) \rightarrow 2\,I_2(s) + 2\,H_2O(g)$

2.23(a) For the reaction $C_2H_5OH(l) + 3\,O_2(g) \rightarrow 2\,CO_2(g) + 3\,H_2O(g)$, $\Delta_r U^\ominus = -1373\ \text{kJ mol}^{-1}$ at 298 K. Calculate $\Delta_r H^\ominus$.

2.23(b) For the reaction $2\,C_6H_5COOH(s) + 13\,O_2(g) \rightarrow 12\,CO_2(g) + 6\,H_2O(g)$, $\Delta_r U^\ominus = -772.7\ \text{kJ mol}^{-1}$ at 298 K. Calculate $\Delta_r H^\ominus$.

2.24(a) Calculate the standard enthalpies of formation of (a) $KClO_3(s)$ from the enthalpy of formation of KCl, (b) $NaHCO_3(s)$ from the enthalpies of formation of CO_2 and NaOH together with the following information:

$2\,KClO_3(s) \rightarrow 2\,KCl(s) + 3\,O_2(g)$ $\Delta_r H^\ominus = -89.4\ \text{kJ mol}^{-1}$
$NaOH(s) + CO_2(g) \rightarrow NaHCO_3(s)$ $\Delta_r H^\ominus = -127.5\ \text{kJ mol}^{-1}$

2.24(b) Calculate the standard enthalpy of formation of NOCl(g) from the enthalpy of formation of NO given in Table 2.5, together with the following information:

$2\,NOCl(g) \rightarrow 2\,NO(g) + Cl_2(g)$ $\Delta_r H^\ominus = +75.5\ \text{kJ mol}^{-1}$

2.25(a) Use the information in Table 2.5 to predict the standard reaction enthalpy of $2\,NO_2(g) \rightarrow N_2O_4(g)$ at 100°C from its value at 25°C.

2.25(b) Use the information in Table 2.5 to predict the standard reaction enthalpy of $2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(l)$ at 100°C from its value at 25°C.

2.26(a) From the data in Table 2.5, calculate $\Delta_r H^\ominus$ and $\Delta_r U^\ominus$ at (a) 298 K, (b) 378 K for the reaction $C(\text{graphite}) + H_2O(g) \rightarrow CO(g) + H_2(g)$. Assume all heat capacities to be constant over the temperature range of interest.

2.26(b) Calculate $\Delta_r H^\ominus$ and $\Delta_r U^\ominus$ at 298 K and $\Delta_r H^\ominus$ at 348 K for the hydrogenation of ethyne (acetylene) to ethene (ethylene) from the enthalpy of combustion and heat capacity data in Tables 2.5 and 2.7. Assume the heat capacities to be constant over the temperature range involved.

2.27(a) Calculate $\Delta_r H^\ominus$ for the reaction $Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$ from the information in Table 2.7 in the *Data section*.

2.27(b) Calculate $\Delta_r H^\ominus$ for the reaction $NaCl(aq) + AgNO_3(aq) \rightarrow AgCl(s) + NaNO_3(aq)$ from the information in Table 2.7 in the *Data section*.

2.28(a) Set up a thermodynamic cycle for determining the enthalpy of hydration of Mg^{2+} ions using the following data: enthalpy of sublimation of Mg(s), $+167.2\ \text{kJ mol}^{-1}$; first and second ionization enthalpies of Mg(g), 7.646 eV and 15.035 eV; dissociation enthalpy of $Cl_2(g)$, $+241.6\ \text{kJ mol}^{-1}$; electron gain enthalpy of Cl(g), −3.78 eV; enthalpy of solution of $MgCl_2(s)$, $-150.5\ \text{kJ mol}^{-1}$; enthalpy of hydration of $Cl^-(g)$, $-383.7\ \text{kJ mol}^{-1}$.

2.28(b) Set up a thermodynamic cycle for determining the enthalpy of hydration of Ca^{2+} ions using the following data: enthalpy of sublimation of Ca(s), $+178.2\ \text{kJ mol}^{-1}$; first and second ionization enthalpies of Ca(g), $589.7\ \text{kJ mol}^{-1}$ and $1145\ \text{kJ mol}^{-1}$; enthalpy of vaporization of bromine, $+30.91\ \text{kJ mol}^{-1}$; dissociation enthalpy of $Br_2(g)$, $+192.9\ \text{kJ mol}^{-1}$; electron gain enthalpy of Br(g), $-331.0\ \text{kJ mol}^{-1}$; enthalpy of solution of $CaBr_2(s)$, $-103.1\ \text{kJ mol}^{-1}$; enthalpy of hydration of $Br^-(g)$, $-337\ \text{kJ mol}^{-1}$.

2.29(a) When a certain freon used in refrigeration was expanded adiabatically from an initial pressure of 32 atm and 0°C to a final pressure of 1.00 atm, the temperature fell by 22 K. Calculate the Joule–Thomson coefficient, μ, at 0°C, assuming it remains constant over this temperature range.

2.29(b) A vapour at 22 atm and 5°C was allowed to expand adiabatically to a final pressure of 1.00 atm; the temperature fell by 10 K. Calculate the Joule–Thomson coefficient, μ, at 5°C, assuming it remains constant over this temperature range.

2.30(a) For a van der Waals gas, $\pi_T = a/V_m^2$. Calculate ΔU_m for the isothermal expansion of nitrogen gas from an initial volume of $1.00\ \text{dm}^3$ to $24.8\ \text{dm}^3$ at 298 K. What are the values of q and w?

2.30(b) Repeat Exercise 2.30(a) for argon, from an initial volume of $1.00\ \text{dm}^3$ to $22.1\ \text{dm}^3$ at 298 K.

2.31(a) The volume of a certain liquid varies with temperature as

$$V = V'\{0.75 + 3.9 \times 10^{-4}(T/\text{K}) + 1.48 \times 10^{-6}(T/\text{K})^2\}$$

where V' is its volume at 300 K. Calculate its expansion coefficient, α, at 320 K.

2.31(b) The volume of a certain liquid varies with temperature as

$$V = V'\{0.77 + 3.7 \times 10^{-4}(T/\text{K}) + 1.52 \times 10^{-6}(T/\text{K})^2\}$$

where V' is its volume at 298 K. Calculate its expansion coefficient, α, at 310 K.

2.32(a) The isothermal compressibility of copper at 293 K is $7.35 \times 10^{-7}\ \text{atm}^{-1}$. Calculate the pressure that must be applied in order to increase its density by 0.08 per cent.

2.32(b) The isothermal compressibility of lead at 293 K is $2.21 \times 10^{-6}\ \text{atm}^{-1}$. Calculate the pressure that must be applied in order to increase its density by 0.08 per cent.

2.33(a) Given that $\mu = 0.25\ \text{K atm}^{-1}$ for nitrogen, calculate the value of its isothermal Joule–Thomson coefficient. Calculate the energy that must be supplied as heat to maintain constant temperature when 15.0 mol N_2 flows through a throttle in an isothermal Joule–Thomson experiment and the pressure drop is 75 atm.

2.33(b) Given that $\mu = 1.11\ \text{K atm}^{-1}$ for carbon dioxide, calculate the value of its isothermal Joule–Thomson coefficient. Calculate the energy that must be supplied as heat to maintain constant temperature when 12.0 mol CO_2 flows through a throttle in an isothermal Joule–Thomson experiment and the pressure drop is 55 atm.

Problems*

Assume all gases are perfect unless stated otherwise. Note that 1 atm = 1.013 25 bar. Unless otherwise stated, thermochemical data are for 298.15 K.

Numerical problems

2.1 A sample consisting of 1 mol of perfect gas atoms (for which $C_{V,\mathrm{m}} = \frac{3}{2}R$) is taken through the cycle shown in Fig. 2.34. (a) Determine the temperature at the points 1, 2, and 3. (b) Calculate q, w, ΔU, and ΔH for each step and for the overall cycle. If a numerical answer cannot be obtained from the information given, then write in +, –, 0, or ? as appropriate.

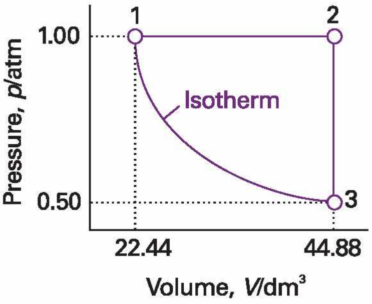

Fig. 2.34

2.2 A sample consisting of 1.0 mol $CaCO_3(s)$ was heated to 800°C, when it decomposed. The heating was carried out in a container fitted with a piston that was initially resting on the solid. Calculate the work done during complete decomposition at 1.0 atm. What work would be done if instead of having a piston the container was open to the atmosphere?

2.3 A sample consisting of 2.0 mol CO_2 occupies a fixed volume of 15.0 dm^3 at 300 K. When it is supplied with 2.35 kJ of energy as heat its temperature increases to 341 K. Assume that CO_2 is described by the van der Waals equation of state, and calculate w, ΔU, and ΔH.

2.4 A sample of 70 mmol Kr(g) expands reversibly and isothermally at 373 K from 5.25 cm^3 to 6.29 cm^3, and the internal energy of the sample is known to increase by 83.5 J. Use the virial equation of state up to the second coefficient $B = -28.7\ \mathrm{cm}^3\ \mathrm{mol}^{-1}$ to calculate w, q, and ΔH for this change of state.

2.5 A sample of 1.00 mol perfect gas molecules with $C_{p,\mathrm{m}} = \frac{7}{2}R$ is put through the following cycle: (a) constant-volume heating to twice its initial volume, (b) reversible, adiabatic expansion back to its initial temperature, (c) reversible isothermal compression back to 1.00 atm. Calculate q, w, ΔU, and ΔH for each step and overall.

2.6 Calculate the work done during the isothermal reversible expansion of a van der Waals gas. Account physically for the way in which the coefficients a and b appear in the final expression. Plot on the same graph the indicator diagrams for the isothermal reversible expansion of (a) a perfect gas, (b) a van der Waals gas in which $a = 0$ and $b = 5.11 \times 10^{-2}\ \mathrm{dm}^3\ \mathrm{mol}^{-1}$, and (c) $a = 4.2\ \mathrm{dm}^6\ \mathrm{atm\ mol}^{-2}$ and $b = 0$. The values selected exaggerate the imperfections but give rise to significant effects on the indicator diagrams. Take $V_\mathrm{i} = 1.0\ \mathrm{dm}^3$, $n = 1.0$ mol, and $T = 298$ K.

2.7 The molar heat capacity of ethane is represented in the temperature range 298 K to 400 K by the empirical expression $C_{p,\mathrm{m}}/(\mathrm{J\ K^{-1}\ mol^{-1}}) = 14.73 + 0.1272(T/\mathrm{K})$. The corresponding expressions for C(s) and $H_2(g)$ are given in Table 2.2. Calculate the standard enthalpy of formation of ethane at 350 K from its value at 298 K.

2.8 A sample of the sugar D-ribose ($C_5H_{10}O_5$) of mass 0.727 g was placed in a calorimeter and then ignited in the presence of excess oxygen. The temperature rose by 0.910 K. In a separate experiment in the same calorimeter, the combustion of 0.825 g of benzoic acid, for which the internal energy of combustion is $-3251\ \mathrm{kJ\ mol^{-1}}$, gave a temperature rise of 1.940 K. Calculate the internal energy of combustion of D-ribose and its enthalpy of formation.

2.9 The standard enthalpy of formation of the metallocene bis(benzene)chromium was measured in a calorimeter. It was found for the reaction $Cr(C_6H_6)_2(s) \rightarrow Cr(s) + 2\ C_6H_6(g)$ that $\Delta_\mathrm{r}U^\ominus(583\ \mathrm{K}) = +8.0\ \mathrm{kJ\ mol^{-1}}$. Find the corresponding reaction enthalpy and estimate the standard enthalpy of formation of the compound at 583 K. The constant-pressure molar heat capacity of benzene is 136.1 $\mathrm{J\ K^{-1}\ mol^{-1}}$ in its liquid range and 81.67 $\mathrm{J\ K^{-1}\ mol^{-1}}$ as a gas.

2.10‡ From the enthalpy of combustion data in Table 2.5 for the alkanes methane through octane, test the extent to which the relation $\Delta_\mathrm{c}H^\ominus = k\{(M/(\mathrm{g\ mol^{-1}})\}^n$ holds and find the numerical values for k and n. Predict $\Delta_\mathrm{c}H^\ominus$ for decane and compare to the known value.

2.11 It is possible to investigate the thermochemical properties of hydrocarbons with molecular modelling methods. (a) Use electronic structure software to predict $\Delta_\mathrm{c}H^\ominus$ values for the alkanes methane through pentane. To calculate $\Delta_\mathrm{c}H^\ominus$ values, estimate the standard enthalpy of formation of $C_nH_{2(n+1)}(g)$ by performing semi-empirical calculations (for example, AM1 or PM3 methods) and use experimental standard enthalpy of formation values for $CO_2(g)$ and $H_2O(l)$. (b) Compare your estimated values with the experimental values of $\Delta_\mathrm{c}H^\ominus$ (Table 2.5) and comment on the reliability of the molecular modelling method. (c) Test the extent to which the relation $\Delta_\mathrm{c}H^\ominus = k\{(M/(\mathrm{g\ mol^{-1}})\}^n$ holds and find the numerical values for k and n.

2.12‡ When 1.3584 g of sodium acetate trihydrate was mixed into 100.0 cm^3 of 0.2000 M HCl(aq) at 25°C in a solution calorimeter, its temperature fell by 0.397°C on account of the reaction:

$$H_3O^+(aq) + NaCH_3CO_2 \cdot 3\ H_2O(s) \rightarrow Na^+(aq) + CH_3COOH(aq) + 4\ H_2O(l).$$

The heat capacity of the calorimeter is 91.0 $\mathrm{J\ K^{-1}}$ and the heat capacity density of the acid solution is 4.144 $\mathrm{J\ K^{-1}\ cm^{-3}}$. Determine the standard enthalpy of formation of the aqueous sodium cation. The standard enthalpy of formation of sodium acetate trihydrate is $-1064\ \mathrm{kJ\ mol^{-1}}$.

2.13‡ Since their discovery in 1985, fullerenes have received the attention of many chemical researchers. Kolesov *et al.* reported the standard enthalpy of combustion and of formation of crystalline C_{60} based on calorimetric measurements (V.P. Kolesov, S.M. Pimenova, V.K. Pavlovich, N.B. Tamm, and A.A. Kurskaya, *J. Chem. Thermodynamics* **28**, 1121 (1996)). In one of their runs, they found the standard specific internal energy of combustion to be $-36.0334\ \mathrm{kJ\ g^{-1}}$ at 298.15 K Compute $\Delta_\mathrm{c}H^\ominus$ and $\Delta_\mathrm{f}H^\ominus$ of C_{60}.

2.14‡ A thermodynamic study of $DyCl_3$ (E.H.P. Cordfunke, A.S. Booji, and M. Yu. Furkaliouk, *J. Chem. Thermodynamics* **28**, 1387 (1996)) determined its standard enthalpy of formation from the following information

(1) $DyCl_3(s) \rightarrow DyCl_3(aq, \text{in } 4.0\ \mathrm{M\ HCl})$ $\quad \Delta_\mathrm{r}H^\ominus = -180.06\ \mathrm{kJ\ mol^{-1}}$
(2) $Dy(s) + 3\ HCl(aq, 4.0\ \mathrm{M}) \rightarrow$
$DyCl_3(aq, \text{in } 4.0\ \mathrm{M\ HCl(aq)}) + \frac{3}{2}H_2(g)$ $\quad \Delta_\mathrm{r}H^\ominus = -699.43\ \mathrm{kJ\ mol^{-1}}$
(3) $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightarrow HCl(aq, 4.0\ \mathrm{M})$ $\quad \Delta_\mathrm{r}H^\ominus = -158.31\ \mathrm{kJ\ mol^{-1}}$

Determine $\Delta_\mathrm{f}H^\ominus(DyCl_3, s)$ from these data.

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

2.15‡ Silylene (SiH_2) is a key intermediate in the thermal decomposition of silicon hydrides such as silane (SiH_4) and disilane (Si_2H_6). Moffat *et al.* (H.K. Moffat, K.F. Jensen, and R.W. Carr, *J. Phys. Chem.* **95**, 145 (1991)) report $\Delta_f H^\ominus(SiH_2) = +274\ \mathrm{kJ\ mol^{-1}}$. If $\Delta_f H^\ominus(SiH_4) = +34.3\ \mathrm{kJ\ mol^{-1}}$ and $\Delta_f H^\ominus(Si_2H_6) = +80.3\ \mathrm{kJ\ mol^{-1}}$ (*CRC Handbook* (2004)), compute the standard enthalpies of the following reactions:

(a) $SiH_4(g) \rightarrow SiH_2(g) + H_2(g)$

(b) $Si_2H_6(g) \rightarrow SiH_2(g) + SiH_4(g)$

2.16‡ Silanone (SiH_2O) and silanol (SiH_3OH) are species believed to be important in the oxidation of silane (SiH_4). These species are much more elusive than their carbon counterparts. C.L. Darling and H.B. Schlegel (*J. Phys. Chem.* **97**, 8207 (1993)) report the following values (converted from calories) from a computational study: $\Delta_f H^\ominus(SiH_2O) = -98.3\ \mathrm{kJ\ mol^{-1}}$ and $\Delta_f H^\ominus(SiH_3OH) = -282\ \mathrm{kJ\ mol^{-1}}$. Compute the standard enthalpies of the following reactions:

(a) $SiH_4(g) + \frac{1}{2}O_2(g) \rightarrow SiH_3OH(g)$

(b) $SiH_4(g) + O_2(g) \rightarrow SiH_2O(g) + H_2O(l)$

(c) $SiH_3OH(g) \rightarrow SiH_2O(g) + H_2(g)$

Note that $\Delta_f H^\ominus(SiH_4, g) = +34.3\ \mathrm{kJ\ mol^{-1}}$ (*CRC Handbook* (2004)).

2.17 The constant-volume heat capacity of a gas can be measured by observing the decrease in temperature when it expands adiabatically and reversibly. If the decrease in pressure is also measured, we can use it to infer the value of $\gamma = C_p/C_V$ and hence, by combining the two values, deduce the constant-pressure heat capacity. A fluorocarbon gas was allowed to expand reversibly and adiabatically to twice its volume; as a result, the temperature fell from 298.15 K to 248.44 K and its pressure fell from 202.94 kPa to 81.840 kPa. Evaluate C_p.

2.18 A sample consisting of 1.00 mol of a van der Waals gas is compressed from $20.0\ \mathrm{dm^3}$ to $10.0\ \mathrm{dm^3}$ at 300 K. In the process, 20.2 kJ of work is done on the gas. Given that $\mu = \{(2a/RT) - b\}/C_{p,\mathrm{m}}$, with $C_{p,\mathrm{m}} = 38.4\ \mathrm{J\ K^{-1}\ mol^{-1}}$, $a = 3.60\ \mathrm{dm^6\ atm\ mol^{-2}}$, and $b = 0.44\ \mathrm{dm^3\ mol^{-1}}$, calculate ΔH for the process.

2.19 Take nitrogen to be a van der Waals gas with $a = 1.352\ \mathrm{dm^6\ atm\ mol^{-2}}$ and $b = 0.0387\ \mathrm{dm^3\ mol^{-1}}$, and calculate ΔH_m when the pressure on the gas is decreased from 500 atm to 1.00 atm at 300 K. For a van der Waals gas, $\mu = \{(2a/RT) - b\}/C_{p,\mathrm{m}}$. Assume $C_{p,\mathrm{m}} = \frac{7}{2}R$.

Theoretical problems

2.20 Show that the following functions have exact differentials: (a) $x^2y + 3y^2$, (b) $x \cos xy$, (c) x^3y^2, (d) $t(t + e^s) + s$.

2.21 (a) What is the total differential of $z = x^2 + 2y^2 - 2xy + 2x - 4y - 8$? (b) Show that $\partial^2 z/\partial y\partial x = \partial^2 z/\partial x\partial y$ for this function. (c) Let $z = xy - y + \ln x + 2$. Find $\mathrm{d}z$ and show that it is exact.

2.22 (a) Express $(\partial C_V/\partial V)_T$ as a second derivative of U and find its relation to $(\partial U/\partial V)_T$ and $(\partial C_p/\partial p)_T$ as a second derivative of H and find its relation to $(\partial H/\partial p)_T$. (b) From these relations show that $(\partial C_V/\partial V)_T = 0$ and $(\partial C_p/\partial p)_T = 0$ for a perfect gas.

2.23 (a) Derive the relation $C_V = -(\partial U/\partial V)_T(\partial V/\partial T)_U$ from the expression for the total differential of $U(T,V)$ and (b) starting from the expression for the total differential of $H(T,p)$, express $(\partial H/\partial p)_T$ in terms of C_p and the Joule–Thomson coefficient, μ.

2.24 Starting from the expression $C_p - C_V = T(\partial p/\partial T)_V(\partial V/\partial T)_p$, use the appropriate relations between partial derivatives to show that

$$C_p - C_V = \frac{T(\partial V/\partial T)_p^2}{(\partial V/\partial T)_T}$$

Evaluate $C_p - C_V$ for a perfect gas.

2.25 (a) By direct differentiation of $H = U + pV$, obtain a relation between $(\partial H/\partial U)_p$ and $(\partial U/\partial V)_p$. (b) Confirm that $(\partial H/\partial U)_p = 1 + p(\partial V/\partial U)_p$ by expressing $(\partial H/\partial U)_p$ as the ratio of two derivatives with respect to volume and then using the definition of enthalpy.

2.26 (a) Write expressions for $\mathrm{d}V$ and $\mathrm{d}p$ given that V is a function of p and T and p is a function of V and T. (b) Deduce expressions for $\mathrm{d}\ln V$ and $\mathrm{d}\ln p$ in terms of the expansion coefficient and the isothermal compressibility.

2.27 Calculate the work done during the isothermal reversible expansion of a gas that satisfies the virial equation of state, eqn 1.19. Evaluate (a) the work for 1.0 mol Ar at 273 K (for data, see Table 1.3) and (b) the same amount of a perfect gas. Let the expansion be from $500\ \mathrm{cm^3}$ to $1000\ \mathrm{cm^3}$ in each case.

2.28 Express the work of isothermal reversible expansion of a van der Waals gas in reduced variables and find a definition of reduced work that makes the overall expression independent of the identity of the gas. Calculate the work of isothermal reversible expansion along the critical isotherm from V_c to xV_c.

2.29‡ A gas obeying the equation of state $p(V - nb) = nRT$ is subjected to a Joule–Thomson expansion. Will the temperature increase, decrease, or remain the same?

2.30 Use the fact that $(\partial U/\partial V)_T = a/V_\mathrm{m}^2$ for a van der Waals gas to show that $\mu C_{p,\mathrm{m}} \approx (2a/RT) - b$ by using the definition of μ and appropriate relations between partial derivatives. (*Hint.* Use the approximation $pV_\mathrm{m} \approx RT$ when it is justifiable to do so.)

2.31 Rearrange the van der Waals equation of state to give an expression for T as a function of p and V (with n constant). Calculate $(\partial T/\partial p)_V$ and confirm that $(\partial T/\partial p)_V = 1/(\partial p/\partial T)_V$. Go on to confirm Euler's chain relation.

2.32 Calculate the isothermal compressibility and the expansion coefficient of a van der Waals gas. Show, using Euler's chain relation, that $\kappa_T R = \alpha(V_\mathrm{m} - b)$.

2.33 Given that $\mu C_p = T(\partial V/\partial T)_p - V$, derive an expression for μ in terms of the van der Waals parameters a and b, and express it in terms of reduced variables. Evaluate μ at 25°C and 1.0 atm, when the molar volume of the gas is $24.6\ \mathrm{dm^3\ mol^{-1}}$. Use the expression obtained to derive a formula for the inversion temperature of a van der Waals gas in terms of reduced variables, and evaluate it for the xenon sample.

2.34 The thermodynamic equation of state $(\partial U/\partial V)_T = T(\partial p/\partial T)_V - p$ was quoted in the chapter. Derive its partner

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

from it and the general relations between partial differentials.

2.35 Show that for a van der Waals gas,

$$C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = \lambda R \qquad \frac{1}{\lambda} = 1 - \frac{(3V_\mathrm{r} - 1)^2}{4V_\mathrm{r}^3 T_\mathrm{r}}$$

and evaluate the difference for xenon at 25°C and 10.0 atm.

2.36 The speed of sound, c_s, in a gas of molar mass M is related to the ratio of heat capacities γ by $c_\mathrm{s} = (\gamma RT/M)^{1/2}$. Show that $c_\mathrm{s} = (\gamma p/\rho)^{1/2}$, where ρ is the mass density of the gas. Calculate the speed of sound in argon at 25°C.

2.37‡ A gas obeys the equation of state $V_\mathrm{m} = RT/p + aT^2$ and its constant-pressure heat capacity is given by $C_{p,\mathrm{m}} = A + BT + Cp$, where a, A, B, and C are constants independent of T and p. Obtain expressions for (a) the Joule–Thomson coefficient and (b) its constant-volume heat capacity.

Applications: to biology, materials science, and the environment

2.38 It is possible to see with the aid of a powerful microscope that a long piece of double-stranded DNA is flexible, with the distance between the ends of the chain adopting a wide range of values. This flexibility is important because it allows DNA to adopt very compact conformations as it is packaged in a chromosome (see Chapter 18). It is convenient to visualize a long piece of DNA as a *freely jointed chain*, a chain of N small, rigid units of length l that are free to make any angle with respect to each other. The length l, the *persistence length*, is approximately 45 nm, corresponding to approximately 130 base pairs. You will now explore the work associated with extending a DNA molecule. (a) Suppose that a DNA molecule resists being extended from an equilibrium, more compact conformation with a *restoring force* $F=-k_F x$, where x is the difference in the end-to-end distance of the chain from an equilibrium value and k_F is the *force constant*. Systems showing this behaviour are said to obey *Hooke's law*. (i) What are the limitations of this model of the DNA molecule? (ii) Using this model, write an expression for the work that must be done to extend a DNA molecule by x. Draw a graph of your conclusion. (b) A better model of a DNA molecule is the *one-dimensional freely jointed chain*, in which a rigid unit of length l can only make an angle of 0° or 180° with an adjacent unit. In this case, the restoring force of a chain extended by $x=nl$ is given by

$$F=\frac{kT}{2l}\ln\left(\frac{1+\nu}{1-\nu}\right) \qquad \nu=n/N$$

where $k=1.381\times10^{-23}\ \mathrm{J\ K^{-1}}$ is *Boltzmann's constant* (not a force constant). (i) What are the limitations of this model? (ii) What is the magnitude of the force that must be applied to extend a DNA molecule with $N=200$ by 90 nm? (iii) Plot the restoring force against ν, noting that ν can be either positive or negative. How is the variation of the restoring force with end-to-end distance different from that predicted by Hooke's law? (iv) Keeping in mind that the difference in end-to-end distance from an equilibrium value is $x=nl$ and, consequently, $dx=l dn=Nl d\nu$, write an expression for the work of extending a DNA molecule. (v) Calculate the work of extending a DNA molecule from $\nu=0$ to $\nu=1.0$. *Hint.* You must integrate the expression for w. The task can be accomplished easily with mathematical software. (c) Show that for small extensions of the chain, when $\nu\ll1$, the restoring force is given by

$$F\approx\frac{\nu kT}{l}=\frac{nkT}{Nl}$$

Hint. See *Appendix* 2 for a review of series expansions of functions. (d) Is the variation of the restoring force with extension of the chain given in part (c) different from that predicted by Hooke's law? Explain your answer.

2.39 There are no dietary recommendations for consumption of carbohydrates. Some nutritionists recommend diets that are largely devoid of carbohydrates, with most of the energy needs being met by fats. However, the most common recommendation is that at least 65 per cent of our food calories should come from carbohydrates. A $\frac{3}{4}$-cup serving of pasta contains 40 g of carbohydrates. What percentage of the daily calorie requirement for a person on a 2200 Calorie diet (1 Cal = 1 kcal) does this serving represent?

2.40 An average human produces about 10 MJ of heat each day through metabolic activity. If a human body were an isolated system of mass 65 kg with the heat capacity of water, what temperature rise would the body experience? Human bodies are actually open systems, and the main mechanism of heat loss is through the evaporation of water. What mass of water should be evaporated each day to maintain constant temperature?

2.41 Glucose and fructose are simple sugars with the molecular formula $C_6H_{12}O_6$. Sucrose, or table sugar, is a complex sugar with molecular formula $C_{12}H_{22}O_{11}$ that consists of a glucose unit covalently bound to a fructose unit (a water molecule is given off as a result of the reaction between glucose and fructose to form sucrose). (a) Calculate the energy released as heat when a typical table sugar cube of mass 1.5 g is burned in air. (b) To what height could you climb on the energy a table sugar cube provides assuming 25 per cent of the energy is available for work? (c) The mass of a typical glucose tablet is 2.5 g. Calculate the energy released as heat when a glucose tablet is burned in air. (d) To what height could you climb on the energy a cube provides assuming 25 per cent of the energy is available for work?

2.42 In biological cells that have a plentiful supply of O_2, glucose is oxidized completely to CO_2 and H_2O by a process called *aerobic oxidation*. Muscle cells may be deprived of O_2 during vigorous exercise and, in that case, one molecule of glucose is converted to two molecules of lactic acid ($CH_3CH(OH)COOH$) by a process called *anaerobic glycolysis* (see *Impact I7.2*). (a) When 0.3212 g of glucose was burned in a bomb calorimeter of calorimeter constant 641 J K^{-1} the temperature rose by 7.793 K. Calculate (i) the standard molar enthalpy of combustion, (ii) the standard internal energy of combustion, and (iii) the standard enthalpy of formation of glucose. (b) What is the biological advantage (in kilojoules per mole of energy released as heat) of complete aerobic oxidation compared with anaerobic glycolysis to lactic acid?

2.43 You have at your disposal a sample of pure polymer P and a sample of P that has just been synthesized in a large chemical reactor and that may contain impurities. Describe how you would use differential scanning calorimetry to determine the mole percentage composition of P in the allegedly impure sample.

2.44‡ Alkyl radicals are important intermediates in the combustion and atmospheric chemistry of hydrocarbons. Seakins *et al.* (P.W. Seakins, M.J. Pilling, J.T. Niiranen, D. Gutman, and L.N. Krasnoperov, *J. Phys. Chem.* **96**, 9847 (1992)) report $\Delta_f H^\ominus$ for a variety of alkyl radicals in the gas phase, information that is applicable to studies of pyrolysis and oxidation reactions of hydrocarbons. This information can be combined with thermodynamic data on alkenes to determine the reaction enthalpy for possible fragmentation of a large alkyl radical into smaller radicals and alkenes. Use the following set of data to compute the standard reaction enthalpies for three possible fates of the *tert*-butyl radical, namely, (a) *tert*-$C_4H_9\rightarrow$ *sec*-C_4H_9, (b) *tert*-$C_4H_9\rightarrow C_3H_6+CH_3$, (c) *tert*-$C_4H_9\rightarrow C_2H_4+C_2H_5$.

Species:	C_2H_5	*sec*-C_4H_9	*tert*-C_4H_9
$\Delta_f H^\ominus/(\mathrm{kJ\ mol^{-1}})$	+121.0	+67.5	+51.3

2.45‡ In 1995, the Intergovernmental Panel on Climate Change (IPCC) considered a global average temperature rise of 1.0–3.5°C likely by the year 2100, with 2.0°C its best estimate. Predict the average rise in sea level due to thermal expansion of sea water based on temperature rises of 1.0°C, 2.0°C, and 3.5°C given that the volume of the Earth's oceans is 1.37×10^9 km^3 and their surface area is 361×10^6 km^2, and state the approximations that go into the estimates.

2.46‡ Concerns over the harmful effects of chlorofluorocarbons on stratospheric ozone have motivated a search for new refrigerants. One such alternative is 2,2-dichloro-1,1,1-trifluoroethane (refrigerant 123). Younglove and McLinden published a compendium of thermophysical properties of this substance (B.A. Younglove and M. McLinden, *J. Phys. Chem. Ref. Data* **23**, 7 (1994)), from which properties such as the Joule–Thomson coefficient μ can be computed. (a) Compute μ at 1.00 bar and 50°C given that $(\partial H/\partial p)_T=-3.29\times10^3\ \mathrm{J\ MPa^{-1}\ mol^{-1}}$ and $C_{p,\mathrm{m}}=110.0\ \mathrm{J\ K^{-1}\ mol^{-1}}$. (b) Compute the temperature change that would accompany adiabatic expansion of 2.0 mol of this refrigerant from 1.5 bar to 0.5 bar at 50°C.

2.47‡ Another alternative refrigerant (see preceding problem) is 1,1,1,2-tetrafluoroethane (refrigerant HFC-134a). Tillner-Roth and Baehr published a compendium of thermophysical properties of this substance (R. Tillner-Roth and H.D. Baehr, *J. Phys. Chem. Ref. Data* **23**, 657 (1994)), from which properties such as the Joule–Thomson coefficient μ can be computed. (a) Compute μ at 0.100 MPa and 300 K from the following data (all referring to 300 K):

p/MPa	0.080	0.100	0.12
Specific enthalpy/(kJ kg^{-1})	426.48	426.12	425.76

(The specific constant-pressure heat capacity is 0.7649 kJ K^{-1} kg^{-1}.)
(b) Compute μ at 1.00 MPa and 350 K from the following data (all referring to 350 K):

p/MPa	0.80	1.00	1.2
Specific enthalpy/(kJ kg^{-1})	461.93	459.12	456.15

(The specific constant-pressure heat capacity is 1.0392 kJ K^{-1} kg^{-1}.)

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 be done to bring it about. A gas can be confined to a smaller volume, an object can be cooled by using a refrigerator, and some reactions can be driven in reverse (as in the electrolysis of water). However, none of these processes is spontaneous; each one must be brought about by doing work. An important point, though, is that throughout this text 'spontaneous' must be interpreted as a natural *tendency* that may or may not be realized in practice. Thermodynamics is silent on the rate at which a spontaneous change in fact occurs, and some spontaneous processes (such as the conversion of diamond to graphite) may be so slow that the tendency is never realized in practice whereas others (such as the expansion of a gas into a vacuum) are almost instantaneous.

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

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

For example, it has proved impossible to construct an engine like that shown in Fig. 3.1, in which heat is drawn from a hot reservoir and completely converted into work. All real heat engines have both a hot source and a cold sink; some energy is always discarded into the cold sink as heat and not converted into work. The Kelvin statement is a generalization of another everyday observation, that a ball at rest on a surface has never been observed to leap spontaneously upwards. An upward leap of the ball would be equivalent to the conversion of heat from the surface into work.

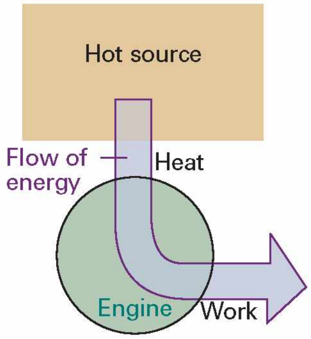

Fig. 3.1 The Kelvin statement of the Second Law denies the possibility of the process illustrated here, in which heat is changed completely into work, there being no other change. The process is not in conflict with the First Law because energy is conserved.

The direction of spontaneous change

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

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

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

3.1 The dispersal of energy

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

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

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

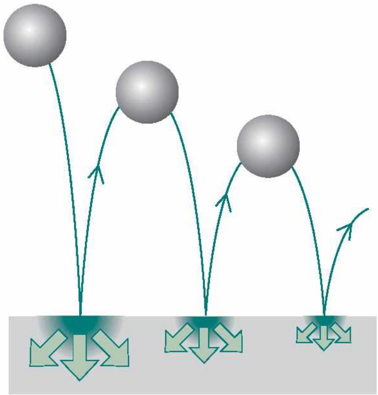

Fig. 3.2 The direction of spontaneous change for a ball bouncing on a floor. On each bounce some of its energy is degraded into the thermal motion of the atoms of the floor, and that energy disperses. The reverse has never been observed to take place on a macroscopic scale.

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

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

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

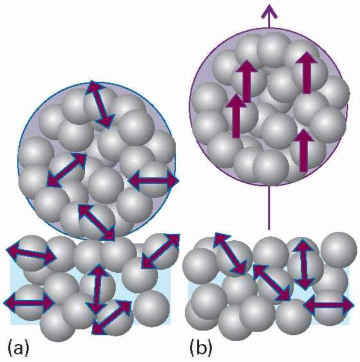

Fig. 3.3 The molecular interpretation of the irreversibility expressed by the Second Law. (a) A ball resting on a warm surface; the atoms are undergoing thermal motion (vibration, in this instance), as indicated by the arrows. (b) For the ball to fly upwards, some of the random vibrational motion would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

3.2 Entropy

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

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

> The entropy of an isolated system increases in the course of a spontaneous change: $\Delta S_{\text{tot}} > 0$

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

(a) The thermodynamic definition of entropy

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

The thermodynamic definition of entropy is based on the expression

$$\mathrm{d}S = \frac{\mathrm{d}q_{\text{rev}}}{T} \qquad [3.1]$$

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

$$\Delta S = \int_{\mathrm{i}}^{\mathrm{f}} \frac{\mathrm{d}q_{\text{rev}}}{T} \qquad (3.2)$$

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.

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

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

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

Answer Because the temperature is constant, eqn 3.2 becomes

$$\Delta S = \frac{1}{T}\int_{\text{i}}^{\text{f}} \text{d}q_{\text{rev}} = \frac{q_{\text{rev}}}{T}$$

From eqn 2.11, we know that

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

It follows that

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

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

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

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

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

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

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

internal energy, $\mathrm{d}U_{\mathrm{sur}}$.[3] The internal energy is a state function, and $\mathrm{d}U_{\mathrm{sur}}$ is an exact differential. As we have seen, these properties imply that $\mathrm{d}U_{\mathrm{sur}}$ 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 $\mathrm{d}q_{\mathrm{sur}}$, to which $\mathrm{d}U_{\mathrm{sur}}$ is equal. Therefore, we can adapt the definition in eqn 3.1 to write

$$\mathrm{d}S_{\mathrm{sur}}=\frac{\mathrm{d}q_{\mathrm{sur,rev}}}{T_{\mathrm{sur}}}=\frac{\mathrm{d}q_{\mathrm{sur}}}{T_{\mathrm{sur}}} \tag{3.3a}$$

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

$$\Delta S_{\mathrm{sur}}=\frac{q_{\mathrm{sur}}}{T_{\mathrm{sur}}} \tag{3.3b}$$

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, $q_{\mathrm{sur}}=0$, so

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

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

Illustration 3.1 *Calculating the entropy change in the surroundings*

To calculate the entropy change in the surroundings when 1.00 mol $H_2O(l)$ is formed from its elements under standard conditions at 298 K, we use $\Delta H^{\ominus} = -286$ kJ from Table 2.7. The energy released as heat is supplied to the surroundings, now regarded as being at constant pressure, so $q_{\mathrm{sur}} = +286$ kJ. Therefore,

$$\Delta S_{\mathrm{sur}}=\frac{2.86\times10^{5}\ \mathrm{J}}{298\ \mathrm{K}}=+960\ \mathrm{J\ K^{-1}}$$

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.

[$-192\ \mathrm{J\ K^{-1}}$]

Molecular interpretation 3.1 *The statistical view of entropy*

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

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[3] Alternatively, the surroundings can be regarded as being at constant pressure, in which case we could equate $\mathrm{d}q_{\mathrm{sur}}$ to $\mathrm{d}H_{\mathrm{sur}}$.

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

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

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

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

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

$$S = k \ln W \tag{3.5}$$

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

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

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

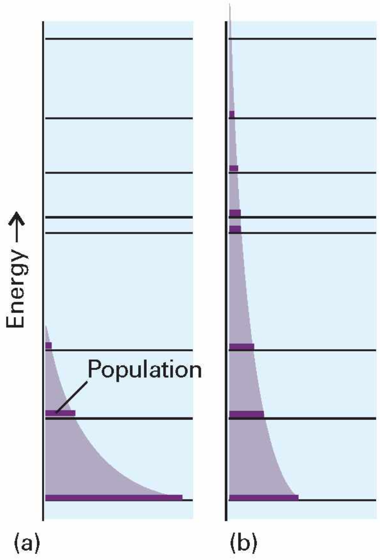

Fig. 3.4 The Boltzmann distribution predicts that the population of a state decreases exponentially with the energy of the state. (a) At low temperatures, only the lowest states are significantly populated; (b) at high temperatures, there is significant population in high-energy states as well as in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

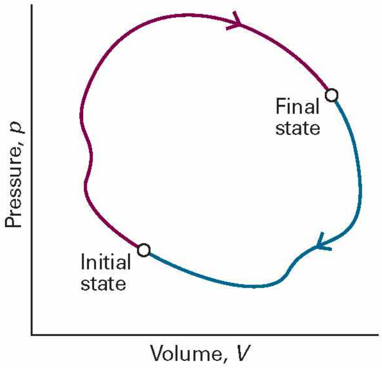

Fig. 3.5 In a thermodynamic cycle, the overall change in a state function (from the initial state to the final state and then back to the initial state again) is zero.

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

(b) The entropy as a state function

Entropy is a state function. To prove this assertion, we need to show that the integral of $\mathrm{d}S$ 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

$$\oint \frac{\mathrm{d}q_{\mathrm{rev}}}{T} = 0 \tag{3.6}$$

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.

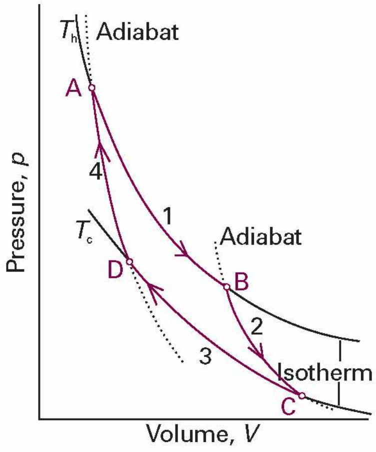

Fig. 3.6 The basic structure of a Carnot cycle. In Step 1, there is isothermal reversible expansion at the temperature T_{h}. Step 2 is a reversible adiabatic expansion in which the temperature falls from T_{h} to T_{c}. In Step 3 there is an isothermal reversible compression at T_{c}, and that isothermal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

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 $q_{\mathrm{h}}/T_{\mathrm{h}}$, 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 $q_{\mathrm{c}}/T_{\mathrm{c}}$; in this expression q_{c} is negative.
4. Reversible adiabatic compression from D to A. No energy enters the system as heat, so the change in entropy is zero. The temperature rises from T_{c} to T_{h}.

The total change in entropy around the cycle is

$$\oint \mathrm{d}S = \frac{q_{\mathrm{h}}}{T_{\mathrm{h}}} + \frac{q_{\mathrm{c}}}{T_{\mathrm{c}}}$$

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

$$\frac{q_{\mathrm{h}}}{q_{\mathrm{c}}} = -\frac{T_{\mathrm{h}}}{T_{\mathrm{c}}} \tag*{(3.7)$_{\mathrm{rev}}$}$$

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

$$q_{\mathrm{h}} = nRT_{\mathrm{h}} \ln \frac{V_{\mathrm{B}}}{V_{\mathrm{A}}} \qquad q_{\mathrm{c}} = nRT_{\mathrm{c}} \ln \frac{V_{\mathrm{D}}}{V_{\mathrm{C}}}$$

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

$$V_{\mathrm{A}} T_{\mathrm{h}}^{c} = V_{\mathrm{D}} T_{\mathrm{c}}^{c} \qquad V_{\mathrm{c}} T_{\mathrm{c}}^{c} = V_{\mathrm{B}} T_{\mathrm{h}}^{c}$$

Multiplication of the first of these expressions by the second gives

$$V_{\mathrm{A}} V_{\mathrm{c}} T_{\mathrm{h}}^{c} T_{\mathrm{c}}^{c} = V_{\mathrm{D}} V_{\mathrm{B}} T_{\mathrm{h}}^{c} T_{\mathrm{c}}^{c}$$

which simplifies to

$$\frac{V_{\mathrm{A}}}{V_{\mathrm{B}}} = \frac{V_{\mathrm{D}}}{V_{\mathrm{C}}}$$

Consequently,

$$q_{\mathrm{c}} = nRT_{\mathrm{c}} \ln \frac{V_{\mathrm{D}}}{V_{\mathrm{C}}} = nRT_{\mathrm{c}} \ln \frac{V_{\mathrm{A}}}{V_{\mathrm{B}}} = -nRT_{\mathrm{c}} \ln \frac{V_{\mathrm{B}}}{V_{\mathrm{A}}}$$

and therefore

$$\frac{q_{\mathrm{h}}}{q_{\mathrm{c}}} = \frac{nRT_{\mathrm{h}} \ln(V_{\mathrm{B}}/V_{\mathrm{A}})}{-nRT_{\mathrm{c}} \ln(V_{\mathrm{B}}/V_{\mathrm{A}})} = -\frac{T_{\mathrm{h}}}{T_{\mathrm{c}}}$$

as in eqn 3.7.

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

$$\varepsilon = \frac{\text{work performed}}{\text{heat absorbed}} = \frac{|w|}{q_{\mathrm{h}}} \qquad [3.8]$$

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

$$\varepsilon = \frac{q_{\mathrm{h}} + q_{\mathrm{c}}}{q_{\mathrm{h}}} = 1 + \frac{q_{\mathrm{c}}}{q_{\mathrm{h}}} \qquad (3.9)$$

(Remember that $q_{\mathrm{c}} < 0$.) It then follows from eqn 3.7 that

$$\varepsilon_{\mathrm{rev}} = 1 - \frac{T_{\mathrm{c}}}{T_{\mathrm{h}}} \qquad (3.10)_{\mathrm{rev}}$$

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

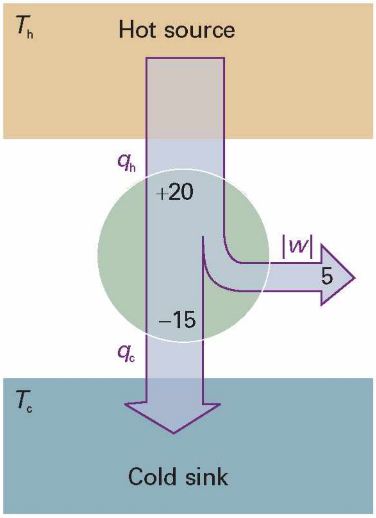

Fig. 3.7 Suppose an energy q_{h} (for example, 20 kJ) is supplied to the engine and q_{c} is lost from the engine (for example, $q_{\mathrm{c}} = -15$ kJ) and discarded into the cold reservoir. The work done by the engine is equal to $q_{\mathrm{h}} + q_{\mathrm{c}}$ (for example, 20 kJ + (−15 kJ) =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

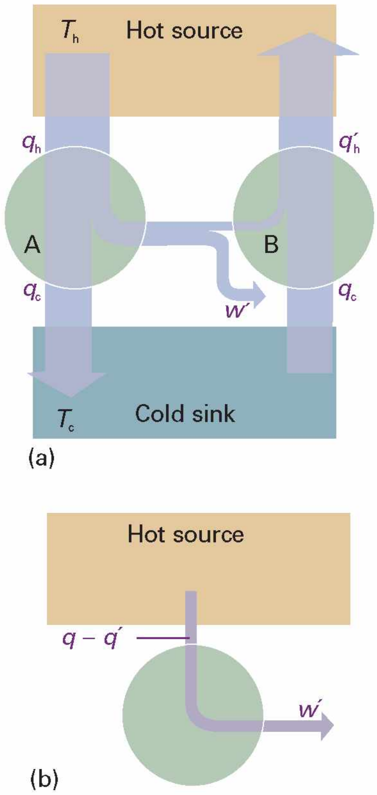

Fig. 3.8 (a) The demonstration of the equivalence of the efficiencies of all reversible engines working between the same thermal reservoirs is based on the flow of energy represented in this diagram. (b) The net effect of the processes is the conversion of heat into work without there being a need for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

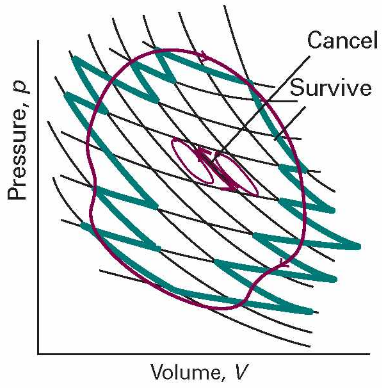

Fig. 3.9 A general cycle can be divided into small Carnot cycles. The match is exact in the limit of infinitesimally small cycles. Paths cancel in the interior of the collection, and only the perimeter, an increasingly good approximation to the true cycle as the number of cycles increases, survives.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

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

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

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

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

IMPACT ON ENGINEERING

I3.1 Refrigeration

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

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

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

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

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

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

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

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

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

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

for the thermodynamically optimum coefficient of performance. For a refrigerator withdrawing heat from ice-cold water ($T_c = 273$ 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.

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

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

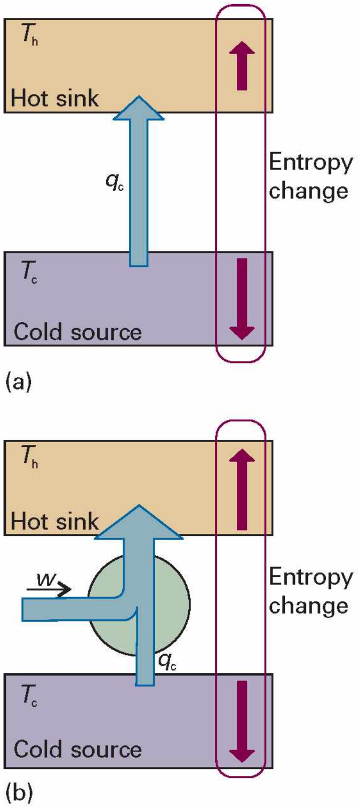

Fig. 3.10 (a) The flow of energy as heat from a cold source to a hot sink is not spontaneous. As shown here, the entropy increase of the hot sink is smaller than the entropy increase of the cold source, so there is a net decrease in entropy. (b) The process becomes feasible if work is provided to add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

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

(c) The thermodynamic temperature

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

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

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

Comment 3.1

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

(d) The Clausius inequality

We now show that the definition of entropy is consistent with the Second Law. To begin, we recall that more energy flows as work under reversible conditions than under irreversible conditions. That is, $-\mathrm{d}w_{\mathrm{rev}} \geq -\mathrm{d}w$, or $\mathrm{d}w - \mathrm{d}w_{\mathrm{rev}} \geq 0$. 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:

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

It follows that $\mathrm{d}q_{\mathrm{rev}} - \mathrm{d}q = \mathrm{d}w - \mathrm{d}w_{\mathrm{rev}} \geq 0$, or $\mathrm{d}q_{\mathrm{rev}} \geq \mathrm{d}q$, and therefore that $\mathrm{d}q_{\mathrm{rev}}/T \geq \mathrm{d}q/T$. Now we use the thermodynamic definition of the entropy (eqn 3.1; $\mathrm{d}S = \mathrm{d}q_{\mathrm{rev}}/T$) to write

$$\mathrm{d}S \geq \frac{\mathrm{d}q}{T} \tag{3.12}$$

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

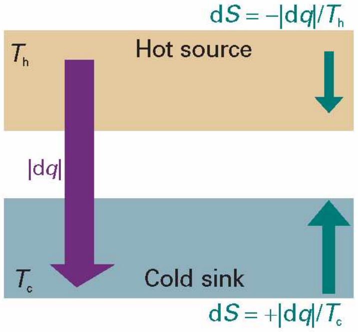

Fig. 3.11 When energy leaves a hot reservoir as heat, the entropy of the reservoir decreases. When the same quantity of energy enters a cooler reservoir, the entropy increases by a larger amount. Hence, overall there is an increase in entropy and the process is spontaneous. Relative changes in entropy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

Illustration 3.2 *Spontaneous cooling*

Consider the transfer of energy as heat from one system—the hot source—at a temperature T_h to another system—the cold sink—at a temperature T_c (Fig. 3.11). When $|\mathrm{d}q|$ leaves the hot source (so $\mathrm{d}q_h < 0$), the Clausius inequality implies that $\mathrm{d}S \geq \mathrm{d}q_h/T_h$. When $|\mathrm{d}q|$ enters the cold sink the Clausius inequality implies that $\mathrm{d}S \geq \mathrm{d}q_c/T_c$ (with $\mathrm{d}q_c > 0$). Overall, therefore,

$$\mathrm{d}S \geq \frac{\mathrm{d}q_h}{T_h} + \frac{\mathrm{d}q_c}{T_c}$$

However, $\mathrm{d}q_h = -\mathrm{d}q_c$, so

$$\mathrm{d}S \geq -\frac{\mathrm{d}q_c}{T_h} + \frac{\mathrm{d}q_c}{T_c} = \mathrm{d}q_c\left(\frac{1}{T_c} - \frac{1}{T_h}\right)$$

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

We now suppose that the system is isolated from its surroundings, so that $\mathrm{d}q = 0$. The Clausius inequality implies that

$$\mathrm{d}S \geq 0$$

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

3.3 Entropy changes accompanying specific processes

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

(a) Expansion

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

$$\Delta S = nR \ln \frac{V_\mathrm{f}}{V_\mathrm{i}} \qquad (3.13)^\circ$$

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

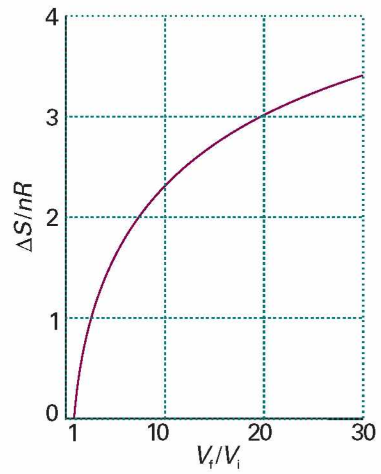

Fig. 3.12 The logarithmic increase in entropy of a perfect gas as it expands isothermally.

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

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

$$\Delta S_\mathrm{sur} = \frac{q_\mathrm{sur}}{T} = -\frac{q_\mathrm{rev}}{T} = -nR \ln \frac{V_\mathrm{f}}{V_\mathrm{i}} \qquad (3.14)^\circ_\mathrm{rev}$$

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

$$\Delta S_\mathrm{tot} = nR \ln \frac{V_\mathrm{f}}{V_\mathrm{i}} \qquad (3.15)^\circ$$

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

(b) Phase transition

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

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

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

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

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

Synoptic Table 3.2* The standard entropies of vaporization of liquids

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

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

because the two phases in the system are in equilibrium. Because at constant pressure $q = \Delta_{trs}H$, the change in molar entropy of the system is[4]

$$\Delta_{trs}S = \frac{\Delta_{trs}H}{T_{trs}} \tag{3.16}$$

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

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

Molecular interpretation 3.2 *Trouton's rule*

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

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

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

Methane has an unusually low entropy of vaporization. A part of the reason is that the entropy of the gas itself is slightly low (186 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 13, small molecules are difficult to excite into rotation; as a result, only a few rotational states are accessible at room temperature and, consequently, the number of rotational energy levels among which energy can be dispersed is low.

Illustration 3.3 *Using Trouton's rule*

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

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

Substitution of the data then gives

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

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

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

(c) Heating

We can use eqn 3.2 to calculate the entropy of a system at a temperature T_{f} from a knowledge of its entropy at a temperature T_{i} and the heat supplied to change its temperature from one value to the other:

$$S(T_{\text{f}}) = S(T_{\text{i}}) + \int_{T_{\text{i}}}^{T_{\text{f}}} \frac{\text{d}q_{\text{rev}}}{T} \tag{3.17}$$

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

$$S(T_{\text{f}}) = S(T_{\text{i}}) + \int_{T_{\text{i}}}^{T_{\text{f}}} \frac{C_p\text{d}T}{T} \tag{3.18}$$

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

$$S(T_\mathrm{f}) = S(T_\mathrm{i}) + C_p\int_{T_\mathrm{i}}^{T_\mathrm{f}}\frac{\mathrm{d}T}{T} = S(T_\mathrm{i}) + C_p\ln\frac{T_\mathrm{f}}{T_\mathrm{i}} \tag{3.19}$$

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

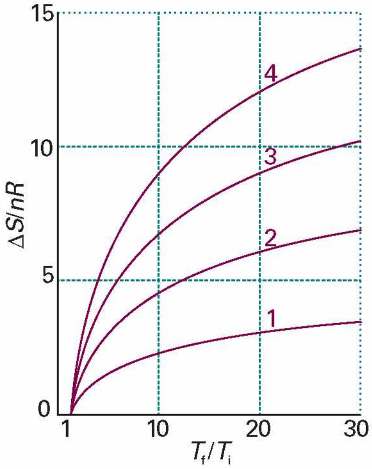

Fig. 3.13 The logarithmic increase in entropy of a substance as it is heated at constant volume. Different curves correspond to different values of the constant-volume heat capacity (which is assumed constant over the temperature range) expressed as $C_{V,\mathrm{m}}/R$.

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

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 3.13 and that of the second step, provided C_V is independent of temperature, by eqn 3.19 (with C_V in place of C_p). In each case we need to know n, the amount of gas molecules, and can calculate it from the perfect gas equation and the data for the initial state from $n = p_\mathrm{i}V_\mathrm{i}/RT_\mathrm{i}$. The heat capacity at constant volume is given by the equipartition theorem as $\frac{3}{2}R$. (The equipartition theorem is reliable for monatomic gases: for others and in general use experimental data like that in Table 2.7, converting to the value at constant volume by using the relation $C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = R$.)

Answer Because $n = p_\mathrm{i}V_\mathrm{i}/RT_\mathrm{i}$, from eqn 3.13

$$\Delta S(\text{Step 1}) = \left(\frac{p_\mathrm{i}V_\mathrm{i}}{RT_\mathrm{i}}\right)\times R\ln\frac{V_\mathrm{f}}{V_\mathrm{i}} = \frac{p_\mathrm{i}V_\mathrm{i}}{T_\mathrm{i}}\ln\frac{V_\mathrm{f}}{V_\mathrm{i}}$$

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

$$\Delta S(\text{Step 2}) = \left(\frac{p_\mathrm{i}V_\mathrm{i}}{RT_\mathrm{i}}\right)\times\tfrac{3}{2}R\ln\frac{T_\mathrm{f}}{T_\mathrm{i}} = \frac{p_\mathrm{i}V_\mathrm{i}}{T_\mathrm{i}}\ln\left(\frac{T_\mathrm{f}}{T_\mathrm{i}}\right)^{3/2}$$

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

$$\Delta S = \frac{p_\mathrm{i}V_\mathrm{i}}{T_\mathrm{i}}\ln\frac{V_\mathrm{f}}{V_\mathrm{i}} + \frac{p_\mathrm{i}V_\mathrm{i}}{T_\mathrm{i}}\ln\left(\frac{T_\mathrm{f}}{T_\mathrm{i}}\right)^{3/2} = \frac{p_\mathrm{i}V_\mathrm{i}}{T_\mathrm{i}}\ln\left\{\frac{V_\mathrm{f}}{V_\mathrm{i}}\left(\frac{T_\mathrm{f}}{T_\mathrm{i}}\right)^{3/2}\right\}$$

At this point we substitute the data and obtain (by using 1 Pa m^3 = 1 J)

$$\Delta S = \frac{(1.00\times10^{5}\ \mathrm{Pa})\times(0.500\times10^{-3}\ \mathrm{m^3})}{298\ \mathrm{K}}\ln\left\{\frac{1.000}{0.500}\left(\frac{373}{298}\right)^{3/2}\right\}$$

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

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. [−0.44 J K^{-1}]

(d) The measurement of entropy

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

$$S(T) = S(0) + \int_0^{T_{\rm f}} \frac{C_p({\rm s})\,{\rm d}T}{T} + \frac{\Delta_{\rm fus}H}{T_{\rm f}} + \int_{T_{\rm f}}^{T_{\rm b}} \frac{C_p({\rm l})\,{\rm d}T}{T} + \frac{\Delta_{\rm vap}H}{T_{\rm b}} + \int_{T_{\rm b}}^{T} \frac{C_p({\rm g})\,{\rm d}T}{T} \qquad (3.20)$$

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

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

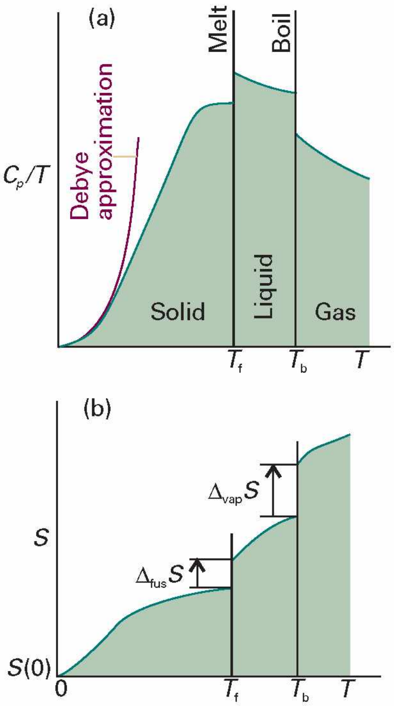

Fig. 3.14 The calculation of entropy from heat capacity data. (a) The variation of C_p/T with the temperature for a sample. (b) The entropy, which is equal to the area beneath the upper curve up to the corresponding temperature, plus the entropy of each phase transition passed.

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

Illustration 3.4 *Calculating a standard molar entropy*

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

	$S^{\ominus}_{\rm m}/({\rm J\,K^{-1}\,mol^{-1}})$
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,

$$S_{\rm m}(298.15\ {\rm K}) = S_{\rm m}(0) + 192.1\ {\rm J\,K^{-1}\,mol^{-1}}$$

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 3.18 to calculate the entropy at a temperature T in terms of the entropy at $T = 0$ and the constant a. When the integration is carried out, it turns out that the result can be expressed in terms of the heat capacity at the temperature T, so the data can be used directly to calculate the entropy.

Answer The integration required is

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

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

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

from which it follows that

$$S_\mathrm{m}(10\ \mathrm{K}) = S_\mathrm{m}(0) + 0.14\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

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

3.4 The Third Law of thermodynamics

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

(a) The Nernst heat theorem

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

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

Illustration 3.5 *Using the Nernst heat theorem*

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

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

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 $S_\mathrm{m}(\alpha) = S_\mathrm{m}(\alpha,0) + 37\ \mathrm{J\ K^{-1}\ mol^{-1}}$

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

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

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

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

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

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

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

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

(b) Third-Law entropies

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

The **standard reaction entropy**, $\Delta_r S^\ominus$, 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:

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

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

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

	$S_m^\ominus/(\text{J K}^{-1}\ \text{mol}^{-1})$
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, $NH_3(g)$	126.2

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

Illustration 3.6 *Calculating a standard reaction entropy*

To calculate the standard reaction entropy of $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ at 25°C, we use the data in Table 2.7 of the *Data Section* to write

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

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

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

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

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

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

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

Concentrating on the system

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

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

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

3.5 The Helmholtz and Gibbs energies

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

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

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

(a) Criteria for spontaneity

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

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

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

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

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

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

where the subscripts indicate the constant conditions.

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

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

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

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

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

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

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

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

Because eqns 3.25 and 3.27 have the forms $\mathrm{d}U - T\mathrm{d}S \le 0$ and $\mathrm{d}H - T\mathrm{d}S \le 0$, respectively, they can be expressed more simply by introducing two more thermodynamic quantities. One is the **Helmholtz energy**, A, which is defined as

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

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

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

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

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

$$\text{(a)}\ \mathrm{d}A = \mathrm{d}U - T\mathrm{d}S \qquad \text{(b)}\ \mathrm{d}G = \mathrm{d}H - T\mathrm{d}S \qquad (3.31)$$

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

$$\text{(a)}\ \mathrm{d}A_{T,V} \le 0 \qquad \text{(b)}\ \mathrm{d}G_{T,p} \le 0 \qquad (3.32)$$

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

(b) Some remarks on the Helmholtz energy

A change in a system at constant temperature and volume is spontaneous if $\mathrm{d}A_{T,V} \le 0$. 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

$$\mathrm{d}A_{T,V} = 0 \qquad (3.33)$$

The expressions $\mathrm{d}A = \mathrm{d}U - T\mathrm{d}S$ and $\mathrm{d}A < 0$ are sometimes interpreted as follows. A negative value of $\mathrm{d}A$ is favoured by a negative value of $\mathrm{d}U$ and a positive value of $T\mathrm{d}S$. 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 $\mathrm{d}A$) 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 $\mathrm{d}A$ may give the impression that systems favour lower energy, but that is misleading: $\mathrm{d}S$ is the entropy change of the system, $-\mathrm{d}U/T$ is the entropy change of the surroundings (when the volume of the system is constant), and their total tends to a maximum.

(c) Maximum work

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

$$\mathrm{d}w_{\text{max}} = \mathrm{d}A \qquad (3.34)$$

As a result, A is sometimes called the 'maximum work function', or the 'work function'.[7]

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

Justification 3.2 *Maximum work*

To demonstrate that maximum work can be expressed in terms of the changes in Helmholtz energy, we combine the Clausius inequality $\mathrm{d}S \geq \mathrm{d}q/T$ in the form $T\mathrm{d}S \geq \mathrm{d}q$ with the First Law, $\mathrm{d}U = \mathrm{d}q + \mathrm{d}w$, and obtain

$$\mathrm{d}U \leq T\mathrm{d}S + \mathrm{d}w$$

($\mathrm{d}U$ is smaller than the term on the right because we are replacing $\mathrm{d}q$ by $T\mathrm{d}S$, which in general is larger.) This expression rearranges to

$$\mathrm{d}w \geq \mathrm{d}U - T\mathrm{d}S$$

It follows that the most negative value of $\mathrm{d}w$, and therefore the maximum energy that can be obtained from the system as work, is given by

$$\mathrm{d}w_{\mathrm{max}} = \mathrm{d}U - T\mathrm{d}S$$

and that this work is done only when the path is traversed reversibly (because then the equality applies). Because at constant temperature $\mathrm{d}A = \mathrm{d}U - T\mathrm{d}S$, we conclude that $\mathrm{d}w_{\mathrm{max}} = \mathrm{d}A$.

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

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

with

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

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

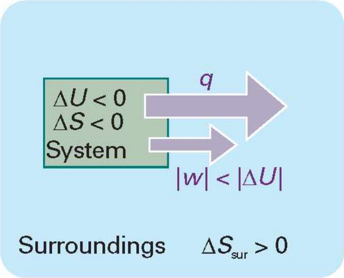

Fig. 3.15 In a system not isolated from its surroundings, the work done may be different from the change in internal energy. Moreover, the process is spontaneous if overall the entropy of the global, isolated system increases. In the process depicted here, the entropy of the system decreases, so that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

Molecular interpretation 3.4 *Maximum work and the Helmholtz energy*

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

If the change occurs with an increase of entropy of the system (in which case $T\Delta S > 0$), the right-hand side of the equation is more negative than ΔU. In this case, the maximum work that can be obtained from the system is greater than ΔU. The explanation of this apparent paradox is that the system is not isolated and energy may flow in as heat as work is done. Because the entropy of the system increases, we can afford a reduction of the entropy of the surroundings yet still have, overall, a spontaneous process. Therefore, some energy (no more than the value of $T\Delta S$) may leave the surroundings as heat and contribute to the work the change is generating (Fig. 3.16). Nature is now providing a tax refund.

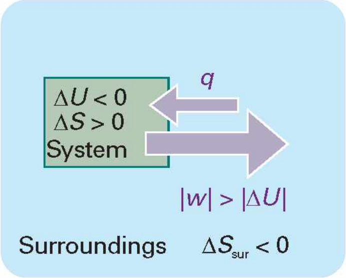

Fig. 3.16 In this process, the entropy of the system increases; hence we can afford to lose some entropy of the surroundings. That is, some of their energy may be lost as heat to the system. This energy can be returned to them as work. Hence the work done can exceed ΔU.

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 $\Delta_r S = +182.4$ 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 3.34.

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

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

Therefore, the combustion of 1.000 mol $C_6H_{12}O_6$ can be used to produce up to 2862 kJ of work. The maximum work available is greater than the change in internal energy on account of the positive entropy of reaction (which is partly due to the generation of a large number of small molecules from one big one). The system can therefore draw in energy from the surroundings (so reducing their entropy) and make it available for doing work.

Self-test 3.7 Repeat the calculation for the combustion of 1.000 mol $CH_4(g)$ under the same conditions, using data from Table 2.5. [$|q_p| = 890$ kJ, $|w_{\max}| = 813$ 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 $\mathrm{d}G_{T,p} \leq 0$ 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 $\mathrm{d}H > 0$. Because the reaction is spontaneous we know that $\mathrm{d}G < 0$ despite $\mathrm{d}H > 0$; it follows that the entropy of the system increases so much that $T\mathrm{d}S$ outweighs $\mathrm{d}H$ in $\mathrm{d}G = \mathrm{d}H - T\mathrm{d}S$. 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 ($\mathrm{d}S_{\text{sur}} = -\mathrm{d}H/T$ at constant pressure).

(e) Maximum non-expansion work

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

$$\mathrm{d}w_{\text{add,max}} = \mathrm{d}G \tag{3.37}$$

The corresponding expression for a measurable change is

$$w_{\text{add,max}} = \Delta G \tag{3.38}$$

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

Justification 3.3 *Maximum non-expansion work*

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

$$\mathrm{d}H = \mathrm{d}q + \mathrm{d}w + \mathrm{d}(pV)$$

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

$$\mathrm{d}G = \mathrm{d}H - T\mathrm{d}S - S\mathrm{d}T = \mathrm{d}q + \mathrm{d}w + \mathrm{d}(pV) - T\mathrm{d}S - S\mathrm{d}T$$

When the change is isothermal we can set $\mathrm{d}T = 0$; then

$$\mathrm{d}G = \mathrm{d}q + \mathrm{d}w + \mathrm{d}(pV) - T\mathrm{d}S$$

When the change is reversible, $\mathrm{d}w = \mathrm{d}w_{\text{rev}}$ and $\mathrm{d}q = \mathrm{d}q_{\text{rev}} = T\mathrm{d}S$, so for a reversible, isothermal process

$$\mathrm{d}G = T\mathrm{d}S + \mathrm{d}w_{\text{rev}} + \mathrm{d}(pV) - T\mathrm{d}S = \mathrm{d}w_{\text{rev}} + \mathrm{d}(pV)$$

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 $\mathrm{d}w_{\text{add}}$. Therefore, with $\mathrm{d}(pV) = p\mathrm{d}V + V\mathrm{d}p$,

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

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

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

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

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 Table 2.5, 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 $-2808\ \mathrm{kJ\ mol^{-1}}$, it follows that the standard reaction Gibbs energy is

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

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

Self-test 3.8 How much non-expansion work can be obtained from the combustion of 1.00 mol $CH_4(g)$ under standard conditions at 298 K? Use $\Delta_r S^{\ominus} = -243\ \text{J K}^{-1}\ \text{mol}^{-1}$. [818 kJ]

3.6 Standard reaction Gibbs energies

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

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

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

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

with each term weighted by the appropriate stoichiometric coefficient.

Illustration 3.7 *Calculating a standard Gibbs energy of reaction*

To calculate the standard Gibbs energy of the reaction $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$ 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. [$-818\ \text{kJ mol}^{-1}$]

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:

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

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

	$\Delta_f G^{\ominus}/(\text{kJ mol}^{-1})$
Diamond, C(s)	+2.9
Benzene, $C_6H_6(l)$	+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*.

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

In essence, this definition adjusts the actual values of the Gibbs energies of formation of ions by a fixed amount, which is chosen so that the standard value for one of them, $H^+(aq)$, has the value zero. Then 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}. All the Gibbs energies of formation of ions tabulated in the *Data section* were calculated in the same way.

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

With the value of $\Delta_f G^\ominus(Cl^-, aq)$ 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}.

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

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}X_2(g) \rightarrow H^+(aq) + X^-(aq)$$

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

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

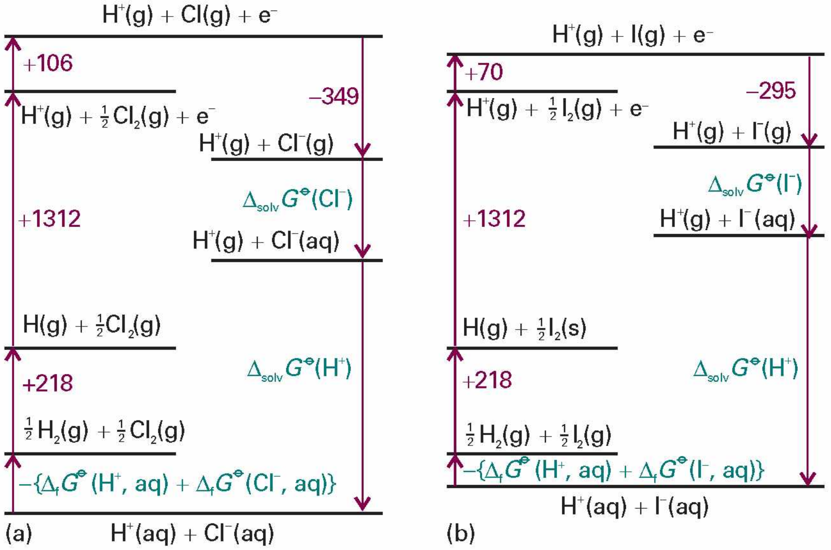

Fig. 3.17 The thermodynamic cycles for the discussion of the Gibbs energies of solvation (hydration) and formation of (a) chloride ions, (b) iodide ions in aqueous solution. The sum of the changes in Gibbs energies around the cycle sum to zero because G is a state function.

Comment 3.2

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

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

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

$$\Delta_{\text{solv}}G^\ominus = -\frac{z_i^2 e^2 N_A}{8\pi\varepsilon_0 r_i}\left(1 - \frac{1}{\varepsilon_r}\right) \qquad (3.42a)$$

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

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

Illustration 3.9 *Using the Born equation*

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

$$\Delta_{\text{solv}}G^\ominus(\text{Cl}^-) - \Delta_{\text{solv}}G^\ominus(\text{I}^-) = -\left(\frac{1}{181} - \frac{1}{220}\right) \times (6.86 \times 10^4\ \text{kJ mol}^{-1})$$

$$= -67\ \text{kJ mol}^{-1}$$

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

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

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

Comment 3.3

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

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

Combining the First and Second Laws

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

3.7 The fundamental equation

We have seen that the First Law of thermodynamics may be written $\mathrm{d}U = \mathrm{d}q + \mathrm{d}w$. For a reversible change in a closed system of constant composition, and in the absence of any additional (non-expansion) work, we may set $\mathrm{d}w_{\mathrm{rev}} = -p\mathrm{d}V$ and (from the definition of entropy) $\mathrm{d}q_{\mathrm{rev}} = T\mathrm{d}S$, where p is the pressure of the system and T its temperature. Therefore, for a reversible change in a closed system,

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V \tag{3.43}$$

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

The fact that the fundamental equation applies to both reversible and irreversible changes may be puzzling at first sight. The reason is that only in the case of a reversible change may $T\mathrm{d}S$ be identified with $\mathrm{d}q$ and $-p\mathrm{d}V$ with $\mathrm{d}w$. When the change is irreversible, $T\mathrm{d}S > \mathrm{d}q$ (the Clausius inequality) and $-p\mathrm{d}V > \mathrm{d}w$. The sum of $\mathrm{d}w$ and $\mathrm{d}q$ remains equal to the sum of $T\mathrm{d}S$ and $-p\mathrm{d}V$, provided the composition is constant.

3.8 Properties of the internal energy

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

The *mathematical* consequence of U being a function of S and V is that we can express an infinitesimal change $\mathrm{d}U$ in terms of changes $\mathrm{d}S$ and $\mathrm{d}V$ by

$$\mathrm{d}U = \left(\frac{\partial U}{\partial S}\right)_V \mathrm{d}S + \left(\frac{\partial U}{\partial V}\right)_S \mathrm{d}V \tag{3.44}$$

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

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

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

Comment 3.4

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

(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

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

Because the fundamental equation, eqn 3.43, 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

Comment 3.5

To illustrate the criterion set by eqn 3.46, let's test whether $\mathrm{d}f = 2xy\mathrm{d}x + x^2\mathrm{d}y$ is an exact differential. We identify $g = 2xy$ and $h = x^2$ and form

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

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

Because these two coefficients are equal, $\mathrm{d}f$ is exact.

Table 3.5 The Maxwell relations

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

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

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

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

(b) The variation of internal energy with volume

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

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

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

Justification 3.4 *The thermodynamic equation of state*

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

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

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

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

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

Example 3.6 *Deriving a thermodynamic relation*

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

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

Answer For a perfect gas we write

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

Then, eqn 3.48 becomes

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

The equation of state of a van der Waals gas is

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

Because a and b are independent of temperature,

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

Therefore, from eqn 3.48,

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

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

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

3.9 Properties of the Gibbs energy

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

(a) General considerations

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

$$\mathrm{d}G = \mathrm{d}H - \mathrm{d}(TS) = \mathrm{d}H - T\mathrm{d}S - S\mathrm{d}T$$

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

$$\mathrm{d}H = \mathrm{d}U + \mathrm{d}(pV) = \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p$$

and therefore

$$\mathrm{d}G = \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p - T\mathrm{d}S - S\mathrm{d}T$$

For a closed system doing no non-expansion work, we can replace $\mathrm{d}U$ by the fundamental equation $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$ and obtain

$$\mathrm{d}G = T\mathrm{d}S - p\mathrm{d}V + p\mathrm{d}V + V\mathrm{d}p - T\mathrm{d}S - S\mathrm{d}T$$

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,

$$dG = Vdp - SdT \tag{3.49}$$

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

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

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

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

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

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

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

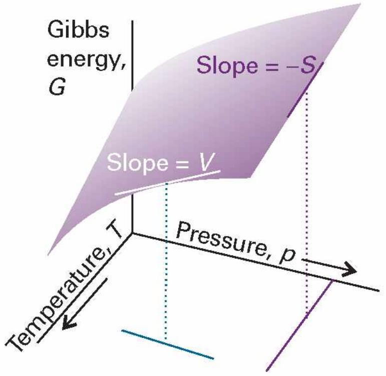

Fig. 3.18 The variation of the Gibbs energy of a system with (a) temperature at constant pressure and (b) pressure at constant temperature. The slope of the former is equal to the negative of the entropy of the system and that of the latter is equal to the volume.

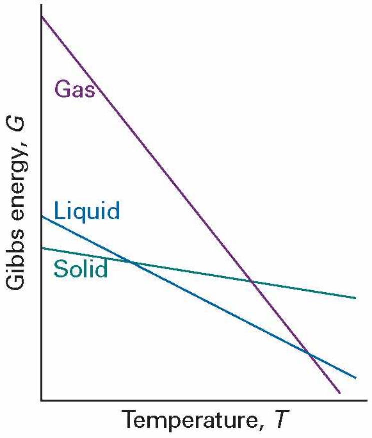

Fig. 3.19 The variation of the Gibbs energy with the temperature is determined by the entropy. Because the entropy of the gaseous phase of a substance is greater than that of the liquid phase, and the entropy of the solid phase is smallest, the Gibbs energy changes most steeply for the gas phase, followed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

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

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

(b) The variation of the Gibbs energy with temperature

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

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

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

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

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

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

Justification 3.5 *The Gibbs–Helmholtz equation*

First, we note that

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

Then we use eqn 3.51 in the form

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

It follows that

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

which is eqn 3.52.

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

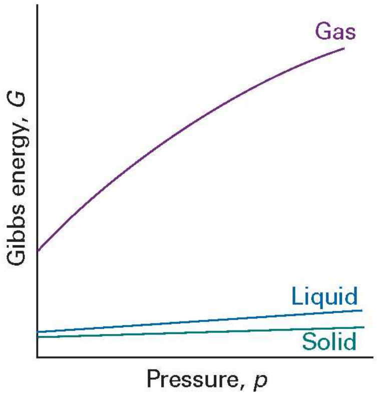

Fig. 3.20 The variation of the Gibbs energy with the pressure is determined by the volume of the sample. Because the volume of the gaseous phase of a substance is greater than that of the same amount of liquid phase, and the entropy of the solid phase is smallest (for most substances), the Gibbs energy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

Comment 3.6

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

$$\frac{\mathrm{d}uv}{\mathrm{d}x} = u\frac{\mathrm{d}v}{\mathrm{d}x} + v\frac{\mathrm{d}u}{\mathrm{d}x}$$

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

$$\frac{\mathrm{d}(\overbrace{x^2}^{u}\overbrace{e^{ax}}^{v})}{\mathrm{d}x} = x^2\frac{\mathrm{d}e^{ax}}{\mathrm{d}x} + e^{ax}\frac{\mathrm{d}x^2}{\mathrm{d}x}$$
$$= ax^2e^{ax} + 2xe^{ax}$$

---

[9] In Section 7.2b we derive the result that the equilibrium constant for a reaction is related to its standard reaction Gibbs energy by $\Delta_\mathrm{r}G^\ominus/T = -R\ln K$.

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

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

(c) The variation of the Gibbs energy with pressure

To find the Gibbs energy at one pressure in terms of its value at another pressure, the temperature being constant, we set $\mathrm{d}T = 0$ in eqn 3.49, which gives $\mathrm{d}G = V\mathrm{d}p$, and integrate:

$$G(p_\mathrm{f}) = G(p_\mathrm{i}) + \int_{p_\mathrm{i}}^{p_\mathrm{f}} V\,\mathrm{d}p \tag{3.54a}$$

For molar quantities,

$$G_\mathrm{m}(p_\mathrm{f}) = G_\mathrm{m}(p_\mathrm{i}) + \int_{p_\mathrm{i}}^{p_\mathrm{f}} V_\mathrm{m}\,\mathrm{d}p \tag{3.54b}$$

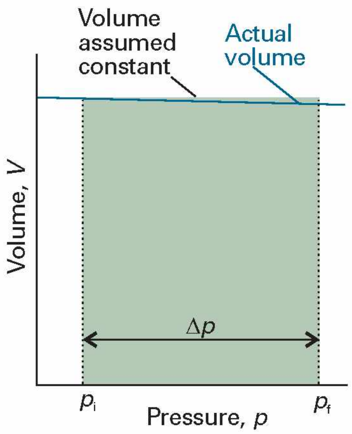

Fig. 3.21 The difference in Gibbs energy of a solid or liquid at two pressures is equal to the rectangular area shown. We have assumed that the variation of volume with pressure is negligible.

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

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

$$G_\mathrm{m}(p_\mathrm{f}) = G_\mathrm{m}(p_\mathrm{i}) + V_\mathrm{m}\int_{p_\mathrm{i}}^{p_\mathrm{f}} \mathrm{d}p = G_\mathrm{m}(p_\mathrm{i}) + (p_\mathrm{f} - p_\mathrm{i})V_\mathrm{m} \tag{3.55}$$

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 $(p_\mathrm{f} - p_\mathrm{i})V_\mathrm{m}$ is very small and may be neglected. Hence, we may usually suppose that the Gibbs energies of solids and liquids are independent of pressure. However, if we are interested in geophysical problems, then because pressures in the Earth's interior are huge, their effect on the Gibbs energy cannot be ignored. If the pressures are so great that there are substantial volume changes over the range of integration, then we must use the complete expression, eqn 3.54.

Illustration 3.10 *Gibbs energies at high pressures*

Suppose that for a certain phase transition of a solid $\Delta_\mathrm{trs}V = +1.0\ \mathrm{cm^3\,mol^{-1}}$ 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 $\Delta_\mathrm{trs}G(1\ \mathrm{bar})$ to

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

where we have used 1 Pa m^3 = 1 J.

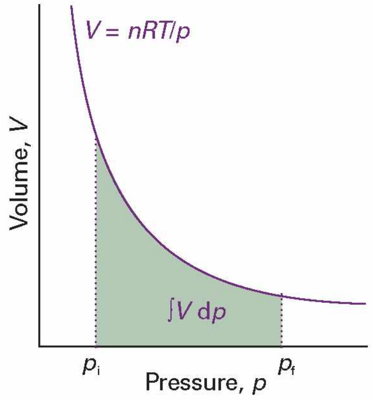

Fig. 3.22 The difference in Gibbs energy for a perfect gas at two pressures is equal to the area shown below the perfect-gas isotherm.

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

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

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

This expression shows that when the pressure is increased tenfold at room temperature, the molar Gibbs energy increases by $RT \ln 10 \approx 6$ 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

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

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

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

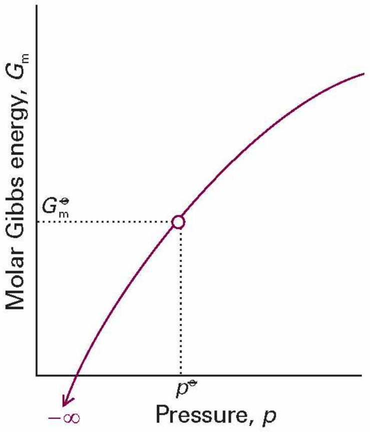

Fig. 3.23 The molar Gibbs energy potential of a perfect gas is proportional to ln p, and the standard state is reached at $p^\ominus$. Note that, as $p \to 0$, the molar Gibbs energy becomes negatively infinite.

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

Checklist of key ideas

☐ 1. Kelvin statement of the Second Law of thermodynamics: No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work.

☐ 2. The Second Law in terms of entropy: The entropy of an isolated system increases in the course of a spontaneous change: $\Delta S_{tot} > 0$.

☐ 3. The thermodynamic definition of entropy is $dS = dq_{rev}/T$. The statistical definition of entropy is given by the Boltzmann formula, $S = k \ln W$.

☐ 4. A Carnot cycle is a cycle composed of a sequence of isothermal and adiabatic reversible expansions and compressions.

☐ 5. The efficiency of a heat engine is $\varepsilon = |w|/q_h$. The Carnot efficiency is $\varepsilon_{rev} = 1 - T_c/T_h$.

☐ 6. The Kelvin scale is a thermodynamic temperature scale in which the triple point of water defines the point 273.16 K.

☐ 7. The Clausius inequality is $dS \geq dq/T$.

☐ 8. The normal transition temperature, T_{trs}, is the temperature at which two phases are in equilibrium at 1 atm. The entropy of transition at the transition temperature, $\Delta_{trs}S = \Delta_{trs}H/T_{trs}$.

☐ 9. Trouton's rule states that many normal liquids have approximately the same standard entropy of vaporization (about 85 J K^{-1} mol^{-1}).

☐ 10. The variation of entropy with temperature is given by

$$S(T_f) = S(T_i) + \int_{T_i}^{T_f} (C_p/T)dT.$$

☐ 11. The entropy of a substance is measured from the area under a graph of C_p/T against T, using the Debye extrapolation at low temperatures, $C_p = aT^3$ as $T \to 0$.

☐ 12. The Nernst heat theorem states that the entropy change accompanying any physical or chemical transformation approaches zero as the temperature approaches zero: $\Delta S \to 0$ as $T \to 0$ provided all the substances involved are perfectly ordered.

☐ 13. Third Law of thermodynamics: The entropy of all perfect crystalline substances is zero at $T = 0$.

☐ 14. The standard reaction entropy is calculated from $\Delta_r S^\ominus = \sum_{\text{Products}} \nu S_m^\ominus - \sum_{\text{Reactants}} \nu S_m^\ominus$.

☐ 15. The standard molar entropies of ions in solution are reported on a scale in which $S^\ominus(\text{H}^+, \text{aq}) = 0$ at all temperatures.

☐ 16. The Helmholtz energy is $A = U - TS$. The Gibbs energy is $G = H - TS$.

☐ 17. The criteria of spontaneity may be written as: (a) $\mathrm{d}S_{U,V} \geq 0$ and $\mathrm{d}U_{S,V} \leq 0$, or (b) $\mathrm{d}A_{T,V} \leq 0$ and $\mathrm{d}G_{T,p} \leq 0$.

☐ 18. The criterion of equilibrium at constant temperature and volume, $\mathrm{d}A_{T,V} = 0$. The criterion of equilibrium at constant temperature and pressure, $\mathrm{d}G_{T,p} = 0$.

☐ 19. The maximum work and the Helmholtz energy are related by $w_{\mathrm{max}} = \Delta A$. The maximum additional (non-expansion) work and the Gibbs energy are related by $w_{\mathrm{add,max}} = \Delta G$.

☐ 20. The standard Gibbs energy of reaction is given by $\Delta_r G^{\ominus} = \Delta_r H^{\ominus} - T\Delta_r S^{\ominus} = \sum_{\mathrm{Products}} \nu G_{\mathrm{m}}^{\ominus} - \sum_{\mathrm{Reactants}} \nu G_{\mathrm{m}}^{\ominus}$.

☐ 21. The standard Gibbs energy of formation ($\Delta_f G^{\ominus}$) is the standard reaction Gibbs energy for the formation of a compound from its elements in their reference states.

☐ 22. The standard Gibbs energy of reaction may be expressed in terms of $\Delta_f G^{\ominus}$, $\Delta_r G^{\ominus} = \sum_{\mathrm{Products}} \nu \Delta_f G^{\ominus} - \sum_{\mathrm{Reactants}} \nu \Delta_f G^{\ominus}$.

☐ 23. The standard Gibbs energies of formation of ions are reported on a scale in which $\Delta_f G^{\ominus}(\mathrm{H}^+, \mathrm{aq}) = 0$ at all temperatures.

☐ 24. The fundamental equation is $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$.

☐ 25. The Maxwell relations are listed in Table 3.5.

☐ 26. A thermodynamic equation of state is an expression for pressure in terms of thermodynamic quantities, $\pi_T = T(\partial p/\partial T)_V - p$.

☐ 27. The Gibbs energy is best described as a function of pressure and temperature, $\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T$. The variation of Gibbs energy with pressure and temperature are, respectively, $(\partial G/\partial p)_T = V$ and $(\partial G/\partial T)_p = -S$.

☐ 28. The temperature dependence of the Gibbs energy is given by the Gibbs–Helmholtz equation, $(\partial(G/T)/\partial T)_p = -H/T^2$.

☐ 29. For a condensed phase, the Gibbs energy varies with pressure as $G(p_f) = G(p_i) + V_{\mathrm{m}}\Delta p$. For a perfect gas, $G(p_f) = G(p_i) + nRT\ln(p_f/p_i)$.

Further reading[10]

Articles and texts

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Further information

Further information 3.1 *The Born equation*

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

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

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

where ε is the medium's permittivity. The permittivity of vacuum is $\varepsilon_0 = 8.854 \times 10^{-12}\ \mathrm{J^{-1}\ C^2\ m^{-1}}$. The relative permittivity (formerly called the 'dielectric constant') of a substance is defined as $\varepsilon_r = \varepsilon/\varepsilon_0$. Ions do not interact as strongly in a solvent of high relative permittivity (such as water, with $\varepsilon_r = 80$ at 293 K) as they do in a solvent of lower relative permittivity (such as ethanol, with $\varepsilon_r = 25$ at 293 K). See Chapter 18 for more details. The potential energy of a charge q_1 in the presence of a charge q_2 can be expressed in terms of the *Coulomb potential*, ϕ:

$$V = q_1\phi \qquad \phi = \frac{q_2}{4\pi\varepsilon r}$$

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

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

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

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

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

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

The work of charging an ion in a vacuum is obtained by setting $\varepsilon = \varepsilon_0$, the vacuum permittivity. The corresponding value for charging the ion in a medium is obtained by setting $\varepsilon = \varepsilon_r \varepsilon_0$, where ε_r is the relative permittivity of the medium. It follows that the change in molar Gibbs energy that accompanies the transfer of ions from a vacuum to a solvent is the difference of these two quantities:

$$\Delta_{solv}G^\ominus = \frac{z_i^2 e^2 N_A}{8\pi\varepsilon r_i} - \frac{z_i^2 e^2 N_A}{8\pi\varepsilon_0 r_i} = \frac{z_i^2 e^2 N_A}{8\pi\varepsilon_r\varepsilon_0 r_i} - \frac{z_i^2 e^2 N_A}{8\pi\varepsilon_0 r_i} = -\frac{z_i^2 e^2 N_A}{8\pi\varepsilon_0 r_i}\left(1 - \frac{1}{\varepsilon_r}\right)$$

which is eqn 3.42.

Further information 3.2 *Real gases: the fugacity*

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

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

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

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

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

Equation 3.54b is true for all gases whether real or perfect. Expressing it in terms of the fugacity by using eqn 3.58 turns it into

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

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

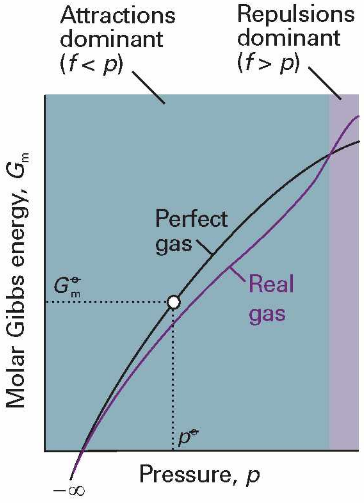

Fig. 3.24 The molar Gibbs energy of a real gas. As $p \to 0$, the molar Gibbs energy coincides with the value for a perfect gas (shown by the black line). When attractive forces are dominant (at intermediate pressures), the molar Gibbs energy is less than that of a perfect gas and the molecules have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

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

The difference between the two equations is

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

which can be rearranged into

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

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

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

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

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

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

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

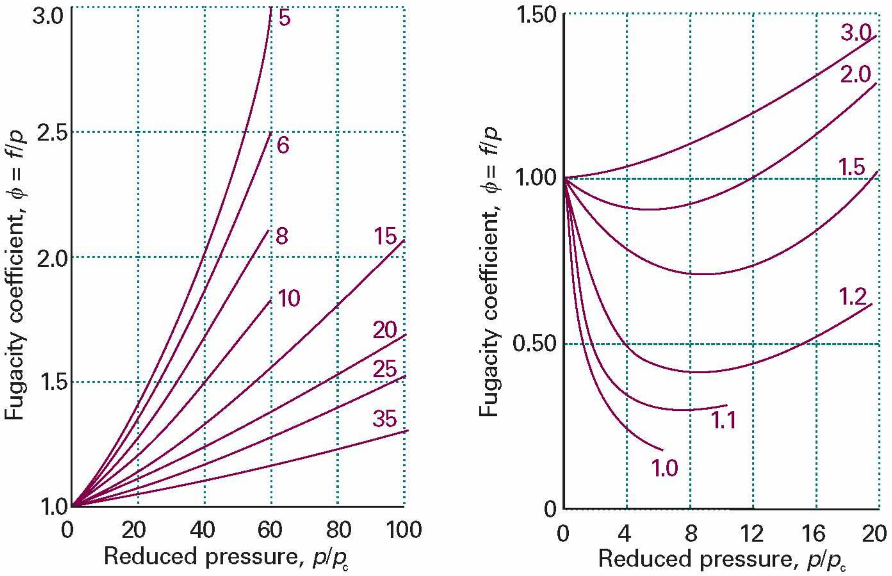

Fig. 3.25 The fugacity coefficient of a van der Waals gas plotted using the reduced variables of the gas. The curves are labelled with the reduced temperature $T_r = T/T_c$.

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

$$\ln \phi = \int_0^p \frac{Z-1}{p}\,\mathrm{d}p \qquad (3.60)$$

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

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

Figure 3.25, which has been calculated using the full van der Waals equation of state, shows how the fugacity coefficient depends on the pressure in terms of the reduced variables (Section 1.5). Because critical constants are available in Table 1.6, the graphs can be used for quick estimates of the fugacities of a wide range of gases. Table 3.6 gives some explicit values for nitrogen.

Synoptic table 3.6* The fugacity of nitrogen at 273 K

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

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

Discussion questions

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

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

3.3 The following expressions have been used to establish criteria for spontaneous change: $\Delta S_{\text{tot}} > 0$, $\mathrm{d}S_{U,V} \ge 0$ and $\mathrm{d}U_{S,V} \le 0$, $\mathrm{d}A_{T,V} \le 0$, and $\mathrm{d}G_{T,p} \le 0$. Discuss the origin, significance, and applicability of each criterion.

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

3.5 Discuss the physical interpretation of any one Maxwell relation.

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

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

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

Exercises

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

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

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

3.2(a) Calculate the molar entropy of a constant-volume sample of neon at 500 K given that it is 146.22 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 $C_{p,\mathrm{m}} = \frac{5}{2}R$, 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 $C_{p,\mathrm{m}} = \frac{7}{2}R$, 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 $C_{V,\mathrm{m}} = 27.5$ 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 $C_{V,\mathrm{m}} = 27.5$ 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 $C_{V,\mathrm{m}} = 28.8$ 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 $C_{V,\mathrm{m}} = 28.8$ 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 $p_{\mathrm{ex}} = 0$, 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 $p_{\mathrm{ex}} = 0$, 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.

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

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

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

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

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

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

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

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

Problems*

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

Numerical problems

3.1 Calculate the difference in molar entropy (a) between liquid water and ice at −5°C, (b) between liquid water and its vapour at 95°C and 1.00 atm. The differences in heat capacities on melting and on vaporization are 37.3 $J\ K^{-1}\ mol^{-1}$ 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 is 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

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

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

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

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

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

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

3.12 From standard enthalpies of formation, standard entropies, and standard heat capacities available from tables in the *Data section*, calculate the standard enthalpies and entropies at 298 K and 398 K for the reaction $\mathrm{CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)}$. Assume that the heat capacities are constant over the temperature range involved.

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

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

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

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

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

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

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

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

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

3.16 Calculate $\Delta_\mathrm{r}G^\ominus(375\ \mathrm{K})$ for the reaction $\mathrm{2\,CO(g) + O_2(g) \rightarrow 2\,CO_2(g)}$ from the value of $\Delta_\mathrm{r}G^\ominus(298\ \mathrm{K})$, $\Delta_\mathrm{r}H^\ominus(298\ \mathrm{K})$, and the Gibbs–Helmholtz equation.

3.17 Estimate the standard reaction Gibbs energy of $\mathrm{N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g)}$ at (a) 500 K, (b) 1000 K from their values at 298 K.

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

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

Theoretical problems

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

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

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

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

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

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

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

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

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

3.28 Derive the thermodynamic equation of state

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

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

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

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

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

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

3.33 Suppose that S is regarded as a function of p and T. Show that $TdS = C_p dT - \alpha TVdp$. Hence, show that the energy transferred as heat when the pressure on an incompressible liquid or solid is increased by Δp is equal to $-\alpha TV\Delta p$. Evaluate q when the pressure acting on 100 cm^3 of mercury at 0°C is increased by 1.0 kbar. ($\alpha = 1.82 \times 10^{-4}\ \text{K}^{-1}$.)

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

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

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

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

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

3.38 In biological cells, the energy released by the oxidation of foods (*Impact on Biology I2.2*) is stored in adenosine triphosphate (ATP or ATP^{4-}). The essence of ATP's action is its ability to lose its terminal phosphate group by hydrolysis and to form adenosine diphosphate (ADP or ADP^{3-}):

$$\text{ATP}^{4-}(\text{aq}) + \text{H}_2\text{O(l)} \rightarrow \text{ADP}^{3-}(\text{aq}) + \text{HPO}_4^{2-}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$$

At pH = 7.0 and 37°C (310 K, blood temperature) the enthalpy and Gibbs energy of hydrolysis are $\Delta_r H = -20$ kJ mol^{-1} and $\Delta_r G = -31$ kJ mol^{-1}, respectively. Under these conditions, the hydrolysis of 1 mol ATP^{4-}(aq) results in the extraction of up to 31 kJ of energy that can be used to do non-expansion work, such as the synthesis of proteins from amino acids, muscular contraction, and the activation of neuronal circuits in our brains. (a) Calculate and account for the sign of the entropy of hydrolysis of ATP at pH = 7.0 and 310 K. (b) Suppose that the radius of a typical biological cell is 10 μm and that inside it 10^6 ATP molecules are hydrolysed each second. What is the power density of the cell in watts per cubic metre (1 W = 1 J s^{-1})? A computer battery delivers about 15 W and has a volume of 100 cm^3. Which has the greater power density, the cell or the battery? (c) The formation of glutamine from glutamate and ammonium ions requires 14.2 kJ mol^{-1} of energy input. It is driven by the hydrolysis of ATP to ADP mediated by the enzyme glutamine synthetase. How many moles of ATP must be hydrolysed to form 1 mol glutamine?

3.39‡ In 1995, the Intergovernmental Panel on Climate Change (IPCC) considered a global average temperature rise of 1.0–3.5°C likely by the year 2100, with 2.0°C its best estimate. Because water vapour is itself a greenhouse gas, the increase in water vapour content of the atmosphere is of some concern to climate change experts. Predict the relative increase in water vapour in the atmosphere based on a temperature rises of 2.0 K, assuming that the relative humidity remains constant. (The present global mean temperature is 290 K, and the equilibrium vapour pressure of water at that temperature is 0.0189 bar.)

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

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

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

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

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

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

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

4

Physical transformations of pure substances

The discussion of the phase transitions of pure substances is among the simplest applications of thermodynamics to chemistry. We shall see that a phase diagram is a map of the pressures and temperatures at which each phase of a substance is the most stable. First, we describe the interpretation of empirically determined phase diagrams for a selection of materials. Then we turn to a consideration of the factors that determine the positions and shapes of the boundaries between the regions on a phase diagram. The practical importance of the expressions we derive is that they show how the vapour pressure of a substance varies with temperature and how the melting point varies with pressure. We shall see that the transitions between phases can be classified by noting how various thermodynamic functions change when the transition occurs. This chapter also introduces the chemical potential, a property that is at the centre of discussions of phase transitions and chemical reactions.

Vaporization, melting, and the conversion of graphite to diamond are all examples of changes of phase without change of chemical composition. In this chapter we describe such processes thermodynamically, using as the guiding principle the tendency of systems at constant temperature and pressure to minimize their Gibbs energy.

Phase diagrams

One of the most succinct ways of presenting the physical changes of state that a substance can undergo is in terms of its phase diagram. We present the concept in this section.

4.1 The stabilities of phases

A **phase** of a substance is a form of matter that is uniform throughout in chemical composition and physical state. Thus, we speak of solid, liquid, and gas phases of a substance, and of its various solid phases, such as the white and black allotropes of phosphorus. A **phase transition**, the spontaneous conversion of one phase into another phase, occurs at a characteristic temperature for a given pressure. Thus, at 1 atm, ice is the stable phase of water below 0°C, but above 0°C liquid water is more stable. This difference indicates that below 0°C the Gibbs energy decreases as liquid water changes into ice and that above 0°C the Gibbs energy decreases as ice changes into liquid water. The **transition temperature**, T_{trs}, is the temperature at which the two phases are in equilibrium and the Gibbs energy is minimized at the prevailing pressure.

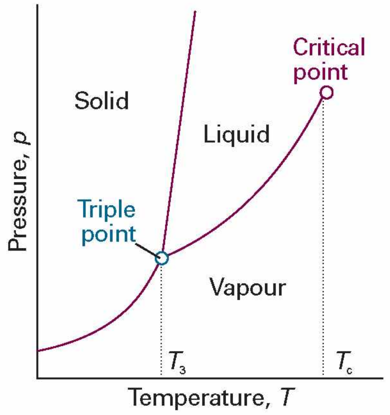

Fig. 4.1 The general regions of pressure and temperature where solid, liquid, or gas is stable (that is, has minimum molar Gibbs energy) are shown on this phase diagram. For example, the solid phase is the most stable phase at low temperatures and high pressures. In the following paragraphs we locate the precise boundaries between the regions.

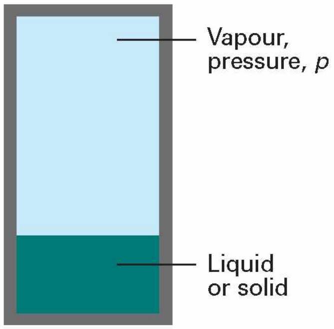

Fig. 4.2 The vapour pressure of a liquid or solid is the pressure exerted by the vapour in equilibrium with the condensed phase.

Comment 4.1

The *NIST Chemistry WebBook* is a good source of links to online databases of data on phase transitions.

As we stressed at the beginning of Chapter 3, we must distinguish between the thermodynamic description of a phase transition and the rate at which the transition occurs. A transition that is predicted from thermodynamics to be spontaneous may occur too slowly to be significant in practice. For instance, at normal temperatures and pressures the molar Gibbs energy of graphite is lower than that of diamond, so there is a thermodynamic tendency for diamond to change into graphite. However, for this transition to take place, the C atoms must change their locations, which is an immeasurably slow process in a solid except at high temperatures. The discussion of the rate of attainment of equilibrium is a kinetic problem and is outside the range of thermodynamics. In gases and liquids the mobilities of the molecules allow phase transitions to occur rapidly, but in solids thermodynamic instability may be frozen in. Thermodynamically unstable phases that persist because the transition is kinetically hindered are called **metastable phases**. Diamond is a metastable phase of carbon under normal conditions.

4.2 Phase boundaries

The **phase diagram** of a substance shows the regions of pressure and temperature at which its various phases are thermodynamically stable (Fig. 4.1). The lines separating the regions, which are called **phase boundaries**, show the values of p and T at which two phases coexist in equilibrium.

Consider a liquid sample of a pure substance in a closed vessel. The pressure of a vapour in equilibrium with the liquid is called the **vapour pressure** of the substance (Fig. 4.2). Therefore, the liquid–vapour phase boundary in a phase diagram shows how the vapour pressure of the liquid varies with temperature. Similarly, the solid–vapour phase boundary shows the temperature variation of the **sublimation vapour pressure**, the vapour pressure of the solid phase. The vapour pressure of a substance increases with temperature because at higher temperatures more molecules have sufficient energy to escape from their neighbours.

(a) Critical points and boiling points

When a liquid is heated in an open vessel, the liquid vaporizes from its surface. At the temperature at which its vapour pressure would be equal to the external pressure, vaporization can occur throughout the bulk of the liquid and the vapour can expand freely into the surroundings. The condition of free vaporization throughout the liquid is called **boiling**. The temperature at which the vapour pressure of a liquid is equal to the external pressure is called the **boiling temperature** at that pressure. For the special case of an external pressure of 1 atm, the boiling temperature is called the **normal boiling point**, T_b. With the replacement of 1 atm by 1 bar as standard pressure, there is some advantage in using the **standard boiling point** instead: this is the temperature at which the vapour pressure reaches 1 bar. Because 1 bar is slightly less than 1 atm (1.00 bar = 0.987 atm), the standard boiling point of a liquid is slightly lower than its normal boiling point. The normal boiling point of water is 100.0°C; its standard boiling point is 99.6°C.

Boiling does not occur when a liquid is heated in a rigid, closed vessel. Instead, the vapour pressure, and hence the density of the vapour, rise as the temperature is raised (Fig. 4.3). At the same time, the density of the liquid decreases slightly as a result of its expansion. There comes a stage when the density of the vapour is equal to that of the remaining liquid and the surface between the two phases disappears. The temperature at which the surface disappears is the **critical temperature**, T_c, of the substance. We first encountered this property in Section 1.3d. The vapour pressure at the critical temperature is called the **critical pressure**, p_c. At and above the critical temperature, a single uniform phase called a **supercritical fluid** fills the container and an interface no longer exists. That is, above the critical temperature, the liquid phase of the substance does not exist.

(b) Melting points and triple points

The temperature at which, under a specified pressure, the liquid and solid phases of a substance coexist in equilibrium is called the **melting temperature**. Because a substance melts at exactly the same temperature as it freezes, the melting temperature of a substance is the same as its **freezing temperature**. The freezing temperature when the pressure is 1 atm is called the **normal freezing point**, T_f, and its freezing point when the pressure is 1 bar is called the **standard freezing point**. The normal and standard freezing points are negligibly different for most purposes. The normal freezing point is also called the **normal melting point**.

There is a set of conditions under which three different phases of a substance (typically solid, liquid, and vapour) all simultaneously coexist in equilibrium. These conditions are represented by the **triple point**, a point at which the three phase boundaries meet. The temperature at the triple point is denoted T_3. The triple point of a pure substance is outside our control: it occurs at a single definite pressure and temperature characteristic of the substance. The triple point of water lies at 273.16 K and 611 Pa (6.11 mbar, 4.58 Torr), and the three phases of water (ice, liquid water, and water vapour) coexist in equilibrium at no other combination of pressure and temperature. This invariance of the triple point is the basis of its use in the definition of the thermodynamic temperature scale (Section 3.2c).

As we can see from Fig. 4.1, the triple point marks the lowest pressure at which a liquid phase of a substance can exist. If (as is common) the slope of the solid–liquid phase boundary is as shown in the diagram, then the triple point also marks the lowest temperature at which the liquid can exist; the critical temperature is the upper limit.

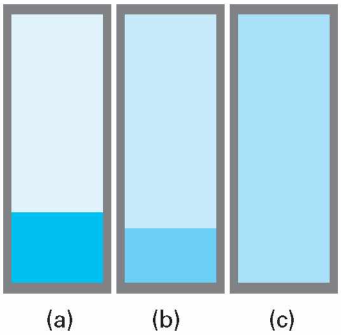

Fig. 4.3 (a) A liquid in equilibrium with its vapour. (b) When a liquid is heated in a sealed container, the density of the vapour phase increases and that of the liquid decreases slightly. There comes a stage, (c), at which the two densities are equal and the interface between the fluids disappears. This disappearance occurs at the critical temperature. The container needs to be strong: the critical temperature of water is 374°C and the vapour pressure is then 218 atm.

IMPACT ON CHEMICAL ENGINEERING AND TECHNOLOGY

I4.1 Supercritical fluids

Supercritical carbon dioxide, $scCO_2$, is the centre of attention for an increasing number of solvent-based processes. The critical temperature of CO_2, 304.2 K (31.0°C) and its critical pressure, 72.9 atm, are readily accessible, it is cheap, and it can readily be recycled. The density of $scCO_2$ at its critical point is 0.45 g cm^{-3}. However, the transport properties of any supercritical fluid depend strongly on its density, which in turn is sensitive to the pressure and temperature. For instance, densities may be adjusted from a gas-like 0.1 g cm^{-3} to a liquid-like 1.2 g cm^{-3}. A useful rule of thumb is that the solubility of a solute is an exponential function of the density of the supercritical fluid, so small increases in pressure, particularly close to the critical point, can have very large effects on solubility.

A great advantage of $scCO_2$ is that there are no noxious residues once the solvent has been allowed to evaporate, so, coupled with its low critical temperature, $scCO_2$ is ideally suited to food processing and the production of pharmaceuticals. It is used, for instance, to remove caffeine from coffee. The supercritical fluid is also increasingly being used for dry cleaning, which avoids the use of carcinogenic and environmentally deleterious chlorinated hydrocarbons.

Supercritical CO_2 has been used since the 1960s as a mobile phase in *supercritical fluid chromatography* (SFC), but it fell out of favour when the more convenient technique of high-performance liquid chromatography (HPLC) was introduced. However, interest in SFC has returned, and there are separations possible in SFC that cannot easily be achieved by HPLC, such as the separation of lipids and of phospholipids. Samples as small as 1 pg can be analysed. The essential advantage of SFC is that diffusion coefficients in supercritical fluids are an order of magnitude greater than in liquids, so there is less resistance to the transfer of solutes through the column, with the result that separations may be effected rapidly or with high resolution.

The principal problem with $scCO_2$, though, is that the fluid is not a very good solvent and surfactants are needed to induce many potentially interesting solutes to dissolve. Indeed, $scCO_2$-based dry cleaning depends on the availability of cheap surfactants; so too does the use of $scCO_2$ as a solvent for homogeneous catalysts, such as metal complexes. There appear to be two principal approaches to solving the solubilization problem. One solution is to use fluorinated and siloxane-based polymeric stabilizers, which allow polymerization reactions to proceed in $scCO_2$. The disadvantage of these stabilizers for commercial use is their great expense. An alternative and much cheaper approach is poly(ether-carbonate) copolymers. The copolymers can be made more soluble in $scCO_2$ by adjusting the ratio of ether and carbonate groups.

The critical temperature of water is 374°C and its pressure is 218 atm. The conditions for using scH_2O are therefore much more demanding than for $scCO_2$ and the properties of the fluid are highly sensitive to pressure. Thus, as the density of scH_2O decreases, the characteristics of a solution change from those of an aqueous solution through those of a non-aqueous solution and eventually to those of a gaseous solution. One consequence is that reaction mechanisms may change from those involving ions to those involving radicals.

4.3 Three typical phase diagrams

We shall now see how these general features appear in the phase diagrams of pure substances.

(a) Carbon dioxide

The phase diagram for carbon dioxide is shown in Fig. 4.4. The features to notice include the positive slope of the solid–liquid boundary (the direction of this line is characteristic of most substances), which indicates that the melting temperature of solid carbon dioxide rises as the pressure is increased. Notice also that, as the triple point lies above 1 atm, the liquid cannot exist at normal atmospheric pressures whatever the temperature, and the solid sublimes when left in the open (hence the name 'dry ice'). To obtain the liquid, it is necessary to exert a pressure of at least 5.11 atm. Cylinders of carbon dioxide generally contain the liquid or compressed gas; at 25°C that implies a vapour pressure of 67 atm if both gas and liquid are present in equilibrium. When the gas squirts through the throttle it cools by the Joule–Thomson effect, so when it emerges into a region where the pressure is only 1 atm, it condenses into a finely divided snow-like solid.

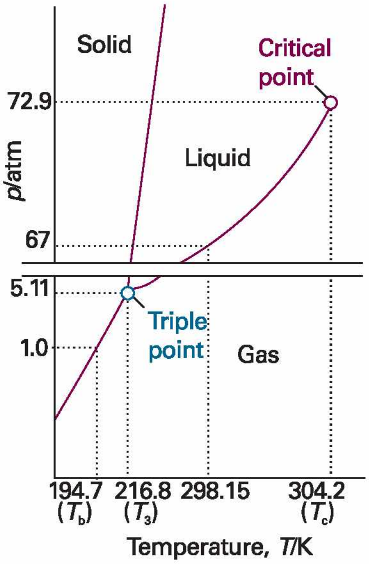

Fig. 4.4 The experimental phase diagram for carbon dioxide. Note that, as the triple point lies at pressures well above atmospheric, liquid carbon dioxide does not exist under normal conditions (a pressure of at least 5.11 atm must be applied).

(b) Water

Figure 4.5 is the phase diagram for water. The liquid–vapour boundary in the phase diagram summarizes how the vapour pressure of liquid water varies with temperature. It also summarizes how the boiling temperature varies with pressure: we simply read off the temperature at which the vapour pressure is equal to the prevailing atmospheric pressure. The solid–liquid boundary shows how the melting temperature varies with the pressure. Its very steep slope indicates that enormous pressures are needed to bring about significant changes. Notice that the line has a negative slope up to 2 kbar, which means that the melting temperature falls as the pressure is raised. The reason for this almost unique behaviour can be traced to the decrease in volume that occurs on melting, and hence it being more favourable for the solid to transform into the liquid as the pressure is raised. The decrease in volume is a result of the very

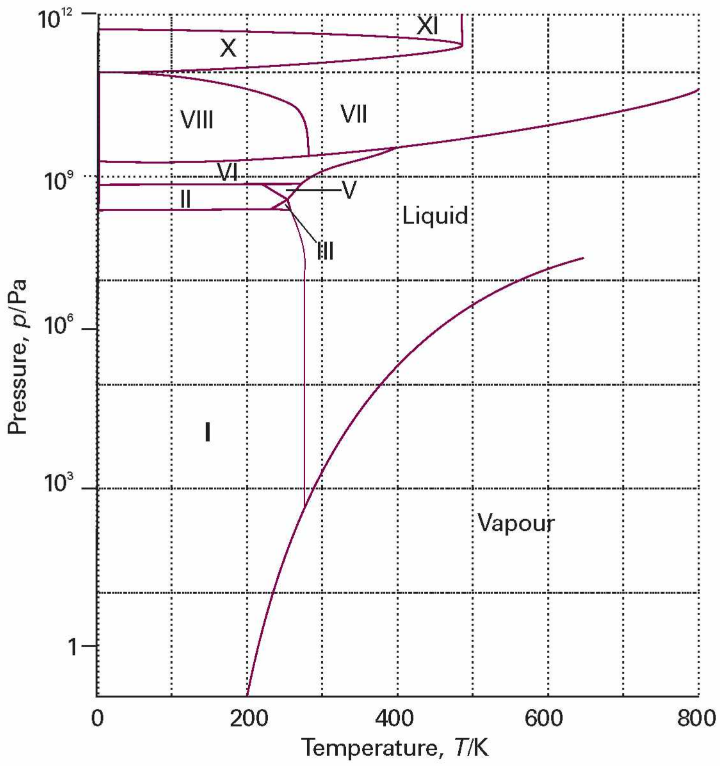

Fig. 4.5 The experimental phase diagram for water showing the different solid phases.

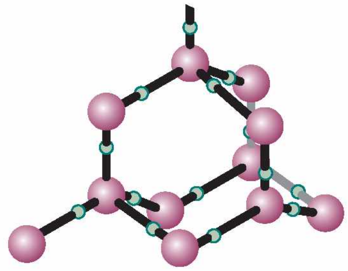

Fig. 4.6 A fragment of the structure of ice (ice-I). Each O atom is linked by two covalent bonds to H atoms and by two hydrogen bonds to a neighbouring O atom, in a tetrahedral array.

open molecular structure of ice: as shown in Fig 4.6, the water molecules are held apart, as well as together, by the hydrogen bonds between them but the structure partially collapses on melting and the liquid is denser than the solid.

Figure 4.5 shows that water has one liquid phase but many different solid phases other than ordinary ice ('ice I', shown in Fig. 4.5). Some of these phases melt at high temperatures. Ice VII, for instance, melts at 100°C but exists only above 25 kbar. Note that five more triple points occur in the diagram other than the one where vapour, liquid, and ice I coexist. Each one occurs at a definite pressure and temperature that cannot be changed. The solid phases of ice differ in the arrangement of the water molecules: under the influence of very high pressures, hydrogen bonds buckle and the H_2O molecules adopt different arrangements. These **polymorphs**, or different solid phases, of ice may be responsible for the advance of glaciers, for ice at the bottom of glaciers experiences very high pressures where it rests on jagged rocks.

(c) Helium

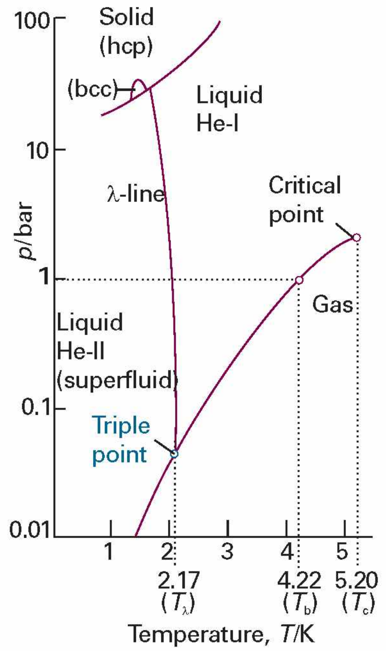

Fig. 4.7 The phase diagram for helium (^{4}He). The λ-line marks the conditions under which the two liquid phases are in equilibrium. Helium-II is the superfluid phase. Note that a pressure of over 20 bar must be exerted before solid helium can be obtained. The labels hcp and bcc denote different solid phases in which the atoms pack together differently: hcp denotes hexagonal closed packing and bcc denotes body-centred cubic (see Section 20.1 for a description of these structures).

Figure 4.7 shows the phase diagram of helium. Helium behaves unusually at low temperatures. For instance, the solid and gas phases of helium are never in equilibrium however low the temperature: the atoms are so light that they vibrate with a large-amplitude motion even at very low temperatures and the solid simply shakes itself apart. Solid helium can be obtained, but only by holding the atoms together by applying pressure.

When considering helium at low temperatures it is necessary to distinguish between the isotopes ^{3}He and ^{4}He. Pure helium-4 has two liquid phases. The phase marked He-I in the diagram behaves like a normal liquid; the other phase, He-II, is a **superfluid**;

it is so called because it flows without viscosity.[1] Provided we discount the liquid crystalline substances discussed in Section 6.6, helium is the only known substance with a liquid–liquid boundary, shown as the **λ-line** (lambda line) in Fig. 4.7. The phase diagram of helium-3 differs from the phase diagram of helium-4, but it also possesses a superfluid phase. Helium-3 is unusual in that the entropy of the liquid is lower than that of the solid, and melting is exothermic.

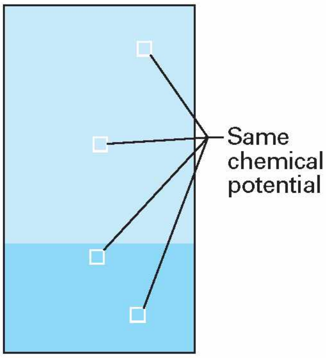

Fig. 4.8 When two or more phases are in equilibrium, the chemical potential of a substance (and, in a mixture, a component) is the same in each phase and is the same at all points in each phase.

Phase stability and phase transitions

We shall now see how thermodynamic considerations can account for the features of the phase diagrams we have just described. All our considerations will be based on the Gibbs energy of a substance, and in particular on its molar Gibbs energy, G_m. In fact, this quantity will play such an important role in this chapter and the rest of the text that we give it a special name and symbol, the **chemical potential**, μ (mu). For a one-component system, 'molar Gibbs energy' and 'chemical potential' are synonyms, so $\mu = G_m$, but in Chapter 5 we shall see that chemical potential has a broader significance and a more general definition. The name 'chemical potential' is also instructive: as we develop the concept, we shall see that μ is a measure of the potential that a substance has for undergoing change in a system. In this chapter, it reflects the potential of a substance to undergo physical change. In Chapter 7 we shall see that μ is the potential of a substance to undergo chemical change.

4.4 The thermodynamic criterion of equilibrium

We base our discussion on the following consequence of the Second Law: *at equilibrium, the chemical potential of a substance is the same throughout a sample, regardless of how many phases are present*. When the liquid and solid phases of a substance are in equilibrium, the chemical potential of the substance is the same throughout the system (Fig. 4.8).

To see the validity of this remark, consider a system in which the chemical potential of a substance is μ_1 at one location and μ_2 at another location. The locations may be in the same or in different phases. When an amount dn of the substance is transferred from one location to the other, the Gibbs energy of the system changes by $-\mu_1 \mathrm{d}n$ when material is removed from location 1, and it changes by $+\mu_2 \mathrm{d}n$ when that material is added to location 2. The overall change is therefore $\mathrm{d}G = (\mu_2 - \mu_1)\mathrm{d}n$. If the chemical potential at location 1 is higher than that at location 2, the transfer is accompanied by a decrease in G, and so has a spontaneous tendency to occur. Only if $\mu_1 = \mu_2$ is there no change in G, and only then is the system at equilibrium. We conclude that the transition temperature, T_{trs}, is the temperature at which the chemical potentials of two phases are equal.

4.5 The dependence of stability on the conditions

At low temperatures and provided the pressure is not too low, the solid phase of a substance has the lowest chemical potential and is therefore the most stable phase. However, the chemical potentials of different phases change with temperature in different ways, and above a certain temperature the chemical potential of another phase (perhaps another solid phase, a liquid, or a gas) may turn out to be the lowest. When that happens, a transition to the second phase is spontaneous and occurs if it is kinetically feasible to do so.

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[1] Recent work has suggested that water may also have a superfluid liquid phase.

(a) The temperature dependence of phase stability

The temperature dependence of the Gibbs energy is expressed in terms of the entropy of the system by eqn 3.50 ($(\partial G/\partial T)_p = -S$). Because the chemical potential of a pure substance is just another name for its molar Gibbs energy, it follows that

$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S_m \tag{4.1}$$

This relation shows that, as the temperature is raised, the chemical potential of a pure substance decreases: $S_m > 0$ for all substances, so the slope of a plot of μ against T is negative.

Equation 4.1 implies that the slope of a plot of μ against temperature is steeper for gases than for liquids, because $S_m(g) > S_m(l)$. The slope is also steeper for a liquid than the corresponding solid, because $S_m(l) > S_m(s)$ almost always. These features are illustrated in Fig. 4.9. The steep negative slope of $\mu(l)$ results in its falling below $\mu(s)$ when the temperature is high enough, and then the liquid becomes the stable phase: the solid melts. The chemical potential of the gas phase plunges steeply downwards as the temperature is raised (because the molar entropy of the vapour is so high), and there comes a temperature at which it lies lowest. Then the gas is the stable phase and vaporization is spontaneous.

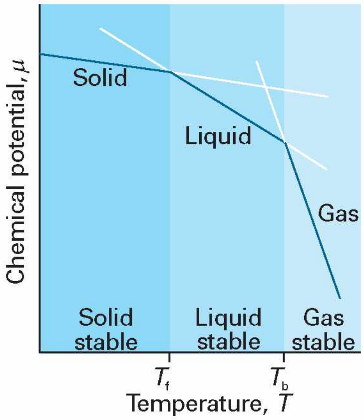

Fig. 4.9 The schematic temperature dependence of the chemical potential of the solid, liquid, and gas phases of a substance (in practice, the lines are curved). The phase with the lowest chemical potential at a specified temperature is the most stable one at that temperature. The transition temperatures, the melting and boiling temperatures (T_f and T_b, respectively), are the temperatures at which the chemical potentials of the two phases are equal.

(b) The response of melting to applied pressure

Most substances melt at a higher temperature when subjected to pressure. It is as though the pressure is preventing the formation of the less dense liquid phase. Exceptions to this behaviour include water, for which the liquid is denser than the solid. Application of pressure to water encourages the formation of the liquid phase. That is, water freezes at a lower temperature when it is under pressure.

We can rationalize the response of melting temperatures to pressure as follows. The variation of the chemical potential with pressure is expressed (from the second of eqn 3.50) by

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V_m \tag{4.2}$$

This equation shows that the slope of a plot of chemical potential against pressure is equal to the molar volume of the substance. An increase in pressure raises the chemical potential of any pure substance (because $V_m > 0$). In most cases, $V_m(l) > V_m(s)$ and the equation predicts that an increase in pressure increases the chemical potential of the liquid more than that of the solid. As shown in Fig. 4.10a, the effect of pressure in such

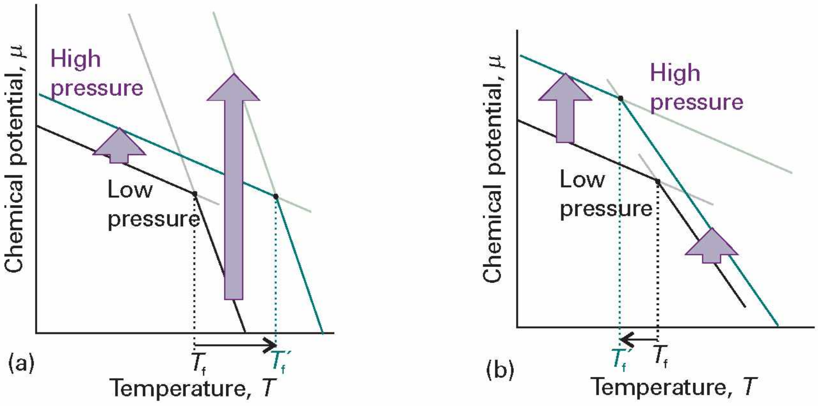

Fig. 4.10 The pressure dependence of the chemical potential of a substance depends on the molar volume of the phase. The lines show schematically the effect of increasing pressure on the chemical potential of the solid and liquid phases (in practice, the lines are curved), and the corresponding effects on the freezing temperatures. (a) In this case the molar volume of the solid is smaller than that of the liquid and $\mu(s)$ increases less than $\mu(l)$. As a result, the freezing temperature rises. (b) Here the molar volume is greater for the solid than the liquid (as for water), $\mu(s)$ increases more strongly than $\mu(l)$, and the freezing temperature is lowered.

a case is to raise the melting temperature slightly. For water, however, $V_m(l) < V_m(s)$, and an increase in pressure increases the chemical potential of the solid more than that of the liquid. In this case, the melting temperature is lowered slightly (Fig. 4.10b).

Example 4.1 *Assessing the effect of pressure on the chemical potential*

Calculate the effect on the chemical potentials of ice and water of increasing the pressure from 1.00 bar to 2.00 bar at 0°C. The density of ice is 0.917 g cm^{-3} and that of liquid water is 0.999 g cm^{-3} under these conditions.

Method From eqn 4.2, we know that the change in chemical potential of an incompressible substance when the pressure is changed by Δp is $\Delta\mu = V_m\Delta p$. Therefore, to answer the question, we need to know the molar volumes of the two phases of water. These values are obtained from the mass density, ρ, and the molar mass, M, by using $V_m = M/\rho$. We therefore use the expression $\Delta\mu = M\Delta p/\rho$.

Answer The molar mass of water is 18.02 g mol^{-1} (1.802×10^{-2} kg mol^{-1}); therefore,

$$\Delta\mu(\text{ice}) = \frac{(1.802\times10^{-2}\ \text{kg mol}^{-1})\times(1.00\times10^{5}\ \text{Pa})}{917\ \text{kg m}^{-3}} = +1.97\ \text{J mol}^{-1}$$

$$\Delta\mu(\text{water}) = \frac{(1.802\times10^{-2}\ \text{kg mol}^{-1})\times(1.00\times10^{5}\ \text{Pa})}{999\ \text{kg m}^{-3}} = +1.80\ \text{J mol}^{-1}$$

We interpret the numerical results as follows: the chemical potential of ice rises more sharply than that of water, so if they are initially in equilibrium at 1 bar, then there will be a tendency for the ice to melt at 2 bar.

Self-test 4.1 Calculate the effect of an increase in pressure of 1.00 bar on the liquid and solid phases of carbon dioxide (of molar mass 44.0 g mol^{-1}) in equilibrium with densities 2.35 g cm^{-3} and 2.50 g cm^{-3}, respectively.

[$\Delta\mu(l) = +1.87$ J mol^{-1}, $\Delta\mu(s) = +1.76$ J mol^{-1}; solid forms]

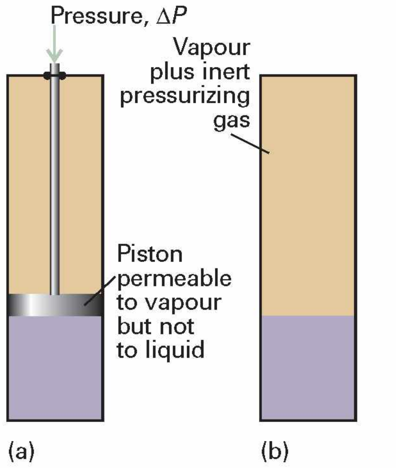

Fig. 4.11 Pressure may be applied to a condensed phases either (a) by compressing the condensed phase or (b) by subjecting it to an inert pressurizing gas. When pressure is applied, the vapour pressure of the condensed phase increases.

(c) The effect of applied pressure on vapour pressure

When pressure is applied to a condensed phase, its vapour pressure rises: in effect, molecules are squeezed out of the phase and escape as a gas. Pressure can be exerted on the condensed phases mechanically or by subjecting it to the applied pressure of an inert gas (Fig. 4.11); in the latter case, the vapour pressure is the partial pressure of the vapour in equilibrium with the condensed phase, and we speak of the **partial vapour pressure** of the substance. One complication (which we ignore here) is that, if the condensed phase is a liquid, then the pressurizing gas might dissolve and change the properties of the liquid. Another complication is that the gas phase molecules might attract molecules out of the liquid by the process of **gas solvation**, the attachment of molecules to gas phase species.

As shown in the following *Justification*, the quantitative relation between the vapour pressure, p, when a pressure ΔP is applied and the vapour pressure, p^*, of the liquid in the absence of an additional pressure is

$$p = p^* e^{V_m(l)\Delta P/RT} \qquad (4.3)$$

This equation shows how the vapour pressure increases when the pressure acting on the condensed phase is increased.

Justification 4.1 *The vapour pressure of a pressurized liquid*

We calculate the vapour pressure of a pressurized liquid by using the fact that at equilibrium the chemical potentials of the liquid and its vapour are equal: $\mu(\mathrm{l}) = \mu(\mathrm{g})$. It follows that, for any change that preserves equilibrium, the resulting change in $\mu(\mathrm{l})$ must be equal to the change in $\mu(\mathrm{g})$; therefore, we can write $\mathrm{d}\mu(\mathrm{g}) = \mathrm{d}\mu(\mathrm{l})$. When the pressure P on the liquid is increased by $\mathrm{d}P$, the chemical potential of the liquid changes by $\mathrm{d}\mu(\mathrm{l}) = V_\mathrm{m}(\mathrm{l})\mathrm{d}P$. The chemical potential of the vapour changes by $\mathrm{d}\mu(\mathrm{g}) = V_\mathrm{m}(\mathrm{g})\mathrm{d}p$ where $\mathrm{d}p$ is the change in the vapour pressure we are trying to find. If we treat the vapour as a perfect gas, the molar volume can be replaced by $V_\mathrm{m}(\mathrm{g}) = RT/p$, and we obtain

$$\mathrm{d}\mu(\mathrm{g}) = \frac{RT\mathrm{d}p}{p}$$

Next, we equate the changes in chemical potentials of the vapour and the liquid:

$$\frac{RT\mathrm{d}p}{p} = V_\mathrm{m}(\mathrm{l})\mathrm{d}P$$

We can integrate this expression once we know the limits of integration.

When there is no additional pressure acting on the liquid, P (the pressure experienced by the liquid) is equal to the normal vapour pressure p^*, so when $P = p^*$, $p = p^*$ too. When there is an additional pressure ΔP on the liquid, with the result that $P = p + \Delta P$, the vapour pressure is p (the value we want to find). Provided the effect of pressure on the vapour pressure is small (as will turn out to be the case) a good approximation is to replace the p in $p + \Delta P$ by p^* itself, and to set the upper limit of the integral to $p^* + \Delta P$. The integrations required are therefore as follows:

$$RT\int_{p^*}^{p}\frac{\mathrm{d}p}{p} = \int_{p^*}^{p^*+\Delta P} V_\mathrm{m}(\mathrm{l})\mathrm{d}P$$

We now divide both sides by RT and assume that the molar volume of the liquid is the same throughout the small range of pressures involved:

$$\int_{p^*}^{p}\frac{\mathrm{d}p}{p} = \frac{V_\mathrm{m}(\mathrm{l})}{RT}\int_{p^*}^{p^*+\Delta P}\mathrm{d}P$$

Then both integrations are straightforward, and lead to

$$\ln\frac{p}{p^*} = \frac{V_\mathrm{m}(\mathrm{l})}{RT}\Delta P$$

which rearranges to eqn 4.3 because $\mathrm{e}^{\ln x} = x$.

Illustration 4.1 *The effect of applied pressure on the vapour pressure of liquid water*

For water, which has density 0.997 g cm^{-3} at 25°C and therefore molar volume 18.1 cm^3 mol^{-1}, when the pressure is increased by 10 bar (that is, $\Delta P = 1.0 \times 10^5$ Pa)

$$\frac{V_\mathrm{m}(\mathrm{l})\Delta P}{RT} = \frac{(1.81\times10^{-5}\ \mathrm{m^3\ mol^{-1}})\times(1.0\times10^{6}\ \mathrm{Pa})}{(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})\times(298\ \mathrm{K})} = \frac{1.81\times1.0\times10}{8.3145\times298}$$

where we have used 1 J = 1 Pa m^3. It follows that $p = 1.0073p^*$, an increase of 0.73 per cent.

Self-test 4.2 Calculate the effect of an increase in pressure of 100 bar on the vapour pressure of benzene at 25°C, which has density 0.879 g cm^{-3}. [43 per cent]

4.6 The location of phase boundaries

We can find the precise locations of the phase boundaries—the pressures and temperatures at which two phases can coexist—by making use of the fact that, when two phases are in equilibrium, their chemical potentials must be equal. Therefore, where the phases α and β are in equilibrium,

$$\mu_\alpha(p,T) = \mu_\beta(p,T) \tag{4.4}$$

By solving this equation for p in terms of T, we get an equation for the phase boundary.

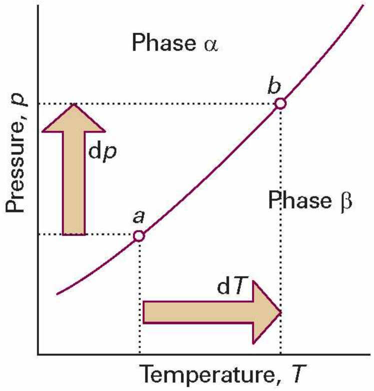

Fig. 4.12 When pressure is applied to a system in which two phases are in equilibrium (at a), the equilibrium is disturbed. It can be restored by changing the temperature, so moving the state of the system to b. It follows that there is a relation between dp and dT that ensures that the system remains in equilibrium as either variable is changed.

(a) The slopes of the phase boundaries

It turns out to be simplest to discuss the phase boundaries in terms of their slopes, $\mathrm{d}p/\mathrm{d}T$. Let p and T be changed infinitesimally, but in such a way that the two phases α and β remain in equilibrium. The chemical potentials of the phases are initially equal (the two phases are in equilibrium). They remain equal when the conditions are changed to another point on the phase boundary, where the two phases continue to be in equilibrium (Fig. 4.12). Therefore, the changes in the chemical potentials of the two phases must be equal and we can write $\mathrm{d}\mu_\alpha = \mathrm{d}\mu_\beta$. Because, from eqn 3.49 ($\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T$), we know that $\mathrm{d}\mu = -S_\mathrm{m}\mathrm{d}T + V_\mathrm{m}\mathrm{d}p$ for each phase, it follows that

$$-S_{\alpha,\mathrm{m}}\mathrm{d}T + V_{\alpha,\mathrm{m}}\mathrm{d}p = -S_{\beta,\mathrm{m}}\mathrm{d}T + V_{\beta,\mathrm{m}}\mathrm{d}p$$

where $S_{\alpha,\mathrm{m}}$ and $S_{\beta,\mathrm{m}}$ are the molar entropies of the phases and $V_{\alpha,\mathrm{m}}$ and $V_{\beta,\mathrm{m}}$ are their molar volumes. Hence

$$(V_{\beta,\mathrm{m}} - V_{\alpha,\mathrm{m}})\mathrm{d}p = (S_{\beta,\mathrm{m}} - S_{\alpha,\mathrm{m}})\mathrm{d}T \tag{4.5}$$

which rearranges into the **Clapeyron equation**:

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_\mathrm{trs}S}{\Delta_\mathrm{trs}V} \tag{4.6}$$

In this expression $\Delta_\mathrm{trs}S = S_{\beta,\mathrm{m}} - S_{\alpha,\mathrm{m}}$ and $\Delta_\mathrm{trs}V = V_{\beta,\mathrm{m}} - V_{\alpha,\mathrm{m}}$ are the entropy and volume of transition, respectively. The Clapeyron equation is an exact expression for the slope of the phase boundary and applies to any phase equilibrium of any pure substance. It implies that we can use thermodynamic data to predict the appearance of phase diagrams and to understand their form. A more practical application is to the prediction of the response of freezing and boiling points to the application of pressure.

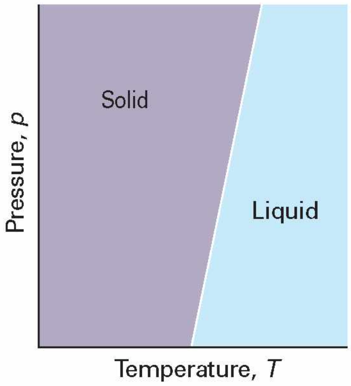

Fig. 4.13 A typical solid–liquid phase boundary slopes steeply upwards. This slope implies that, as the pressure is raised, the melting temperature rises. Most substances behave in this way.

(b) The solid–liquid boundary

Melting (fusion) is accompanied by a molar enthalpy change $\Delta_\mathrm{fus}H$ and occurs at a temperature T. The molar entropy of melting at T is therefore $\Delta_\mathrm{fus}H/T$ (Section 3.3), and the Clapeyron equation becomes

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_\mathrm{fus}H}{T\Delta_\mathrm{fus}V} \tag{4.7}$$

where $\Delta_\mathrm{fus}V$ is the change in molar volume that occurs on melting. The enthalpy of melting is positive (the only exception is helium-3) and the volume change is usually positive and always small. Consequently, the slope $\mathrm{d}p/\mathrm{d}T$ is steep and usually positive (Fig. 4.13).

We can obtain the formula for the phase boundary by integrating $\mathrm{d}p/\mathrm{d}T$, assuming that $\Delta_\mathrm{fus}H$ and $\Delta_\mathrm{fus}V$ change so little with temperature and pressure that they can be treated as constant. If the melting temperature is T^* when the pressure is p^*, and T when the pressure is p, the integration required is

$$\int_{p^*}^{p} \mathrm{d}p = \frac{\Delta_{\mathrm{fus}}H}{\Delta_{\mathrm{fus}}V}\int_{T^*}^{T}\frac{\mathrm{d}T}{T}$$

Therefore, the approximate equation of the solid–liquid boundary is

$$p \approx p^* + \frac{\Delta_{\mathrm{fus}}H}{\Delta_{\mathrm{fus}}V}\ln\frac{T}{T^*} \tag{4.8}$$

This equation was originally obtained by yet another Thomson—James, the brother of William, Lord Kelvin. When T is close to T^*, the logarithm can be approximated by using

$$\ln\frac{T}{T^*} = \ln\left(1 + \frac{T - T^*}{T^*}\right) \approx \frac{T - T^*}{T^*}$$

therefore,

$$p \approx p^* + \frac{\Delta_{\mathrm{fus}}H}{T^*\Delta_{\mathrm{fus}}V}(T - T^*) \tag{4.9}$$

This expression is the equation of a steep straight line when p is plotted against T (as in Fig. 4.13).

Comment 4.2

Calculations involving natural logarithms often become simpler if we note that, provided $-1 < x < 1$, $\ln(1+x) = x - \frac{1}{2}x^2 + \frac{1}{3}x^3 \cdots$. If $x \ll 1$, a good approximation is $\ln(1+x) \approx x$.

(c) The liquid–vapour boundary

The entropy of vaporization at a temperature T is equal to $\Delta_{\mathrm{vap}}H/T$; the Clapeyron equation for the liquid–vapour boundary is therefore

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{vap}}H}{T\Delta_{\mathrm{vap}}V} \tag{4.10}$$

The enthalpy of vaporization is positive; $\Delta_{\mathrm{vap}}V$ is large and positive. Therefore, $\mathrm{d}p/\mathrm{d}T$ is positive, but it is much smaller than for the solid–liquid boundary. It follows that $\mathrm{d}T/\mathrm{d}p$ is large, and hence that the boiling temperature is more responsive to pressure than the freezing temperature.

Example 4.2 *Estimating the effect of pressure on the boiling temperature*

Estimate the typical size of the effect of increasing pressure on the boiling point of a liquid.

Method To use eqn 4.10 we need to estimate the right-hand side. At the boiling point, the term $\Delta_{\mathrm{vap}}H/T$ is Trouton's constant (Section 3.3b). Because the molar volume of a gas is so much greater than the molar volume of a liquid, we can write

$$\Delta_{\mathrm{vap}}V = V_{\mathrm{m}}(\mathrm{g}) - V_{\mathrm{m}}(\mathrm{l}) \approx V_{\mathrm{m}}(\mathrm{g})$$

and take for $V_{\mathrm{m}}(\mathrm{g})$ the molar volume of a perfect gas (at low pressures, at least).

Answer Trouton's constant has the value 85 J K^{-1} mol^{-1}. The molar volume of a perfect gas is about 25 dm^3 mol^{-1} at 1 atm and near but above room temperature. Therefore,

$$\frac{\mathrm{d}p}{\mathrm{d}T} \approx \frac{85\ \mathrm{J\ K^{-1}\ mol^{-1}}}{2.5\times10^{-2}\ \mathrm{m^3\ mol^{-1}}} = 3.4\times10^{3}\ \mathrm{Pa\ K^{-1}}$$

We have used 1 J = 1 Pa m^3. This value corresponds to 0.034 atm K^{-1}, and hence to $\mathrm{d}T/\mathrm{d}p = 29$ K atm^{-1}. Therefore, a change of pressure of +0.1 atm can be expected to change a boiling temperature by about +3 K.

Self-test 4.3 Estimate $\mathrm{d}T/\mathrm{d}p$ for water at its normal boiling point using the information in Table 3.2 and $V_\mathrm{m}(\mathrm{g}) = RT/p$. [28 K atm^{-1}]

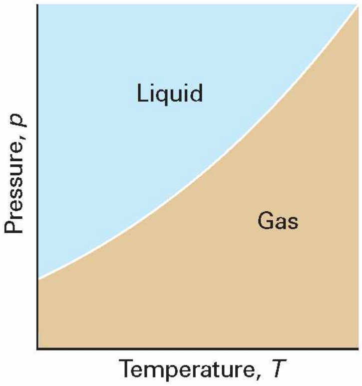

Fig. 4.14 A typical liquid–vapour phase boundary. The boundary can be regarded as a plot of the vapour pressure against the temperature. Note that, in some depictions of phase diagrams in which a logarithmic pressure scale is used, the phase boundary has the opposite curvature (see Fig. 4.7). This phase boundary terminates at the critical point (not shown).

Because the molar volume of a gas is so much greater than the molar volume of a liquid, we can write $\Delta_\mathrm{vap}V \approx V_\mathrm{m}(\mathrm{g})$ (as in *Example 4.2*). Moreover, if the gas behaves perfectly, $V_\mathrm{m}(\mathrm{g}) = RT/p$. These two approximations turn the exact Clapeyron equation into

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_\mathrm{vap}H}{T(RT/p)}$$

which rearranges into the **Clausius–Clapeyron equation** for the variation of vapour pressure with temperature:

$$\frac{\mathrm{d}\ln p}{\mathrm{d}T} = \frac{\Delta_\mathrm{vap}H}{RT^2} \qquad (4.11)^\circ$$

(We have used $\mathrm{d}x/x = \mathrm{d}\ln x$.) Like the Clapeyron equation, the Clausius–Clapeyron equation is important for understanding the appearance of phase diagrams, particularly the location and shape of the liquid–vapour and solid–vapour phase boundaries. It lets us predict how the vapour pressure varies with temperature and how the boiling temperature varies with pressure. For instance, if we also assume that the enthalpy of vaporization is independent of temperature, this equation can be integrated as follows:

$$\int_{\ln p^*}^{\ln p} \mathrm{d}\ln p = \frac{\Delta_\mathrm{vap}H}{R}\int_{T^*}^{T}\frac{\mathrm{d}T}{T^2} = -\frac{\Delta_\mathrm{vap}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)$$

where p^* is the vapour pressure when the temperature is T^* and p the vapour pressure when the temperature is T. Therefore, because the integral on the left evaluates to $\ln(p/p^*)$, the two vapour pressures are related by

$$p = p^*\mathrm{e}^{-\chi} \qquad \chi = \frac{\Delta_\mathrm{vap}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right) \qquad (4.12)^\circ$$

Equation 4.12 is plotted as the liquid–vapour boundary in Fig. 4.14. The line does not extend beyond the critical temperature T_c, because above this temperature the liquid does not exist.

Illustration 4.2 *The effect of temperature on the vapour pressure of a liquid*

Equation 4.12 can be used to estimate the vapour pressure of a liquid at any temperature from its normal boiling point, the temperature at which the vapour pressure is 1.00 atm (101 kPa). Thus, because the normal boiling point of benzene is 80°C (353 K) and (from Table 2.3), $\Delta_\mathrm{vap}H^\ominus = 30.8$ kJ mol^{-1}, to calculate the vapour pressure at 20°C (293 K), we write

$$\chi = \frac{3.08\times10^4\ \mathrm{J\ mol^{-1}}}{8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}}\left(\frac{1}{293\ \mathrm{K}} - \frac{1}{353\ \mathrm{K}}\right) = \frac{3.08\times10^4}{8.3145}\left(\frac{1}{293} - \frac{1}{353}\right)$$

and substitute this value into eqn 4.12 with $p^* = 101$ kPa. The result is 12 kPa. The experimental value is 10 kPa.

A note on good practice Because exponential functions are so sensitive, it is good practice to carry out numerical calculations like this without evaluating the intermediate steps and using rounded values.

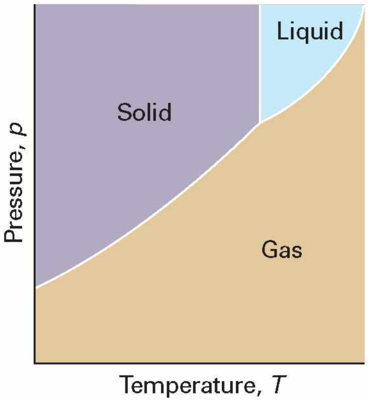

Fig. 4.15 Near the point where they coincide (at the triple point), the solid–gas boundary has a steeper slope than the liquid–gas boundary because the enthalpy of sublimation is greater than the enthalpy of vaporization and the temperatures that occur in the Clausius–Clapeyron equation for the slope have similar values.

(d) The solid–vapour boundary

The only difference between this case and the last is the replacement of the enthalpy of vaporization by the enthalpy of sublimation, $\Delta_{\rm sub}H$. Because the enthalpy of sublimation is greater than the enthalpy of vaporization ($\Delta_{\rm sub}H = \Delta_{\rm fus}H + \Delta_{\rm vap}H$), the equation predicts a steeper slope for the sublimation curve than for the vaporization curve at similar temperatures, which is near where they meet at the triple point (Fig. 4.15).

4.7 The Ehrenfest classification of phase transitions

There are many different types of phase transition, including the familiar examples of fusion and vaporization and the less familiar examples of solid–solid, conducting–superconducting, and fluid–superfluid transitions. We shall now see that it is possible to use thermodynamic properties of substances, and in particular the behaviour of the chemical potential, to classify phase transitions into different types. The classification scheme was originally proposed by Paul Ehrenfest, and is known as the **Ehrenfest classification**.

Many familiar phase transitions, like fusion and vaporization, are accompanied by changes of enthalpy and volume. These changes have implications for the slopes of the chemical potentials of the phases at either side of the phase transition. Thus, at the transition from a phase α to another phase β,

$$\begin{aligned}\left(\frac{\partial\mu_\beta}{\partial p}\right)_T-\left(\frac{\partial\mu_\alpha}{\partial p}\right)_T&=V_{\beta,\rm m}-V_{\alpha,\rm m}=\Delta_{\rm trs}V\\ \left(\frac{\partial\mu_\beta}{\partial T}\right)_p-\left(\frac{\partial\mu_\alpha}{\partial T}\right)_p&=-S_{\beta,\rm m}+S_{\alpha,\rm m}=\Delta_{\rm trs}S=\frac{\Delta_{\rm trs}H}{T_{\rm trs}}\end{aligned}\qquad(4.13)$$

Because $\Delta_{\rm trs}V$ and $\Delta_{\rm trs}H$ are non-zero for melting and vaporization, it follows that for such transitions the slopes of the chemical potential plotted against either pressure or temperature are different on either side of the transition (Fig. 4.16a). In other words, the first derivatives of the chemical potentials with respect to pressure and temperature are discontinuous at the transition.

A transition for which the first derivative of the chemical potential with respect to temperature is discontinuous is classified as a **first-order phase transition**. The constant-pressure heat capacity, $C_{\rm p}$, of a substance is the slope of a plot of the enthalpy with respect to temperature. At a first-order phase transition, H changes by a finite amount for an infinitesimal change of temperature. Therefore, at the transition the heat capacity is infinite. The physical reason is that heating drives the transition rather than raising the temperature. For example, boiling water stays at the same temperature even though heat is being supplied.

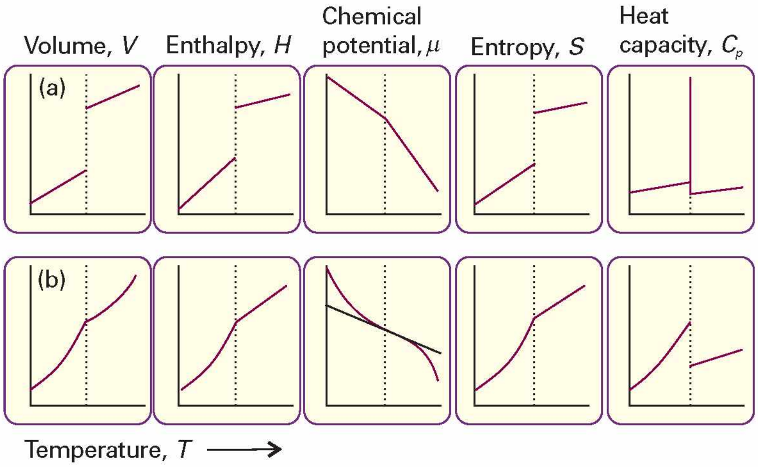

Fig. 4.16 The changes in thermodynamic properties accompanying (a) first-order and (b) second-order phase transitions.

A **second-order phase transition** in the Ehrenfest sense is one in which the first derivative of μ with respect to temperature is continuous but its second derivative is discontinuous. A continuous slope of μ (a graph with the same slope on either side of the transition) implies that the volume and entropy (and hence the enthalpy) do not change at the transition (Fig. 4.16b). The heat capacity is discontinuous at the transition but does not become infinite there. An example of a second-order transition is the conducting–superconducting transition in metals at low temperatures.[2]

The term **λ-transition** is applied to a phase transition that is not first-order yet the heat capacity becomes infinite at the transition temperature. Typically, the heat capacity of a system that shows such a transition begins to increase well before the transition (Fig. 4.17), and the shape of the heat capacity curve resembles the Greek letter lambda. This type of transition includes order–disorder transitions in alloys, the onset of ferromagnetism, and the fluid–superfluid transition of liquid helium.

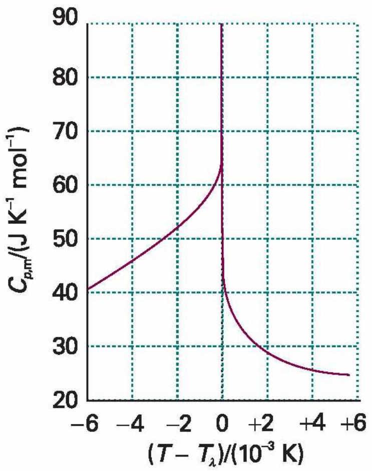

Fig. 4.17 The λ-curve for helium, where the heat capacity rises to infinity. The shape of this curve is the origin of the name λ-transition.

Molecular interpretation 4.1 *Second-order phase transitions and λ-transitions*

One type of second-order transition is associated with a change in symmetry of the crystal structure of a solid. Thus, suppose the arrangement of atoms in a solid is like that represented in Fig. 4.18a, with one dimension (technically, of the unit cell) longer than the other two, which are equal. Such a crystal structure is classified as tetragonal (see Section 20.1). Moreover, suppose the two shorter dimensions increase more than the long dimension when the temperature is raised. There may come a stage when the three dimensions become equal. At that point the crystal has cubic symmetry (Fig. 4.18b), and at higher temperatures it will expand equally in all three directions (because there is no longer any distinction between them). The tetragonal → cubic phase transition has occurred, but as it has not involved a discontinuity in the interaction energy between the atoms or the volume they occupy, the transition is not first-order.

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[2] A metallic conductor is a substance with an electrical conductivity that decreases as the temperature increases. A superconductor is a solid that conducts electricity without resistance. See Chapter 20 for more details.

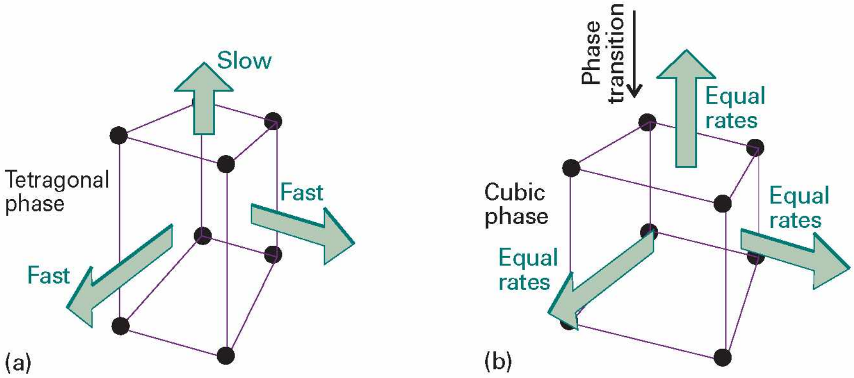

Fig. 4.18 One version of a second-order phase transition in which (a) a tetragonal phase expands more rapidly in two directions than a third, and hence becomes a cubic phase, which (b) expands uniformly in three directions as the temperature is raised. There is no rearrangement of atoms at the transition temperature, and hence no enthalpy of transition.

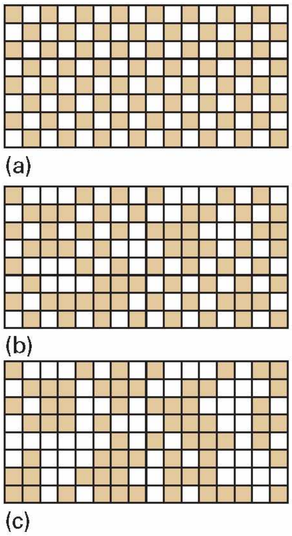

Fig. 4.19 An order–disorder transition. (a) At $T = 0$, there is perfect order, with different kinds of atoms occupying alternate sites. (b) As the temperature is increased, atoms exchange locations and islands of each kind of atom form in regions of the solid. Some of the original order survives. (c) At and above the transition temperature, the islands occur at random throughout the sample.

The order–disorder transition in β-brass (CuZn) is an example of a λ-transition. The low-temperature phase is an orderly array of alternating Cu and Zn atoms. The high-temperature phase is a random array of the atoms (Fig. 4.19). At $T = 0$ the order is perfect, but islands of disorder appear as the temperature is raised. The islands form because the transition is cooperative in the sense that, once two atoms have exchanged locations, it is easier for their neighbours to exchange their locations. The islands grow in extent, and merge throughout the crystal at the transition temperature (742 K). The heat capacity increases as the transition temperature is approached because the cooperative nature of the transition means that it is increasingly easy for the heat supplied to drive the phase transition rather than to be stored as thermal motion.

Checklist of key ideas

☐ 1. A phase is a form of matter that is uniform throughout in chemical composition and physical state.

☐ 2. A transition temperature is the temperature at which the two phases are in equilibrium.

☐ 3. A metastable phase is a thermodynamically unstable phase that persists because the transition is kinetically hindered.

☐ 4. A phase diagram is a diagram showing the regions of pressure and temperature at which its various phases are thermodynamically stable.

☐ 5. A phase boundary is a line separating the regions in a phase diagram showing the values of p and T at which two phases coexist in equilibrium.

☐ 6. The vapour pressure is the pressure of a vapour in equilibrium with the condensed phase.

☐ 7. Boiling is the condition of free vaporization throughout the liquid.

☐ 8. The boiling temperature is the temperature at which the vapour pressure of a liquid is equal to the external pressure.

☐ 9. The critical temperature is the temperature at which a liquid surface disappears and above which a liquid does not exist whatever the pressure. The critical pressure is the vapour pressure at the critical temperature.

☐ 10. A supercritical fluid is a dense fluid phase above the critical temperature.

☐ 11. The melting temperature (or freezing temperature) is the temperature at which, under a specified pressure, the liquid and solid phases of a substance coexist in equilibrium.

☐ 12. The triple point is a point on a phase diagram at which the three phase boundaries meet and all three phases are in mutual equilibrium.

☐ 13. The chemical potential μ of a pure substance is the molar Gibbs energy of the substance.

☐ 14. The chemical potential is uniform throughout a system at equilibrium.

☐ 15. The chemical potential varies with temperature as $(\partial\mu/\partial T)_p = -S_m$ and with pressure as $(\partial\mu/\partial p)_T = V_m$.

☐ 16. The vapour pressure in the presence of applied pressure is given by $p = p^* e^{V_m \Delta P/RT}$.

☐ 17. The temperature dependence of the vapour pressure is given by the Clapeyron equation, $dp/dT = \Delta_{trs}S/\Delta_{trs}V$.

☐ 18. The temperature dependence of the vapour pressure of a condensed phase is given by the Clausius–Clapeyron equation, $d\ln p/dT = \Delta_{vap}H/RT^2$.

☐ 19. The Ehrenfest classification is a classification of phase transitions based on the behaviour of the chemical potential.

Further reading

Articles and texts

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Sources of data and information[3]

T. Boublik, V. Fried, and E. Hála, *The vapor pressures of pure substances*. Elsevier, Amsterdam (1984).

R.C. Weast (ed.), *Handbook of chemistry and physics*, Vol. 81. CRC Press, Boca Raton (2004).

Discussion questions

4.1 Discuss the implications for phase stability of the variation of chemical potential with temperature and pressure.

4.2 Suggest a physical interpretation of the phenomena of superheating and supercooling.

4.3 Discuss what would be observed as a sample of water is taken along a path that encircles and is close to its critical point.

4.4 Use the phase diagram in Fig. 4.4 to state what would be observed when a sample of carbon dioxide, initially at 1.0 atm and 298 K, is subjected to the following cycle: (a) isobaric (constant–pressure) heating to 320 K, (b) isothermal compression to 100 atm, (c) isobaric cooling to 210 K, (d) isothermal decompression to 1.0 atm, (e) isobaric heating to 298 K.

4.5 The use of supercritical fluids for the extraction of a component from a complicated mixture is not confined to the decaffeination of coffee. Consult library and internet resources and prepare a discussion of the principles, advantages, disadvantages, and current uses of supercritical fluid extraction technology.

4.6 Explain the significance of the Clapeyron equation and of the Clausius–Clapeyron equation.

4.7 Distinguish between a first-order phase transition, a second-order phase transition, and a λ-transition at both molecular and macroscopic levels.

Exercises

4.1(a) The vapour pressure of dichloromethane at 24.1°C is 53.3 kPa and its enthalpy of vaporization is 28.7 kJ mol^{-1}. Estimate the temperature at which its vapour pressure is 70.0 kPa.

4.1(b) The vapour pressure of a substance at 20.0°C is 58.0 kPa and its enthalpy of vaporization is 32.7 kJ mol^{-1}. Estimate the temperature at which its vapour pressure is 66.0 kPa.

4.2(a) The molar volume of a certain solid is 161.0 cm^3 mol^{-1} at 1.00 atm and 350.75 K, its melting temperature. The molar volume of the liquid at this temperature and pressure is 163.3 cm^3 mol^{-1}. At 100 atm the melting temperature changes to 351.26 K. Calculate the enthalpy and entropy of fusion of the solid.

4.2(b) The molar volume of a certain solid is 142.0 cm^3 mol^{-1} at 1.00 atm and 427.15 K, its melting temperature. The molar volume of the liquid at this temperature and pressure is 152.6 cm^3 mol^{-1}. At 1.2 MPa the melting temperature changes to 429.26 K. Calculate the enthalpy and entropy of fusion of the solid.

4.3(a) The vapour pressure of a liquid in the temperature range 200 K to 260 K was found to fit the expression $\ln(p/\text{Torr}) = 16.255 - 2501.8/(T/\text{K})$. Calculate the enthalpy of vaporization of the liquid.

4.3(b) The vapour pressure of a liquid in the temperature range 200 K to 260 K was found to fit the expression $\ln(p/\text{Torr}) = 18.361 - 3036.8/(T/\text{K})$. Calculate the enthalpy of vaporization of the liquid.

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[3] See *Further reading* in Chapter 2 for additional sources of thermochemical data.

4.4(a) The vapour pressure of benzene between 10°C and 30°C fits the expression $\log(p/\text{Torr}) = 7.960 - 1780/(T/\text{K})$. Calculate (a) the enthalpy of vaporization and (b) the normal boiling point of benzene.

4.4(b) The vapour pressure of a liquid between 15°C and 35°C fits the expression $\log(p/\text{Torr}) = 8.750 - 1625/(T/\text{K})$. Calculate (a) the enthalpy of vaporization and (b) the normal boiling point of the liquid.

4.5(a) When benzene freezes at 5.5°C its density changes from 0.879 g cm^{-3} to 0.891 g cm^{-3}. Its enthalpy of fusion is 10.59 kJ mol^{-1}. Estimate the freezing point of benzene at 1000 atm.

4.5(b) When a certain liquid freezes at −3.65°C its density changes from 0.789 g cm^{-3} to 0.801 g cm^{-3}. Its enthalpy of fusion is 8.68 kJ mol^{-1}. Estimate the freezing point of the liquid at 100 MPa.

4.6(a) In July in Los Angeles, the incident sunlight at ground level has a power density of 1.2 kW m^{-2} at noon. A swimming pool of area 50 m^2 is directly exposed to the sun. What is the maximum rate of loss of water? Assume that all the radiant energy is absorbed.

4.6(b) Suppose the incident sunlight at ground level has a power density of 0.87 kW m^{-2} at noon. What is the maximum rate of loss of water from a lake of area 1.0 ha? (1 ha = 10^4 m^2.) Assume that all the radiant energy is absorbed.

4.7(a) An open vessel containing (a) water, (b) benzene, (c) mercury stands in a laboratory measuring 5.0 m × 5.0 m × 3.0 m at 25°C. What mass of each substance will be found in the air if there is no ventilation? (The vapour pressures are (a) 3.2 kPa, (b) 13.1 kPa, (c) 0.23 Pa.)

4.7(b) On a cold, dry morning after a frost, the temperature was −5°C and the partial pressure of water in the atmosphere fell to 0.30 kPa. Will the frost sublime? What partial pressure of water would ensure that the frost remained?

4.8(a) Naphthalene, $C_{10}H_8$, melts at 80.2°C. If the vapour pressure of the liquid is 1.3 kPa at 85.8°C and 5.3 kPa at 119.3°C, use the Clausius–Clapeyron equation to calculate (a) the enthalpy of vaporization, (b) the normal boiling point, and (c) the enthalpy of vaporization at the boiling point.

4.8(b) The normal boiling point of hexane is 69.0°C. Estimate (a) its enthalpy of vaporization and (b) its vapour pressure at 25°C and 60°C.

4.9(a) Calculate the melting point of ice under a pressure of 50 bar. Assume that the density of ice under these conditions is approximately 0.92 g cm^{-3} and that of liquid water is 1.00 g cm^{-3}.

4.9(b) Calculate the melting point of ice under a pressure of 10 MPa. Assume that the density of ice under these conditions is approximately 0.915 g cm^{-3} and that of liquid water is 0.998 g cm^{-3}.

4.10(a) What fraction of the enthalpy of vaporization of water is spent on expanding the water vapour?

4.10(b) What fraction of the enthalpy of vaporization of ethanol is spent on expanding its vapour?

Problems*

Numerical problems

4.1 The temperature dependence of the vapour pressure of solid sulfur dioxide can be approximately represented by the relation $\log(p/\text{Torr}) = 10.5916 - 1871.2/(T/\text{K})$ and that of liquid sulfur dioxide by $\log(p/\text{Torr}) = 8.3186 - 1425.7/(T/\text{K})$. Estimate the temperature and pressure of the triple point of sulfur dioxide.

4.2 Prior to the discovery that freon-12 (CF_2Cl_2) was harmful to the Earth's ozone layer, it was frequently used as the dispersing agent in spray cans for hair spray, etc. Its enthalpy of vaporization at its normal boiling point of −29.2°C is 20.25 kJ mol^{-1}. Estimate the pressure that a can of hair spray using freon-12 had to withstand at 40°C, the temperature of a can that has been standing in sunlight. Assume that $\Delta_{\text{vap}}H$ is a constant over the temperature range involved and equal to its value at −29.2°C.

4.3 The enthalpy of vaporization of a certain liquid is found to be 14.4 kJ mol^{-1} at 180 K, its normal boiling point. The molar volumes of the liquid and the vapour at the boiling point are 115 cm^3 mol^{-1} and 14.5 dm^3 mol^{-1}, respectively. (a) Estimate $\mathrm{d}p/\mathrm{d}T$ from the Clapeyron equation and (b) the percentage error in its value if the Clausius–Clapeyron equation is used instead.

4.4 Calculate the difference in slope of the chemical potential against temperature on either side of (a) the normal freezing point of water and (b) the normal boiling point of water. (c) By how much does the chemical potential of water supercooled to −5.0°C exceed that of ice at that temperature?

4.5 Calculate the difference in slope of the chemical potential against pressure on either side of (a) the normal freezing point of water and (b) the normal boiling point of water. The densities of ice and water at 0°C are 0.917 g cm^{-3} and 1.000 g cm^{-3}, and those of water and water vapour at 100°C are 0.958 g cm^{-3} and 0.598 g dm^{-3}, respectively. By how much does the chemical potential of water vapour exceed that of liquid water at 1.2 atm and 100°C?

4.6 The enthalpy of fusion of mercury is 2.292 kJ mol^{-1}, and its normal freezing point is 234.3 K with a change in molar volume of +0.517 cm^{-3} mol^{-1} on melting. At what temperature will the bottom of a column of mercury (density 13.6 g cm^{-3}) of height 10.0 m be expected to freeze?

4.7 50.0 dm^3 of dry air was slowly bubbled through a thermally insulated beaker containing 250 g of water initially at 25°C. Calculate the final temperature. (The vapour pressure of water is approximately constant at 3.17 kPa throughout, and its heat capacity is 75.5 J K^{-1} mol^{-1}. Assume that the air is not heated or cooled and that water vapour is a perfect gas.)

4.8 The vapour pressure, p, of nitric acid varies with temperature as follows:

θ/°C	0	20	40	50	70	80	90	100
p/kPa	1.92	6.38	17.7	27.7	62.3	89.3	124.9	170.9

What are (a) the normal boiling point and (b) the enthalpy of vaporization of nitric acid?

4.9 The vapour pressure of the ketone carvone ($M = 150.2$ g mol^{-1}), a component of oil of spearmint, is as follows:

θ/°C	57.4	100.4	133.0	157.3	203.5	227.5
p/Torr	1.00	10.0	40.0	100	400	760

What are (a) the normal boiling point and (b) the enthalpy of vaporization of carvone?

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

4.10 Construct the phase diagram for benzene near its triple point at 36 Torr and 5.50°C using the following data: $\Delta_{\rm fus}H = 10.6\ {\rm kJ\ mol^{-1}}$, $\Delta_{\rm vap}H = 30.8\ {\rm kJ\ mol^{-1}}$, $\rho({\rm s}) = 0.891\ {\rm g\ cm^{-3}}$, $\rho({\rm l}) = 0.879\ {\rm g\ cm^{-3}}$.

4.11‡ In an investigation of thermophysical properties of toluene (R.D. Goodwin *J. Phys. Chem. Ref. Data* **18**, 1565 (1989)) presented expressions for two coexistence curves (phase boundaries). The solid–liquid coexistence curve is given by

$$p/{\rm bar} = p_3/{\rm bar} + 1000 \times (5.60 + 11.727x)x$$

where $x = T/T_3 - 1$ and the triple point pressure and temperature are $p_3 = 0.4362\ \mu{\rm bar}$ and $T_3 = 178.15\ {\rm K}$. The liquid–vapour curve is given by:

$$\ln(p/{\rm bar}) = -10.418/y + 21.157 - 15.996y + 14.015y^2 - 5.0120y^3 \\ + 4.7224(1-y)^{1.70}$$

where $y = T/T_c = T/(593.95\ {\rm K})$. (a) Plot the solid–liquid and liquid–vapour phase boundaries. (b) Estimate the standard melting point of toluene. (c) Estimate the standard boiling point of toluene. (d) Compute the standard enthalpy of vaporization of toluene, given that the molar volumes of the liquid and vapour at the normal boiling point are $0.12\ {\rm dm^3\ mol^{-1}}$ and $30.3\ {\rm dm^3\ mol^{-1}}$, respectively.

4.12‡ In a study of the vapour pressure of chloromethane, A. Bah and N. Dupont-Pavlovsky (*J. Chem. Eng. Data* **40**, 869 (1995)) presented data for the vapour pressure over solid chloromethane at low temperatures. Some of that data is shown below:

T/K	145.94	147.96	149.93	151.94	153.97	154.94
p/Pa	13.07	18.49	25.99	36.76	50.86	59.56

Estimate the standard enthalpy of sublimation of chloromethane at 150 K. (Take the molar volume of the vapour to be that of a perfect gas, and that of the solid to be negligible.)

Theoretical problems

4.13 Show that, for a transition between two incompressible solid phases, ΔG is independent of the pressure.

4.14 The change in enthalpy is given by $dH = C_p dT + V dp$. The Clapeyron equation relates dp and dT at equilibrium, and so in combination the two equations can be used to find how the enthalpy changes along a phase boundary as the temperature changes and the two phases remain in equilibrium. Show that $d(\Delta H/T) = \Delta C_p\, d\ln T$.

4.15 In the 'gas saturation method' for the measurement of vapour pressure, a volume V of gas (as measured at a temperature T and a pressure p) is bubbled slowly through the liquid that is maintained at the temperature T, and a mass loss m is measured. Show that the vapour pressure, p, of the liquid is related to its molar mass, M, by $p = AmP/(1 + Am)$, where $A = RT/MPV$. The vapour pressure of geraniol ($M = 154.2\ {\rm g\ mol^{-1}}$), which is a component of oil of roses, was measured at 110°C. It was found that, when $5.00\ {\rm dm^3}$ of nitrogen at 760 Torr was passed slowly through the heated liquid, the loss of mass was 0.32 g. Calculate the vapour pressure of geraniol.

4.16 Combine the barometric formula (stated in *Impact I1.1*) for the dependence of the pressure on altitude with the Clausius–Clapeyron equation, and predict how the boiling temperature of a liquid depends on the altitude and the ambient temperature. Take the mean ambient temperature as 20°C and predict the boiling temperature of water at 3000 m.

4.17 Figure 4.9 gives a schematic representation of how the chemical potentials of the solid, liquid, and gaseous phases of a substance vary with temperature. All have a negative slope, but it is unlikely that they are truly straight lines as indicated in the illustration. Derive an expression for the curvatures (specifically, the second derivatives with respect to temperature) of these lines. Is there a restriction on the curvature of these lines? Which state of matter shows the greatest curvature?

4.18 The Clapeyron equation does not apply to second-order phase transitions, but there are two analogous equations, the *Ehrenfest equations*, that do. They are:

$$\frac{dp}{dT} = \frac{\alpha_2 - \alpha_1}{\kappa_{T,2} - \kappa_{T,1}} \qquad \frac{dp}{dT} = \frac{C_{p,{\rm m}2} - C_{p,{\rm m}1}}{TV_{\rm m}(\alpha_2 - \alpha_1)}$$

where α is the expansion coefficient, κ_T the isothermal compressibility, and the subscripts 1 and 2 refer to two different phases. Derive these two equations. Why does the Clapeyron equation not apply to second-order transitions?

4.19 For a first-order phase transition, to which the Clapeyron equation does apply, prove the relation

$$C_S = C_p - \frac{\alpha V \Delta_{\rm trs}H}{\Delta_{\rm trs}V}$$

where $C_S = (\partial q/\partial T)_S$ is the heat capacity along the coexistence curve of two phases.

Applications: to biology and engineering

4.20 Proteins are *polypeptides*, polymers of amino acids that can exist in ordered structures stabilized by a variety of molecular interactions. However, when certain conditions are changed, the compact structure of a polypeptide chain may collapse into a random coil. This structural change may be regarded as a phase transition occurring at a characteristic transition temperature, the *melting temperature*, $T_{\rm m}$, which increases with the strength and number of intermolecular interactions in the chain. A thermodynamic treatment allows predictions to be made of the temperature $T_{\rm m}$ for the unfolding of a helical polypeptide held together by hydrogen bonds into a random coil. If a polypeptide has n amino acids, $n - 4$ hydrogen bonds are formed to form an α-helix, the most common type of helix in naturally occurring proteins (see Chapter 19). Because the first and last residues in the chain are free to move, $n - 2$ residues form the compact helix and have restricted motion. Based on these ideas, the molar Gibbs energy of unfolding of a polypeptide with $n \geq 5$ may be written as

$$\Delta G_{\rm m} = (n-4)\Delta_{\rm hb}H_{\rm m} - (n-2)T\Delta_{\rm hb}S_{\rm m}$$

where $\Delta_{\rm hb}H_{\rm m}$ and $\Delta_{\rm hb}S_{\rm m}$ are, respectively, the molar enthalpy and entropy of dissociation of hydrogen bonds in the polypeptide. (a) Justify the form of the equation for the Gibbs energy of unfolding. That is, why are the enthalpy and entropy terms written as $(n-4)\Delta_{\rm hb}H_{\rm m}$ and $(n-2)\Delta_{\rm hb}S_{\rm m}$, respectively? (b) Show that $T_{\rm m}$ may be written as

$$T_{\rm m} = \frac{(n-4)\Delta_{\rm hb}H_{\rm m}}{(n-2)\Delta_{\rm hb}S_{\rm m}}$$

(c) Plot $T_{\rm m}/(\Delta_{\rm hb}H_{\rm m}/\Delta_{\rm hb}S_{\rm m})$ for $5 \leq n \leq 20$. At what value of n does $T_{\rm m}$ change by less than 1% when n increases by one?

4.21‡ The use of supercritical fluids as mobile phases in SFC depends on their properties as nonpolar solvents. The solubility parameter, δ, is defined as $(\Delta U_{\rm cohesive}/V_{\rm m})^{1/2}$, where $\Delta U_{\rm cohesive}$ is the cohesive energy of the solvent, the energy per mole needed to increase the volume isothermally to an infinite value. Diethyl ether, carbon tetrachloride, and dioxane have solubility parameter ranges of 7–8, 8–9, and 10–11, respectively. (a) Derive a practical equation for the computation of the isotherms for the reduced internal energy change, $\Delta U_{\rm r}(T_{\rm r},V_{\rm r})$ defined as

$$\Delta U_{\rm r}(T_{\rm r},V_{\rm r}) = \frac{U_{\rm r}(T_{\rm r},V_{\rm r}) - U_{\rm r}(T_{\rm r},\infty)}{p_{\rm c}V_{\rm c}}$$

(b) Draw a graph of $\Delta U_{\rm r}$ against $p_{\rm r}$ for the isotherms $T_{\rm r} = 1, 1.2$, and 1.5 in the reduced pressure range for which $0.7 \leq V_{\rm r} \leq 2$. (c) Draw a graph of δ against $p_{\rm r}$ for the carbon dioxide isotherms $T_{\rm r} = 1$ and 1.5 in the reduced pressure range for which $1 \leq V_{\rm r} \leq 3$. In what pressure range at $T_{\rm f} = 1$ will carbon dioxide have solvent properties similar to those of liquid carbon tetrachloride? *Hint*. Use mathematical software or a spreadsheet.

4.22‡ A substance as well–known as methane still receives research attention because it is an important component of natural gas, a commonly used fossil fuel . Friend *et al.* have published a review of thermophysical properties of methane (D.G. Friend, J.F. Ely, and H. Ingham, *J. Phys. Chem. Ref. Data* **18**, 583 (1989)), which included the following data describing the liquid–vapour phase boundary.

T/K	100	108	110	112	114	120	130	140	150	160	170	190
p/MPa	0.034	0.074	0.088	0.104	0.122	0.192	0.368	0.642	1.041	1.593	2.329	4.521

(a) Plot the liquid–vapour phase boundary. (b) Estimate the standard boiling point of methane. (c) Compute the standard enthalpy of vaporization of methane, given that the molar volumes of the liquid and vapour at the standard boiling point are 3.80×10^{-2} and 8.89 dm^3 mol^{-1}, respectively.

4.23‡ Diamond, an allotrope of carbon, is the hardest substance and the best conductor of heat yet characterized. For these reasons, diamond is used widely in industrial applications that require a strong abrasive. Unfortunately, it is difficult to synthesize diamond from the more readily available allotropes of carbon, such as graphite. To illustrate this point, calculate the pressure required to convert graphite into diamond at 25°C. The following data apply to 25°C and 100 kPa. Assume the specific volume, V_s, and κ_T are constant with respect to pressure changes.

	Graphite	Diamond
$\Delta_f G^\ominus$/(kJ mol^{-1})	0	+2.8678
V_s/(cm^3 g^{-1})	0.444	0.284
κ_T/kPa	3.04×10^{-8}	0.187×10^{-8}

5

Simple mixtures

This chapter begins by developing the concept of chemical potential to show that it is a particular case of a class of properties called partial molar quantities. Then it explores how to use the chemical potential of a substance to describe the physical properties of mixtures. The underlying principle to keep in mind is that at equilibrium the chemical potential of a species is the same in every phase. We see, by making use of the experimental observations known as Raoult's and Henry's laws, how to express the chemical potential of a substance in terms of its mole fraction in a mixture. With this result established, we can calculate the effect of a solute on certain thermodynamic properties of a solution. These properties include the lowering of vapour pressure of the solvent, the elevation of its boiling point, the depression of its freezing point, and the origin of osmotic pressure. Finally, we see how to express the chemical potential of a substance in a real mixture in terms of a property known as the activity. We see how the activity may be measured, and conclude with a discussion of how the standard states of solutes and solvents are defined and how ion–ion interactions are taken into account in electrolyte solutions.

Chemistry deals with mixtures, including mixtures of substances that can react together. Therefore, we need to generalize the concepts introduced so far to deal with substances that are mingled together. As a first step towards dealing with chemical reactions (which are treated in Chapter 7), here we consider mixtures of substances that do not react together. At this stage we deal mainly with *binary mixtures*, which are mixtures of two components, A and B. We shall therefore often be able to simplify equations by making use of the relation $x_A + x_B = 1$.

The thermodynamic description of mixtures

We have already seen that the partial pressure, which is the contribution of one component to the total pressure, is used to discuss the properties of mixtures of gases. For a more general description of the thermodynamics of mixtures we need to introduce other analogous 'partial' properties.

5.1 Partial molar quantities

The easiest partial molar property to visualize is the 'partial molar volume', the contribution that a component of a mixture makes to the total volume of a sample.

(a) Partial molar volume

Imagine a huge volume of pure water at 25°C. When a further 1 mol H_2O is added, the volume increases by 18 cm^3 and we can report that 18 $cm^3\ mol^{-1}$ is the molar volume of pure water. However, when we add 1 mol H_2O to a huge volume of pure ethanol, the volume increases by only 14 cm^3. The reason for the different increase in volume is that the volume occupied by a given number of water molecules depends on the identity of the molecules that surround them. In the latter case there is so much ethanol present that each H_2O molecule is surrounded by ethanol molecules, and the packing of the molecules results in the H_2O molecules increasing the volume by only 14 cm^3. The quantity 14 $cm^3\ mol^{-1}$ is the partial molar volume of water in pure ethanol. In general, the **partial molar volume** of a substance A in a mixture is the change in volume per mole of A added to a large volume of the mixture.

The partial molar volumes of the components of a mixture vary with composition because the environment of each type of molecule changes as the composition changes from pure A to pure B. It is this changing molecular environment, and the consequential modification of the forces acting between molecules, that results in the variation of the thermodynamic properties of a mixture as its composition is changed. The partial molar volumes of water and ethanol across the full composition range at 25°C are shown in Fig. 5.1.

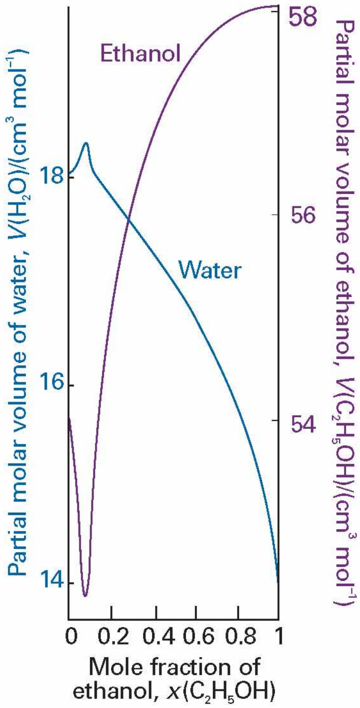

Fig. 5.1 The partial molar volumes of water and ethanol at 25°C. Note the different scales (water on the left, ethanol on the right).

The partial molar volume, V_J , of a substance J at some general composition is defined formally as follows:

$$V_J = \left(\frac{\partial V}{\partial n_J}\right)_{p,T,n'} \qquad [5.1]$$

where the subscript n' signifies that the amounts of all other substances present are constant.[1] The partial molar volume is the slope of the plot of the total volume as the amount of J is changed, the pressure, temperature, and amount of the other components being constant (Fig. 5.2). Its value depends on the composition, as we saw for water and ethanol. The definition in eqn 5.1 implies that, when the composition of the mixture is changed by the addition of dn_A of A and dn_B of B, then the total volume of the mixture changes by

$$dV = \left(\frac{\partial V}{\partial n_A}\right)_{p,T,n_B} dn_A + \left(\frac{\partial V}{\partial n_B}\right)_{p,T,n_A} dn_B = V_A dn_A + V_B dn_B \qquad (5.2)$$

Provided the composition is held constant as the amounts of A and B are increased, the final volume of a mixture can be calculated by integration. Because the partial molar volumes are constant (provided the composition is held constant throughout the integration) we can write

$$V = \int_0^{n_A} V_A dn_A + \int_0^{n_B} V_B dn_B = V_A \int_0^{n_A} dn_A + V_B \int_0^{n_B} dn_B$$
$$= V_A n_A + V_B n_B \qquad (5.3)$$

Although we have envisaged the two integrations as being linked (in order to preserve constant composition), because V is a state function the final result in eqn 5.3 is valid however the solution is in fact prepared.

Partial molar volumes can be measured in several ways. One method is to measure the dependence of the volume on the composition and to fit the observed volume to a function of the amount of the substance. Once the function has been found, its slope can be determined at any composition of interest by differentiation.

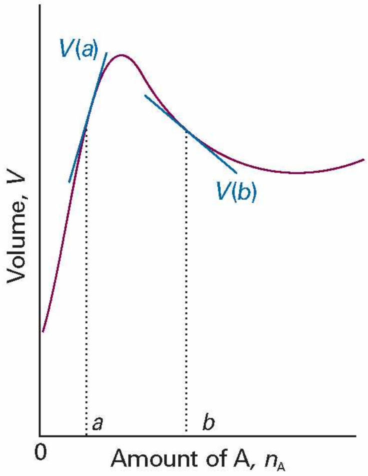

Fig. 5.2 The partial molar volume of a substance is the slope of the variation of the total volume of the sample plotted against the composition. In general, partial molar quantities vary with the composition, as shown by the different slopes at the compositions a and b. Note that the partial molar volume at b is negative: the overall volume of the sample decreases as A is added.

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[1] The IUPAC recommendation is to denote a partial molar quantity by $\bar{X}$, but only when there is the possibility of confusion with the quantity X. For instance, the partial molar volume of NaCl in water could be written $\bar{V}$(NaCl, aq) to distinguish it from the volume of the solution, V(NaCl, aq).

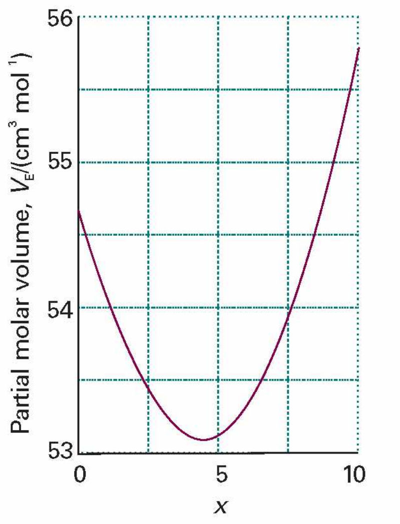

Fig. 5.3 The partial molar volume of ethanol as expressed by the polynomial in *Illustration 5.1*.

Exploration Using the data from *Illustration 5.1*, determine the value of b at which V_E has a minimum value.

Illustration 5.1 *The determination of partial molar volume*

A polynomial fit to measurements of the total volume of a water/ethanol mixture at 25°C that contains 1.000 kg of water is

$$v = 1002.93 + 54.6664x - 0.363\,94x^2 + 0.028\,256x^3$$

where $v = V/\text{cm}^3$, $x = n_E/\text{mol}$, and n_E is the amount of CH_3CH_2OH present. The partial molar volume of ethanol, V_E, is therefore

$$V_E = \left(\frac{\partial V}{\partial n_E}\right)_{p,T,n_W} = \left(\frac{\partial (V/\text{cm}^3)}{\partial (n_E/\text{mol})}\right)_{p,T,n_W} \text{cm}^3\,\text{mol}^{-1} = \left(\frac{\partial v}{\partial x}\right)_{p,T,n_W} \text{cm}^3\,\text{mol}^{-1}$$

Then, because

$$\frac{\mathrm{d}v}{\mathrm{d}x} = 54.6664 - 2(0.36394)x + 3(0.028256)x^2$$

we can conclude that

$$V_E/(\text{cm}^3\,\text{mol}^{-1}) = 54.6664 - 0.72788x + 0.084768x^2$$

Figure 5.3 is a graph of this function.

Self-test 5.1 At 25°C, the density of a 50 per cent by mass ethanol/water solution is 0.914 g cm^{-3}. Given that the partial molar volume of water in the solution is 17.4 cm^3 mol^{-1}, what is the partial molar volume of the ethanol?

[56.4 cm^3 mol^{-1}]

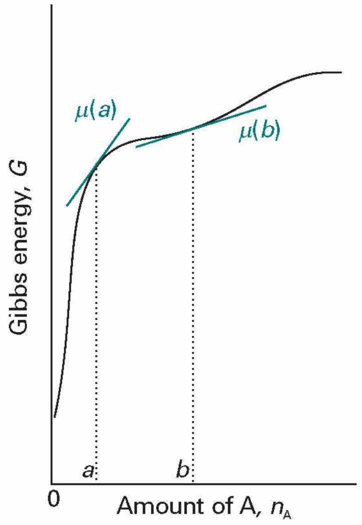

Fig. 5.4 The chemical potential of a substance is the slope of the total Gibbs energy of a mixture with respect to the amount of substance of interest. In general, the chemical potential varies with composition, as shown for the two values at a and b. In this case, both chemical potentials are positive.

Molar volumes are always positive, but partial molar quantities need not be. For example, the limiting partial molar volume of $MgSO_4$ in water (its partial molar volume in the limit of zero concentration) is −1.4 cm^3 mol^{-1}, which means that the addition of 1 mol $MgSO_4$ to a large volume of water results in a decrease in volume of 1.4 cm^3. The mixture contracts because the salt breaks up the open structure of water as the ions become hydrated, and it collapses slightly.

(b) Partial molar Gibbs energies

The concept of a partial molar quantity can be extended to any extensive state function. For a substance in a mixture, the chemical potential is *defined* as the partial molar Gibbs energy:

$$\mu_J = \left(\frac{\partial G}{\partial n_J}\right)_{p,T,n'} \qquad [5.4]$$

That is, the chemical potential is the slope of a plot of Gibbs energy against the amount of the component J, with the pressure and temperature (and the amounts of the other substances) held constant (Fig. 5.4). For a pure substance we can write $G = n_J G_{J,m}$, and from eqn 5.4 obtain $\mu_J = G_{J,m}$: in this case, the chemical potential is simply the molar Gibbs energy of the substance, as we used in Chapter 4.

By the same argument that led to eqn 5.3, it follows that the total Gibbs energy of a binary mixture is

$$G = n_A\mu_A + n_B\mu_B \qquad (5.5)$$

where μ_A and μ_B are the chemical potentials at the composition of the mixture. That is, the chemical potential of a substance in a mixture is the contribution of that substance to the total Gibbs energy of the mixture. Because the chemical potentials depend on composition (and the pressure and temperature), the Gibbs energy of a mixture may change when these variables change, and for a system of components A, B, etc., the equation $\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T$ becomes

$$\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T + \mu_{\mathrm{A}}\mathrm{d}n_{\mathrm{A}} + \mu_{\mathrm{B}}\mathrm{d}n_{\mathrm{B}} + \cdots \tag{5.6}$$

This expression is the **fundamental equation of chemical thermodynamics.** Its implications and consequences are explored and developed in this and the next two chapters.

At constant pressure and temperature, eqn 5.6 simplifies to

$$\mathrm{d}G = \mu_{\mathrm{A}}\mathrm{d}n_{\mathrm{A}} + \mu_{\mathrm{B}}\mathrm{d}n_{\mathrm{B}} + \cdots \tag{5.7}$$

We saw in Section 3.5e that under the same conditions $\mathrm{d}G = \mathrm{d}w_{\mathrm{add,max}}$. Therefore, at constant temperature and pressure,

$$\mathrm{d}w_{\mathrm{add,max}} = \mu_{\mathrm{A}}\mathrm{d}n_{\mathrm{A}} + \mu_{\mathrm{B}}\mathrm{d}n_{\mathrm{B}} + \cdots \tag{5.8}$$

That is, additional (non-expansion) work can arise from the changing composition of a system. For instance, in an electrochemical cell, the chemical reaction is arranged to take place in two distinct sites (at the two electrodes). The electrical work the cell performs can be traced to its changing composition as products are formed from reactants.

(c) The wider significance of the chemical potential

The chemical potential does more than show how G varies with composition. Because $G = U + pV - TS$, and therefore $U = -pV + TS + G$, we can write a general infinitesimal change in U for a system of variable composition as

$$\begin{aligned}\mathrm{d}U &= -p\mathrm{d}V - V\mathrm{d}p + S\mathrm{d}T + T\mathrm{d}S + \mathrm{d}G\\ &= -p\mathrm{d}V - V\mathrm{d}p + S\mathrm{d}T + T\mathrm{d}S + (V\mathrm{d}p - S\mathrm{d}T + \mu_{\mathrm{A}}\mathrm{d}n_{\mathrm{A}} + \mu_{\mathrm{B}}\mathrm{d}n_{\mathrm{B}} + \cdots)\\ &= -p\mathrm{d}V + T\mathrm{d}S + \mu_{\mathrm{A}}\mathrm{d}n_{\mathrm{A}} + \mu_{\mathrm{B}}\mathrm{d}n_{\mathrm{B}} + \cdots\end{aligned}$$

This expression is the generalization of eqn 3.43 (that $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$) to systems in which the composition may change. It follows that at constant volume and entropy,

$$\mathrm{d}U = \mu_{\mathrm{A}}\mathrm{d}n_{\mathrm{A}} + \mu_{\mathrm{B}}\mathrm{d}n_{\mathrm{B}} + \cdots \tag{5.9}$$

and hence that

$$\mu_{\mathrm{J}} = \left(\frac{\partial U}{\partial n_{\mathrm{J}}}\right)_{S,V,n'} \tag{5.10}$$

Therefore, not only does the chemical potential show how G changes when the composition changes, it also shows how the internal energy changes too (but under a different set of conditions). In the same way it is easy to deduce that

$$\text{(a)}\quad \mu_{\mathrm{J}} = \left(\frac{\partial H}{\partial n_{\mathrm{J}}}\right)_{S,p,n'} \qquad \text{(b)}\quad \mu_{\mathrm{J}} = \left(\frac{\partial A}{\partial n_{\mathrm{J}}}\right)_{V,T,n'} \tag{5.11}$$

Thus we see that the μ_{J} shows how all the extensive thermodynamic properties U, H, A, and G depend on the composition. This is why the chemical potential is so central to chemistry.

(d) The Gibbs–Duhem equation

Because the total Gibbs energy of a binary mixture is given by eqn 5.5 and the chemical potentials depend on the composition, when the compositions are changed infinitesimally we might expect G of a binary system to change by

$$\mathrm{d}G = \mu_{\mathrm{A}}\mathrm{d}n_{\mathrm{A}} + \mu_{\mathrm{B}}\mathrm{d}n_{\mathrm{B}} + n_{\mathrm{A}}\mathrm{d}\mu_{\mathrm{A}} + n_{\mathrm{B}}\mathrm{d}\mu_{\mathrm{B}}$$

However, we have seen that at constant pressure and temperature a change in Gibbs energy is given by eqn 5.7. Because G is a state function, these two equations must be equal, which implies that at constant temperature and pressure

$$n_{\rm A}{\rm d}\mu_{\rm A} + n_{\rm B}{\rm d}\mu_{\rm B} = 0 \qquad (5.12{\rm a})$$

This equation is a special case of the **Gibbs–Duhem equation**:

$$\sum_{\rm J} n_{\rm J}{\rm d}\mu_{\rm J} = 0 \qquad (5.12{\rm b})$$

The significance of the Gibbs–Duhem equation is that the chemical potential of one component of a mixture cannot change independently of the chemical potentials of the other components. In a binary mixture, if one partial molar quantity increases, then the other must decrease, with the two changes related by

$${\rm d}\mu_{\rm B} = -\frac{n_{\rm A}}{n_{\rm B}}{\rm d}\mu_{\rm A} \qquad (5.13)$$

The same line of reasoning applies to all partial molar quantities. We can see in Fig. 5.1, for example, that, where the partial molar volume of water increases, that of ethanol decreases. Moreover, as eqn 5.13 shows, and as we can see from Fig. 5.1, a small change in the partial molar volume of A corresponds to a large change in the partial molar volume of B if $n_{\rm A}/n_{\rm B}$ is large, but the opposite is true when this ratio is small. In practice, the Gibbs–Duhem equation is used to determine the partial molar volume of one component of a binary mixture from measurements of the partial molar volume of the second component.

Comment 5.1

The *molar concentration* (colloquially, the 'molarity', [J] or $c_{\rm J}$) is the amount of solute divided by the volume of the solution and is usually expressed in moles per cubic decimetre (mol dm^{-3}). We write $c^\ominus = 1$ mol dm^{-3}. The term *molality*, *b*, is the amount of solute divided by the mass of solvent and is usually expressed in moles per kilogram of solvent (mol kg^{-1}). We write $b^\ominus = 1$ mol kg^{-1}.

Example 5.1 *Using the Gibbs–Duhem equation*

The experimental values of the partial molar volume of K_2SO_4(aq) at 298 K are found to fit the expression

$$v_{\rm B} = 32.280 + 18.216x^{1/2}$$

where $v_{\rm B} = V_{\rm K_2SO_4}/({\rm cm^3\ mol^{-1}})$ and x is the numerical value of the molality of K_2SO_4 ($x = b/b^\ominus$; see *Comment 5.1*). Use the Gibbs–Duhem equation to derive an equation for the molar volume of water in the solution. The molar volume of pure water at 298 K is 18.079 cm^3 mol^{-1}.

Method Let A denote H_2O, the solvent, and B denote K_2SO_4, the solute. The Gibbs–Duhem equation for the partial molar volumes of two components is $n_{\rm A}{\rm d}V_{\rm A} + n_{\rm B}{\rm d}V_{\rm B} = 0$. This relation implies that ${\rm d}v_{\rm A} = -(n_{\rm B}/n_{\rm A}){\rm d}v_{\rm B}$, and therefore that $v_{\rm A}$ can be found by integration:

$$v_{\rm A} = v_{\rm A}^* - \int \frac{n_{\rm B}}{n_{\rm A}}{\rm d}v_{\rm B}$$

where $v_{\rm A}^* = V_{\rm A}/({\rm cm^3\ mol^{-1}})$ is the numerical value of the molar volume of pure A. The first step is to change the variable $v_{\rm B}$ to $x = b/b^\ominus$ and then to integrate the right-hand side between $x = 0$ (pure B) and the molality of interest.

Answer It follows from the information in the question that, with B = K_2SO_4, ${\rm d}v_{\rm B}/{\rm d}x = 9.108x^{-1/2}$. Therefore, the integration required is

$$v_{\rm B} = v_{\rm B}^* - 9.108\int_0^{b/b^\ominus} \frac{n_{\rm B}}{n_{\rm A}} x^{-1/2}{\rm d}x$$

However, the ratio of amounts of A (H_2O) and B (K_2SO_4) is related to the molality of B, $b = n_B/(1\text{ kg water})$ and $n_A = (1\text{ kg water})/M_A$ where M_A is the molar mass of water, by

$$\frac{n_B}{n_A} = \frac{n_B}{(1\text{ kg})/M_A} = \frac{n_B M_A}{1\text{ kg}} = bM_A = xb^{\ominus}M_A$$

and hence

$$v_A = v_A^{\star} - 9.108M_A b^{\ominus}\int_0^{b/b^{\ominus}} x^{1/2}\mathrm{d}x = v_A^{\star} - \tfrac{2}{3}\{9.108M_A b^{\ominus}(b/b^{\ominus})^{3/2}\}$$

It then follows, by substituting the data (including $M_A = 1.802 \times 10^{-2}\text{ kg mol}^{-1}$, the molar mass of water), that

$$V_A/(\text{cm}^3\text{ mol}^{-1}) = 18.079 - 0.1094(b/b^{\ominus})^{3/2}$$

The partial molar volumes are plotted in Fig. 5.5.

Self-test 5.2 Repeat the calculation for a salt B for which $V_B/(\text{cm}^3\text{ mol}^{-1}) = 6.218 + 5.146b - 7.147b^2$. $[V_A/(\text{cm}^3\text{ mol}^{-1}) = 18.079 - 0.0464b^2 + 0.0859b^3]$

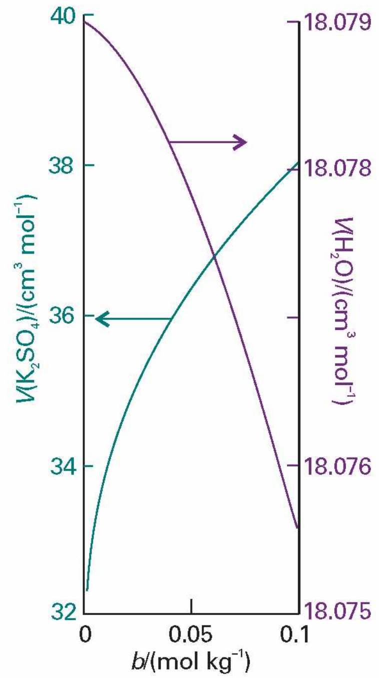

Fig. 5.5 The partial molar volumes of the components of an aqueous solution of potassium sulfate.

5.2 The thermodynamics of mixing

The dependence of the Gibbs energy of a mixture on its composition is given by eqn 5.5, and we know that at constant temperature and pressure systems tend towards lower Gibbs energy. This is the link we need in order to apply thermodynamics to the discussion of spontaneous changes of composition, as in the mixing of two substances. One simple example of a spontaneous mixing process is that of two gases introduced into the same container. The mixing is spontaneous, so it must correspond to a decrease in G. We shall now see how to express this idea quantitatively.

(a) The Gibbs energy of mixing of perfect gases

Let the amounts of two perfect gases in the two containers be n_A and n_B; both are at a temperature T and a pressure p (Fig. 5.6). At this stage, the chemical potentials of the two gases have their 'pure' values, which are obtained by applying the definition $\mu = G_m$ to eqn 3.57:

$$\mu = \mu^{\ominus} + RT\ln\frac{p}{p^{\ominus}} \qquad (5.14a)^{\circ}$$

where $\mu^{\ominus}$ is the **standard chemical potential**, the chemical potential of the pure gas at 1 bar. It will be much simpler notationally if we agree to let p denote the pressure relative to $p^{\ominus}$; that is, to replace $p/p^{\ominus}$ by p, for then we can write

$$\mu = \mu^{\ominus} + RT\ln p \qquad \{5.14b\}^{\circ}$$

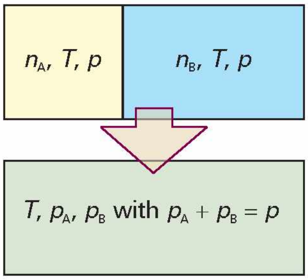

Fig. 5.6 The arrangement for calculating the thermodynamic functions of mixing of two perfect gases.

Equations for which this convention is used will be labelled {1}, {2}, . . . ; to use the equations, we have to remember to replace p by $p/p^{\ominus}$ again. In practice, that simply means using the numerical value of p in bars. The Gibbs energy of the total system is then given by eqn 5.5 as

$$G_i = n_A\mu_A + n_B\mu_B = n_A(\mu_A^{\ominus} + RT\ln p) + n_B(\mu_B^{\ominus} + RT\ln p) \qquad \{5.15\}^{\circ}$$

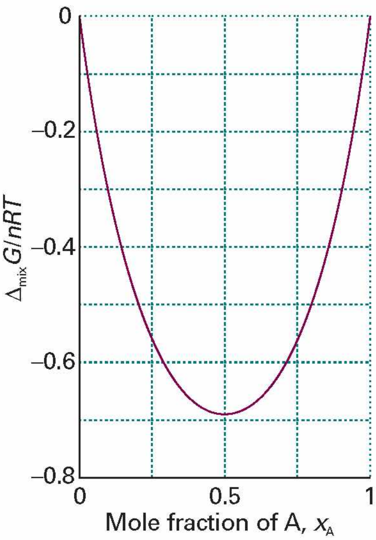

Fig. 5.7 The Gibbs energy of mixing of two perfect gases and (as discussed later) of two liquids that form an ideal solution. The Gibbs energy of mixing is negative for all compositions and temperatures, so perfect gases mix spontaneously in all proportions.

Exploration Draw graphs of $\Delta_{mix}G$ against x_A at different temperatures in the range 298 K to 500 K. For what value of x_A does $\Delta_{mix}G$ depend on temperature most strongly?

After mixing, the partial pressures of the gases are p_A and p_B, with $p_A + p_B = p$. The total Gibbs energy changes to

$$G_f = n_A(\mu_A^\ominus + RT\ln p_A) + n_B(\mu_B^\ominus + RT\ln p_B) \tag*{\{5.16\}°}$$

The difference $G_f - G_i$, the **Gibbs energy of mixing**, $\Delta_{mix}G$, is therefore

$$\Delta_{mix}G = n_ART\ln\frac{p_A}{p} + n_BRT\ln\frac{p_B}{p} \tag*{(5.17)°}$$

At this point we may replace n_J by x_Jn, where n is the total amount of A and B, and use the relation between partial pressure and mole fraction (Section 1.2b) to write $p_J/p = x_J$ for each component, which gives

$$\Delta_{mix}G = nRT(x_A\ln x_A + x_B\ln x_B) \tag*{(5.18)°}$$

Because mole fractions are never greater than 1, the logarithms in this equation are negative, and $\Delta_{mix}G < 0$ (Fig. 5.7). The conclusion that $\Delta_{mix}G$ is negative for all compositions confirms that perfect gases mix spontaneously in all proportions. However, the equation extends common sense by allowing us to discuss the process quantitatively.

Example 5.2 *Calculating a Gibbs energy of mixing*

A container is divided into two equal compartments (Fig. 5.8). One contains 3.0 mol $H_2(g)$ at 25°C; the other contains 1.0 mol $N_2(g)$ at 25°C. Calculate the Gibbs energy of mixing when the partition is removed. Assume perfect behaviour.

Method Equation 5.18 cannot be used directly because the two gases are initially at different pressures. We proceed by calculating the initial Gibbs energy from the chemical potentials. To do so, we need the pressure of each gas. Write the pressure of nitrogen as p; then the pressure of hydrogen as a multiple of p can be found from the gas laws. Next, calculate the Gibbs energy for the system when the partition is removed. The volume occupied by each gas doubles, so its initial partial pressure is halved.

Answer Given that the pressure of nitrogen is p, the pressure of hydrogen is $3p$; therefore, the initial Gibbs energy is

$$G_i = (3.0\text{ mol})\{\mu^\ominus(H_2) + RT\ln 3p\} + (1.0\text{ mol})\{\mu^\ominus(N_2) + RT\ln p\}$$

When the partition is removed and each gas occupies twice the original volume, the partial pressure of nitrogen falls to $\frac{1}{2}p$ and that of hydrogen falls to $\frac{3}{2}p$. Therefore, the Gibbs energy changes to

$$G_f = (3.0\text{ mol})\{\mu^\ominus(H_2) + RT\ln \tfrac{3}{2}p\} + (1.0\text{ mol})\{\mu^\ominus(N_2) + RT\ln \tfrac{1}{2}p\}$$

The Gibbs energy of mixing is the difference of these two quantities:

$$\begin{aligned}\Delta_{mix}G &= (3.0\text{ mol})RT\ln\left(\frac{\frac{3}{2}p}{3p}\right) + (1.0\text{ mol})RT\ln\left(\frac{\frac{1}{2}p}{p}\right)\\ &= -(3.0\text{ mol})RT\ln 2 - (1.0\text{ mol})RT\ln 2\\ &= -(4.0\text{ mol})RT\ln 2 = -6.9\text{ kJ}\end{aligned}$$

In this example, the value of $\Delta_{mix}G$ is the sum of two contributions: the mixing itself, and the changes in pressure of the two gases to their final total pressure, $2p$. When 3.0 mol H_2 mixes with 1.0 mol N_2 at the same pressure, with the volumes of the vessels adjusted accordingly, the change of Gibbs energy is −5.6 kJ.

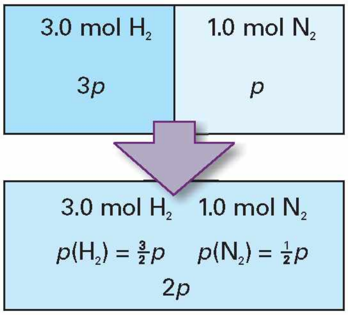

Fig. 5.8 The initial and final states considered in the calculation of the Gibbs energy of mixing of gases at different initial pressures.

Self-test 5.3 Suppose that 2.0 mol H_2 at 2.0 atm and 25°C and 4.0 mol N_2 at 3.0 atm and 25°C are mixed at constant volume. Calculate $\Delta_{mix}G$. What would be the value of $\Delta_{mix}G$ had the pressures been identical initially? [−9.7 kJ, −9.5 kJ]

(b) Other thermodynamic mixing functions

Because $(\partial G/\partial T)_{p,n} = -S$, it follows immediately from eqn 5.18 that, for a mixture of perfect gases initially at the same pressure, the entropy of mixing, $\Delta_{mix}S$, is

$$\Delta_{mix}S = \left(\frac{\partial \Delta_{mix}G}{\partial T}\right)_{p,n_A,n_B} = -nR(x_A \ln x_A + x_B \ln x_B) \qquad (5.19)^\circ$$

Because $\ln x < 0$, it follows that $\Delta_{mix}S > 0$ for all compositions (Fig. 5.9). For equal amounts of gas, for instance, we set $x_A = x_B = \frac{1}{2}$, and obtain $\Delta_{mix}S = nR \ln 2$, with n the total amount of gas molecules. This increase in entropy is what we expect when one gas disperses into the other and the disorder increases.

We can calculate the isothermal, isobaric (constant pressure) **enthalpy of mixing**, $\Delta_{mix}H$, the enthalpy change accompanying mixing, of two perfect gases from $\Delta G = \Delta H - T\Delta S$. It follows from eqns 5.18 and 5.19 that

$$\Delta_{mix}H = 0 \qquad (5.20)^\circ$$

The enthalpy of mixing is zero, as we should expect for a system in which there are no interactions between the molecules forming the gaseous mixture. It follows that the whole of the driving force for mixing comes from the increase in entropy of the system, because the entropy of the surroundings is unchanged.

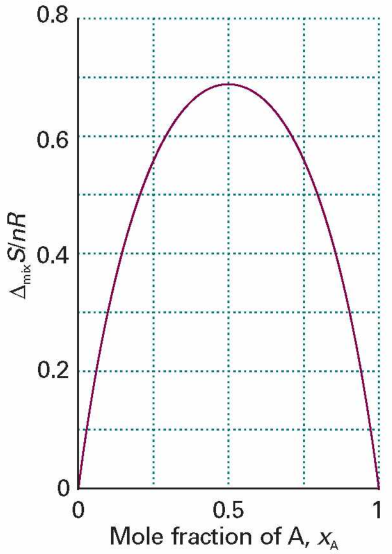

Fig. 5.9 The entropy of mixing of two perfect gases and (as discussed later) of two liquids that form an ideal solution. The entropy increases for all compositions and temperatures, so perfect gases mix spontaneously in all proportions. Because there is no transfer of heat to the surroundings when perfect gases mix, the entropy of the surroundings is unchanged. Hence, the graph also shows the total entropy of the system plus the surroundings when perfect gases mix.

5.3 The chemical potentials of liquids

To discuss the equilibrium properties of liquid mixtures we need to know how the Gibbs energy of a liquid varies with composition. To calculate its value, we use the fact that, at equilibrium, the chemical potential of a substance present as a vapour must be equal to its chemical potential in the liquid.

(a) Ideal solutions

We shall denote quantities relating to pure substances by a superscript *, so the chemical potential of pure A is written μ_A^*, and as $\mu_A^*(l)$ when we need to emphasize that A is a liquid. Because the vapour pressure of the pure liquid is p_A^*, it follows from eqn 5.14 that the chemical potential of A in the vapour (treated as a perfect gas) is $\mu_A^\ominus + RT \ln p_A^*$ (with p_A to be interpreted as the relative pressure $p_A/p^\ominus$). These two chemical potentials are equal at equilibrium (Fig. 5.10), so we can write

$$\mu_A^* = \mu_A^\ominus + RT \ln p_A^* \qquad \{5.21\}$$

If another substance, a solute, is also present in the liquid, the chemical potential of A in the liquid is changed to μ_A and its vapour pressure is changed to p_A. The vapour and solvent are still in equilibrium, so we can write

$$\mu_A = \mu_A^\ominus + RT \ln p_A \qquad \{5.22\}$$

Next, we combine these two equations to eliminate the standard chemical potential of the gas. To do so, we write eqn 5.21 as $\mu_A^\ominus = \mu_A^* - RT \ln p_A^*$ and substitute this expression into eqn 5.22 to obtain

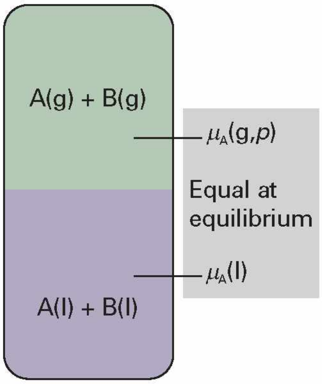

Fig. 5.10 At equilibrium, the chemical potential of the gaseous form of a substance A is equal to the chemical potential of its condensed phase. The equality is preserved if a solute is also present. Because the chemical potential of A in the vapour depends on its partial vapour pressure, it follows that the chemical potential of liquid A can be related to its partial vapour pressure.

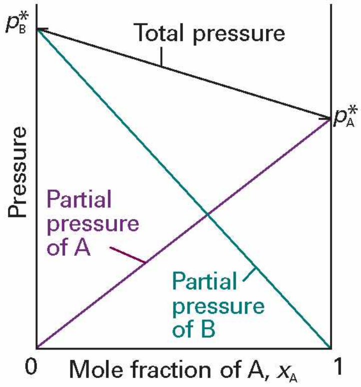

Fig. 5.11 The total vapour pressure and the two partial vapour pressures of an ideal binary mixture are proportional to the mole fractions of the components.

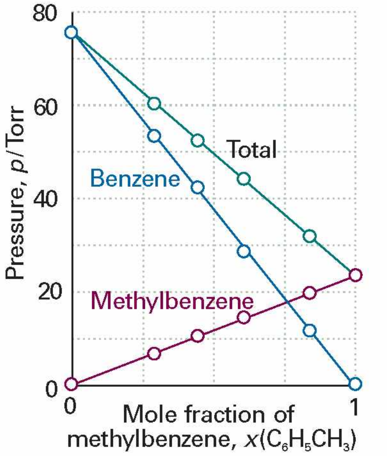

Fig. 5.12 Two similar liquids, in this case benzene and methylbenzene (toluene), behave almost ideally, and the variation of their vapour pressures with composition resembles that for an ideal solution.

$$\mu_A = \mu_A^* - RT\ln p_A^* + RT\ln p_A = \mu_A^* + RT\ln\frac{p_A}{p_A^*} \tag{5.23}$$

In the final step we draw on additional experimental information about the relation between the ratio of vapour pressures and the composition of the liquid. In a series of experiments on mixtures of closely related liquids (such as benzene and methylbenzene), the French chemist François Raoult found that the ratio of the partial vapour pressure of each component to its vapour pressure as a pure liquid, p_A/p_A^*, is approximately equal to the mole fraction of A in the liquid mixture. That is, he established what we now call **Raoult's law**:

$$p_A = x_A p_A^* \tag*{(5.24)°}$$

This law is illustrated in Fig. 5.11. Some mixtures obey Raoult's law very well, especially when the components are structurally similar (Fig. 5.12). Mixtures that obey the law throughout the composition range from pure A to pure B are called **ideal solutions**. When we write equations that are valid only for ideal solutions, we shall label them with a superscript °, as in eqn 5.24.

For an ideal solution, it follows from eqns 5.23 and 5.24 that

$$\mu_A = \mu_A^* + RT\ln x_A \tag*{(5.25)°}$$

This important equation can be used as the *definition* of an ideal solution (so that it implies Raoult's law rather than stemming from it). It is in fact a better definition than eqn 5.24 because it does not assume that the vapour is a perfect gas.

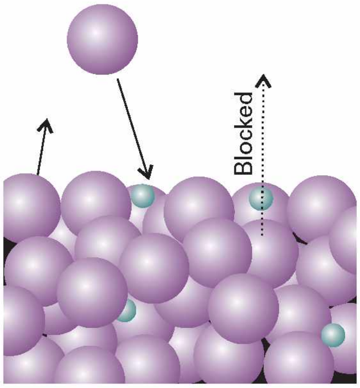

Fig. 5.13 A pictorial representation of the molecular basis of Raoult's law. The large spheres represent solvent molecules at the surface of a solution (the uppermost line of spheres), and the small spheres are solute molecules. The latter hinder the escape of solvent molecules into the vapour, but do not hinder their return.

Molecular interpretation 5.1 *The molecular origin of Raoult's law*

The origin of Raoult's law can be understood in molecular terms by considering the rates at which molecules leave and return to the liquid. The law reflects the fact that the presence of a second component reduces the rate at which A molecules leave the surface of the liquid but does not inhibit the rate at which they return (Fig. 5.13).

The rate at which A molecules leave the surface is proportional to the number of them at the surface, which in turn is proportional to the mole fraction of A:

$$\text{rate of vaporization} = kx_A$$

where k is a constant of proportionality. The rate at which molecules condense is proportional to their concentration in the gas phase, which in turn is proportional to their partial pressure:

$$\text{rate of condensation} = k'p_A$$

At equilibrium, the rates of vaporization and condensation are equal, so $k'p_A = kx_A$. It follows that

$$p_A = \frac{k}{k'}x_A$$

For the pure liquid, $x_A = 1$; so in this special case $p_A^* = k/k'$. Equation 5.24 then follows by substitution of this relation into the line above.

Some solutions depart significantly from Raoult's law (Fig. 5.14). Nevertheless, even in these cases the law is obeyed increasingly closely for the component in excess (the solvent) as it approaches purity. The law is therefore a good approximation for the properties of the solvent if the solution is dilute.

(b) Ideal-dilute solutions

In ideal solutions the solute, as well as the solvent, obeys Raoult's law. However, the English chemist William Henry found experimentally that, for real solutions at low concentrations, although the vapour pressure of the solute is proportional to its mole fraction, the constant of proportionality is not the vapour pressure of the pure substance (Fig. 5.15). **Henry's law** is:

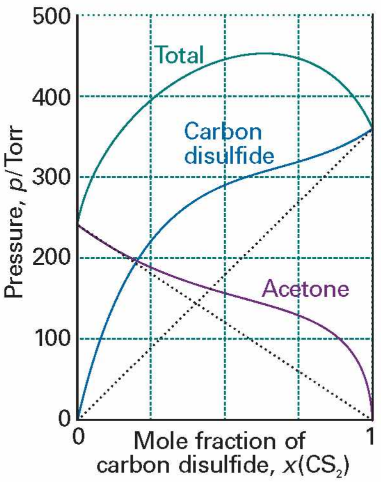

Fig. 5.14 Strong deviations from ideality are shown by dissimilar liquids (in this case carbon disulfide and acetone, propanone).

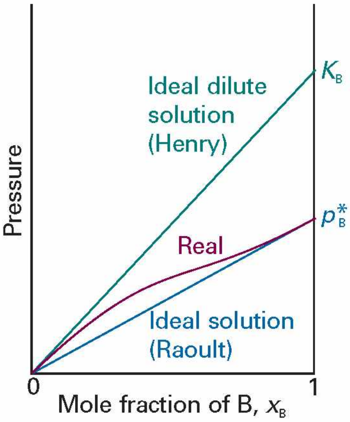

Fig. 5.15 When a component (the solvent) is nearly pure, it has a vapour pressure that is proportional to mole fraction with a slope p_B^* (Raoult's law). When it is the minor component (the solute) its vapour pressure is still proportional to the mole fraction, but the constant of proportionality is now K_B (Henry's law).

$$p_B = x_B K_B \qquad (5.26)^\circ$$

In this expression x_B is the mole fraction of the solute and K_B is an empirical constant (with the dimensions of pressure) chosen so that the plot of the vapour pressure of B against its mole fraction is tangent to the experimental curve at $x_B = 0$.

Mixtures for which the solute obeys Henry's law and the solvent obeys Raoult's law are called **ideal-dilute solutions**. We shall also label equations with a superscript ° when they have been derived from Henry's law. The difference in behaviour of the solute and solvent at low concentrations (as expressed by Henry's and Raoult's laws, respectively) arises from the fact that in a dilute solution the solvent molecules are in an environment very much like the one they have in the pure liquid (Fig. 5.16). In contrast, the solute molecules are surrounded by solvent molecules, which is entirely different from their environment when pure. Thus, the solvent behaves like a slightly modified pure liquid, but the solute behaves entirely differently from its pure state unless the solvent and solute molecules happen to be very similar. In the latter case, the solute also obeys Raoult's law.

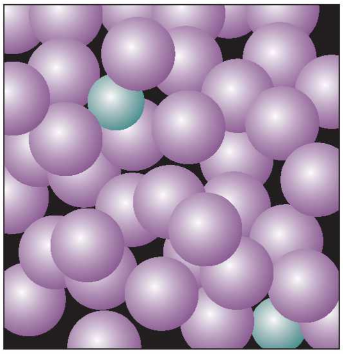

Fig. 5.16 In a dilute solution, the solvent molecules (the purple spheres) are in an environment that differs only slightly from that of the pure solvent. The solute particles, however, are in an environment totally unlike that of the pure solute.

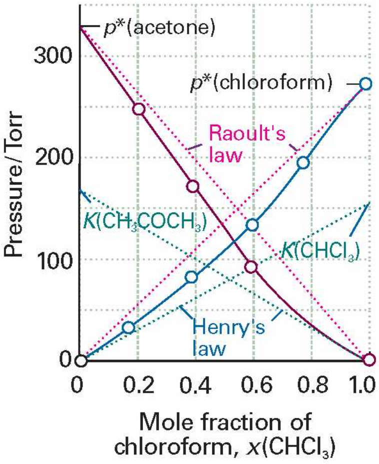

Fig. 5.17 The experimental partial vapour pressures of a mixture of chloroform (trichloromethane) and acetone (propanone) based on the data in *Example 5.3*. The values of *K* are obtained by extrapolating the dilute solution vapour pressures as explained in the *Example*.

Example 5.3 *Investigating the validity of Raoult's and Henry's laws*

The vapour pressures of each component in a mixture of propanone (acetone, A) and trichloromethane (chloroform, C) were measured at 35°C with the following results:

x_C	0	0.20	0.40	0.60	0.80	1
p_C/kPa	0	4.7	11	18.9	26.7	36.4
p_A/kPa	46.3	33.3	23.3	12.3	4.9	0

Confirm that the mixture conforms to Raoult's law for the component in large excess and to Henry's law for the minor component. Find the Henry's law constants.

Method Both Raoult's and Henry's laws are statements about the form of the graph of partial vapour pressure against mole fraction. Therefore, plot the partial vapour pressures against mole fraction. Raoult's law is tested by comparing the data with the straight line $p_J = x_J p_J^*$ for each component in the region in which it is in excess (and acting as the solvent). Henry's law is tested by finding a straight line $p_J = x_J K_J$ that is tangent to each partial vapour pressure at low x, where the component can be treated as the solute.

Answer The data are plotted in Fig. 5.17 together with the Raoult's law lines. Henry's law requires K = 23.3 kPa for propanone and K = 22.0 kPa for trichloromethane. Notice how the system deviates from both Raoult's and Henry's laws even for quite small departures from $x = 1$ and $x = 0$, respectively. We deal with these deviations in Section 5.5.

Self-test 5.4 The vapour pressure of chloromethane at various mole fractions in a mixture at 25°C was found to be as follows:

x	0.005	0.009	0.019	0.024
p/kPa	27.3	48.4	101	126

Estimate Henry's law constant. [5 MPa]

For practical applications, Henry's law is expressed in terms of the molality, b, of the solute,

$$p_B = b_B K_B$$

Some Henry's law data for this convention are listed in Table 5.1. As well as providing a link between the mole fraction of solute and its partial pressure, the data in the table may also be used to calculate gas solubilities. A knowledge of Henry's law constants for gases in blood and fats is important for the discussion of respiration, especially when the partial pressure of oxygen is abnormal, as in diving and mountaineering, and for the discussion of the action of gaseous anaesthetics.

Synoptic Table 5.1* Henry's law constants for gases in water at 298 K

	$K/(\text{kPa kg mol}^{-1})$
CO_2	3.01×10^3
H_2	1.28×10^5
N_2	1.56×10^5
O_2	7.92×10^4

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

Illustration 5.2 *Using Henry's law*

To estimate the molar solubility of oxygen in water at 25°C and a partial pressure of 21 kPa, its partial pressure in the atmosphere at sea level, we write

$$b_{O_2} = \frac{p_{O_2}}{K_{O_2}} = \frac{21\ \text{kPa}}{7.9 \times 10^4\ \text{kPa kg mol}^{-1}} = 2.9 \times 10^{-4}\ \text{mol kg}^{-1}$$

The molality of the saturated solution is therefore 0.29 mmol kg^{-1}. To convert this quantity to a molar concentration, we assume that the mass density of this dilute solution is essentially that of pure water at 25°C, or $\rho_{H_2O} = 0.99709\ \text{kg dm}^{-3}$. It follows that the molar concentration of oxygen is

$$[O_2] = b_{O_2} \times \rho_{H_2O} = 0.29\ \text{mmol kg}^{-1} \times 0.99709\ \text{kg dm}^{-3} = 0.29\ \text{mmol dm}^{-3}$$

A note on good practice The number of significant figures in the result of a calculation should not exceed the number in the data (only two in this case).

Self-test 5.5 Calculate the molar solubility of nitrogen in water exposed to air at 25°C; partial pressures were calculated in *Example 1.3*. [0.51 mmol dm^{-3}]

IMPACT ON BIOLOGY
I5.1 Gas solubility and breathing

We inhale about 500 cm^3 of air with each breath we take. The influx of air is a result of changes in volume of the lungs as the diaphragm is depressed and the chest expands, which results in a decrease in pressure of about 100 Pa relative to atmospheric pressure. Expiration occurs as the diaphragm rises and the chest contracts, and gives rise to a differential pressure of about 100 Pa above atmospheric pressure. The total volume of air in the lungs is about 6 dm^3, and the additional volume of air that can be exhaled forcefully after normal expiration is about 1.5 dm^3. Some air remains in the lungs at all times to prevent the collapse of the alveoli.

Comment 5.2
The web site contains links to online databases of Henry's law constants.

A knowledge of Henry's law constants for gases in fats and lipids is important for the discussion of respiration. The effect of gas exchange between blood and air inside the alveoli of the lungs means that the composition of the air in the lungs changes throughout the breathing cycle. Alveolar gas is in fact a mixture of newly inhaled air and air about to be exhaled. The concentration of oxygen present in arterial blood is equivalent to a partial pressure of about 40 Torr (5.3 kPa), whereas the partial pressure of freshly inhaled air is about 104 Torr (13.9 kPa). Arterial blood remains in the capillary passing through the wall of an alveolus for about 0.75 s, but such is the steepness of the pressure gradient that it becomes fully saturated with oxygen in about 0.25 s. If the lungs collect fluids (as in pneumonia), then the respiratory membrane thickens, diffusion is greatly slowed, and body tissues begin to suffer from oxygen starvation. Carbon dioxide moves in the opposite direction across the respiratory