# Part 1 Equilibrium

*Part 1 of the text develops the concepts that are needed for the discussion of equilibria in chemistry. Equilibria include physical change, such as fusion and vaporization, and chemical change, including electrochemistry. The discussion is in terms of thermodynamics, and particularly in terms of enthalpy and entropy. We shall see that a unified view of equilibrium and the direction of spontaneous change can be obtained in terms of the chemical potential of substances. The chapters of Part 1 deal with the properties of matter in bulk, those of Part 2 will show how these properties stem from the behaviour of individual atoms.*

# 1

# 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 this relation between the properties of the gas can be explained in terms of the kinetic model, in which the gas is represented by a collection of point masses in continuous random motion. Finally, we 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 shall consider only pure gases, but later in the chapter we shall 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 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.

### 0.1 The states of gases

The physical **state** of a sample of a substance is defined by its physical properties, and 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 the values of 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

$$p = f(T, V, n) \tag{1}$$

This equation tells us that, if we know the values of $n$, $T$, and $V$ for a particular substance, then we can find its pressure. 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 for a **perfect gas**, which has the form

$$p = \frac{nRT}{V} \tag{2}$$

where $R$ is a constant. Much of the rest of this chapter will examine the origin and implications of this equation of state.

## *(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.

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

$$1\ \mathrm{Pa} = 1\ \mathrm{N\,m^{-2}} \qquad [3]$$

However, several other units are still widely used; they are summarized in Table 1.1. A pressure of $10^5$ Pa (1 bar) is the **standard pressure** for reporting data, and we shall denote it $p^{\ominus}$.

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 Pa |
| torr | 1 Torr | (101 325/760) Pa = 133.32 ... Pa |
| millimetre of mercury | 1 mmHg | 133.322 ... Pa |
| pound per square inch | 1 psi | 6.894 757 ... kPa |

## **Example 1.1** Calculating pressure

Suppose Isaac Newton weighed 65 kg. Calculate the pressure he exerted on the ground when wearing (a) boots with soles of total area 250 cm$^2$ in contact with the ground, (b) ice skates, of total area 2.0 cm$^2$.

**Method** Pressure is force divided by area ($p = F/A$), so the calculation depends on being able to calculate the force, $F$, that Newton exerts on the ground, and then to divide it by the area, $A$, over which the force is exerted. To calculate the force, we need to know (from elementary physics) that the downward force an object of mass $m$ exerts at the surface of the Earth is $F = mg$, where $g$ is the acceleration of free fall, $9.81\ \mathrm{m\,s^{-2}}$. Note that

$1\ \mathrm{N} = 1\ \mathrm{kg\,m\,s^{-2}}$ and $1\ \mathrm{Pa} = 1\ \mathrm{N\,m^{-2}}$. Convert the areas to metre squared by using $1\ \mathrm{cm^2} = 10^{-4}\ \mathrm{m^2}$.

Answer The force exerted by Newton is

$$F = (65\ \mathrm{kg}) \times (9.81\ \mathrm{m\,s^{-2}}) = 6.4 \times 10^2\ \mathrm{N}$$

The force is the same whatever his footwear. The areas 250 $\mathrm{cm^2}$ and 2.0 $\mathrm{cm^2}$ correspond to $2.50 \times 10^{-2}\ \mathrm{m^2}$ and $2.0 \times 10^{-4}\ \mathrm{m^2}$, respectively. The pressure he exerts in each case is:

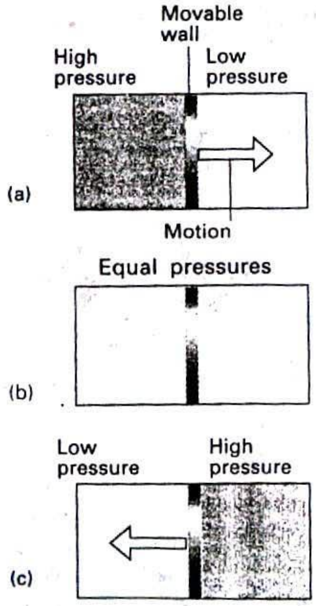
$$\text{(a) } p = \frac{6.4 \times 10^2\ \mathrm{N}}{2.50 \times 10^{-2}\ \mathrm{m^2}} = 2.6 \times 10^4\ \mathrm{Pa}\ (26\ \mathrm{kPa})$$

$$\text{(b) } p = \frac{6.4 \times 10^2\ \mathrm{N}}{2.0 \times 10^{-4}\ \mathrm{m^2}} = 3.2 \times 10^6\ \mathrm{Pa}\ (3.2\ \mathrm{MPa})$$

Comment One Newton exerts a force of much more than 1 newton. A pressure of 26 kPa corresponds to 0.26 atm and a pressure of 3.2 MPa corresponds to 32 atm.

Self-test 1.1 Calculate the pressure 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.

[0.98 GPa, $9.7 \times 10^3$ atm]



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.

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 lower pressure gas. The pressure of the former gas will fall as it expands and that of the latter 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 numerical value of 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.

### *(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 1.2 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 $\rho$ and height $h$ at the surface of the Earth.

Method As in Example 1.1, $p = F/A$ and $F = mg$, so we need to know the mass of a column of liquid. The mass of a column of liquid is its mass density, $\rho$, multiplied by its volume, $V$. So, the first step is to calculate the volume of a cylindrical column of liquid.

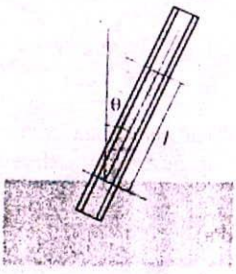
Answer Let the column have cross-sectional area $A$; then its volume is $Ah$ and its mass is $m = \rho Ah$. The force the column of this mass exerts at its base is

$$F = mg = \rho Ahg$$

The pressure at the base of the column is therefore

$$p = \frac{F}{A} = \frac{\rho A h g}{A} = \rho g h$$

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



1

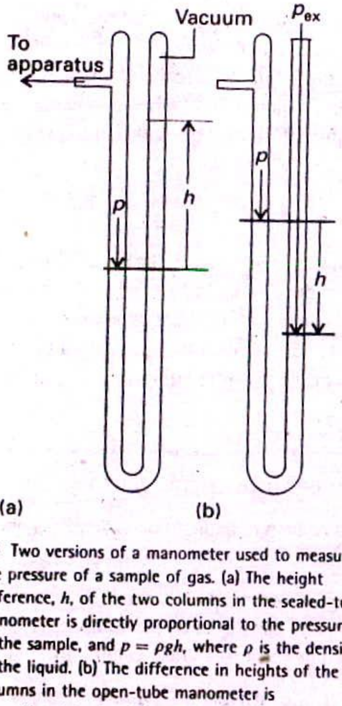
**Self-test 1.2** Derive an expression for the pressure at the base of a column of liquid of length $l$ held at an angle $\theta$ to the vertical (1).

$[p = \rho g l \cos\theta]$

The pressure of a sample of gas inside a container is measured with a **manometer** (Fig. 1.2). In its simplest form, a manometer is a U-tube filled with a liquid of low volatility (such as silicone oil). The pressure, $p$, of the gaseous sample balances the pressure exerted by the column of liquid, which is equal to $\rho g h$ if the column is of height $h$ (see Example 1.2), plus the external pressure, $p_{\mathrm{ex}}$, if one tube is open to the atmosphere:

$$p = p_{\mathrm{ex}} + \rho g h \tag{4}$$

It follows that the pressure of the sample can be obtained by measuring the height of the column and noting the external pressure. More sophisticated techniques are used at lower pressures. Methods that avoid the complication of having to account for the vapour from the manometer fluid are also available. These superior methods include monitoring the deflection of a diaphragm, either mechanically or electrically, or monitoring the change in a pressure-sensitive electrical property.



1.2 Two versions of a manometer used to measure the pressure of a sample of gas. (a) The height difference, $h$, of the two columns in the sealed-tube manometer is directly proportional to the pressure of the sample, and $p = \rho g h$, where $\rho$ is the density of the liquid. (b) The difference in heights of the columns in the open-tube manometer is proportional to the difference in pressure between the sample and the atmosphere. In the example shown, the pressure of the sample is lower than that of the atmosphere.

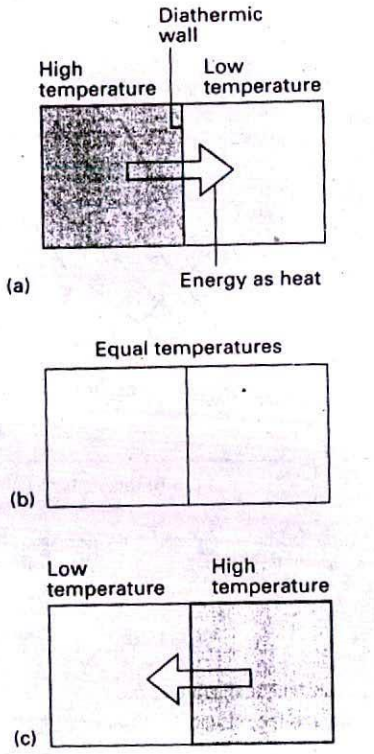
## (c) Temperature

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 tells us the direction of the flow of energy. If energy flows from A to B when they are in contact, then we say that A has a higher temperature than B (Fig. 1.3).

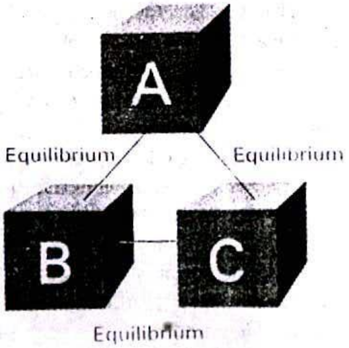
It will prove useful to distinguish between two types of boundary that can separate the objects. A boundary is **diathermic** if a change of state is observed when two objects at different temperatures are brought into contact (the word *dia* is from the Greek for 'through'). A metal container has diathermic walls. A boundary is **adiabatic** if no change occurs even though the two objects have different temperatures.

The temperature is a property that tells us 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 and 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. 1.4). This observation is summarized by the following statement:

**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.



1.3 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.



1.4 The experience summarized by the Zeroth Law of thermodynamics is that, if an object A is in thermal equilibrium with B and if B is in thermal equilibrium with C, then B 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 mercury. 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 contact with another object C, then we can predict that no change of state of A and C will occur when they are in 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 $\theta$ 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 almost independent of the identity of the gas, as we shall explain shortly. The perfect-gas scale turns out to be identical to the **thermodynamic temperature scale** to be introduced in Section 4.2c, 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. Thermodynamic and Celsius temperatures are related by the exact expression

$$T/\mathrm{K} = \theta/^{\circ}\mathrm{C} + 273.15 \qquad (5)$$

This relation is the current definition of the Celsius scale in terms of the more fundamental Kelvin scale.

**Illustration**

To express 25.00 °C as a temperature in kelvins, we write

$$T/\mathrm{K} = 25.00\,^{\circ}\mathrm{C}/^{\circ}\mathrm{C} + 273.15 = 25.00 + 273.15 = 298.15$$

Note how the units 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.

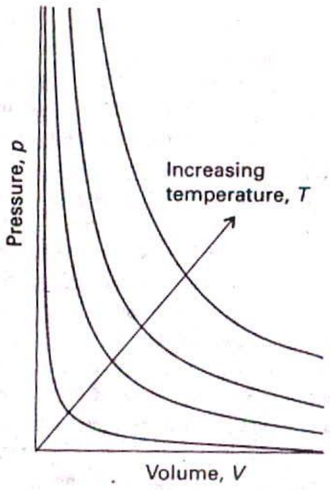
## 1.2 The gas laws

The equation of state of a low-pressure gas was established by combining a series of empirical laws. We shall introduce these laws below, and then show how they can be combined into the single equation of state $pV = nRT$.

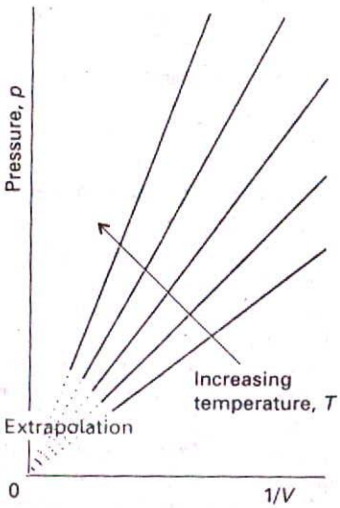
### (a) The individual gas laws

Robert Boyle, acting on the suggestion of a correspondent John Townley, showed in 1661 that, to a good approximation, the pressure and volume of a fixed amount of gas at constant temperature are related by

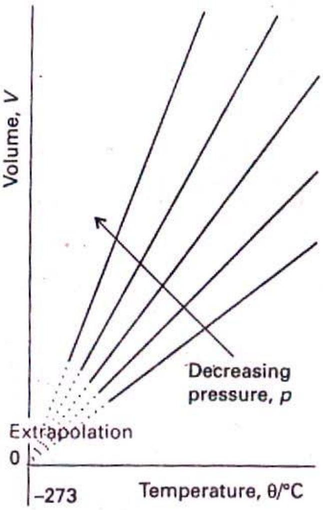
$$pV = \text{constant} \qquad (6)^{\circ}$$



1.5 The pressure–volume dependence of a fixed amount of perfect gas at different temperatures. Each curve is a hyperbola ($pV$ = constant) and is called an isotherm.



1.6 Straight lines are obtained when the pressure is plotted against $1/V$.



1.7 The variation of the volume of a fixed amount of gas with the temperature constant. Note that in each case they extrapolate to zero volume at −273.15°C.

This relation is known as Boyle's law. That is, at constant temperature, the pressure of a sample of gas is inversely proportional to its volume, and the volume it occupies is inversely proportional to its pressure:

$$p \propto \frac{1}{V} \qquad V \propto \frac{1}{p} \tag{7}^{\circ}$$

The variation of the pressure of a sample of gas as the volume is changed is depicted in Fig. 1.5. 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.[1] An alternative depiction, a plot of pressure against 1/volume, is shown in Fig. 1.6.

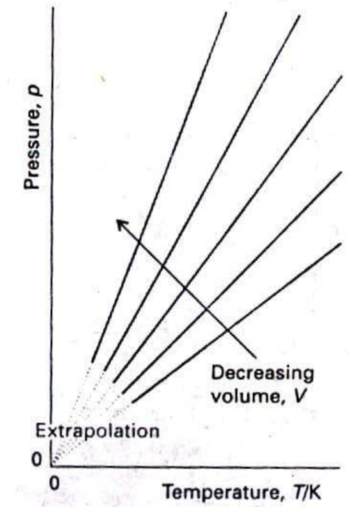
More modern experiments have shown that Boyle's law is valid only at low pressures, and that real gases obey it only in the limit of the pressure approaching zero (which we write $p \to 0$). Boyle's law is therefore an example of a **limiting law**, a law that is strictly true only in a certain limit, in this case $p \to 0$. Equations that are valid in this limiting sense will be signalled by a ° on the equation number, as in eqn 6.

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. The reason why Boyle's law applies to all gases regardless of their chemical identity (provided the pressure is low) is that at low pressures the molecules are so far apart on average that they exert no influence on one another, and hence travel independently.

The French scientist Jacques Charles established the next important property of gases. He studied the effect of temperature on the volume of a sample of gas that was subjected to constant pressure. He found that the volume increased linearly with the temperature,

---

[1] A hyperbola is a curve obtained by plotting $y$ against $x$ with $xy$ = constant.



1.8 The pressure also varies linearly with the temperature, and extrapolates to zero at $T = 0$ ($-273.15\,^\circ\text{C}$).

whatever the identity of the gas, provided it was at low pressure. Specifically, he established that

$$V = \text{constant} \times (\theta + 273\,^\circ\text{C}) \qquad \text{(at constant pressure)} \qquad (8)^\circ$$

(Recall that we use $\theta$ to denote temperatures on the Celsius scale.) The linear variation of volume with temperature summarized by this expression is illustrated in Fig. 1.7. The lines are examples of isobars, or lines showing the variation of properties at constant pressure.

Equation 8 suggests that the volume of any gas should extrapolate to zero at $\theta = -273\,^\circ\text{C}$ and therefore that $-273\,^\circ\text{C}$ is a natural zero of a fundamental temperature scale. As we have already indicated, a scale with 0 set at $-273.15\,^\circ\text{C}$ is equivalent to the thermodynamic temperature scale devised by Kelvin, so **Charles's law** can be written

$$V = \text{constant} \times T \qquad \text{(at constant pressure)} \qquad (9)^\circ$$

An alternative version of Charles's law, in which the pressure of a sample of gas is monitored under conditions of constant volume is

$$p = \text{constant} \times T \qquad \text{(at constant volume)} \qquad (10)^\circ$$

This version of the law indicates that the pressure of a gas falls to zero as the temperature is reduced to zero (Fig. 1.8).

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 do so with greater impact. Therefore they exert a greater pressure on the walls of the container. A problem we leave until later is why the pressure depends so simply on the temperature.

The final piece of experimental information we need is that, at a given pressure and temperature, the molar volume, $V_m = V/n$, the volume per mole of molecules, of a gas is approximately the same regardless of the identity of the gas. This observation implies that the volume of a sample of gas is proportional to the amount of molecules (in moles) present, and that the constant of proportionality is independent of the identity of the gas:

$$V = \text{constant} \times n \qquad \text{(at constant pressure and temperature)} \qquad (11)^\circ$$

This conclusion is a modern form of **Avogadro's principle**, that equal volumes of gases at the same pressure and temperature contain the same numbers of molecules.

### *(b) The combined gas law*

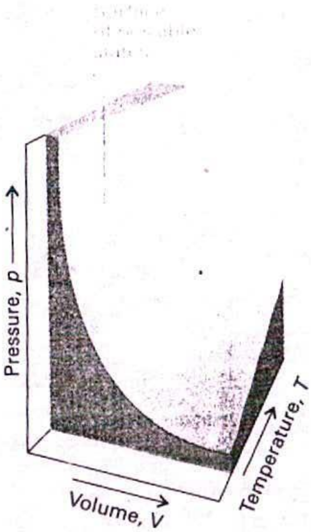
The empirical observations summarized by eqns 6–11 can be combined into a single expression:

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

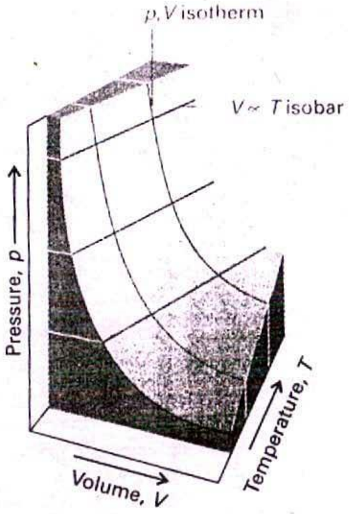
This expression is consistent with Boyle's law ($pV = \text{constant}$) when $n$ and $T$ are constant, with both forms of Charles's law ($p \propto T$, $V \propto T$) when $n$ and either $V$ or $p$ are held constant, and with Avogadro's principle ($V \propto n$) when $p$ and $T$ are constant. The constant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

$$pV = nRT \qquad (12)^\circ$$

is called 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 12 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 12 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).



1.9 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.



1.10 Sections through the surface shown in Fig. 1.9 at constant temperature give the isotherms shown in Fig. 1.5 and the isobars shown in Fig. 1.7.

Table 1.2 The gas constant in various units

| $R$ |
|---|
| $8.31451\ \mathrm{J\,K^{-1}\,mol^{-1}}$ |
| $8.20578 \times 10^{-2}\ \mathrm{L\,atm\,K^{-1}\,mol^{-1}}$ |
| $8.31451 \times 10^{-2}\ \mathrm{L\,bar\,K^{-1}\,mol^{-1}}$ |
| $8.31451\ \mathrm{Pa\,m^3\,K^{-1}\,mol^{-1}}$ |
| $62.364\ \mathrm{L\,Torr\,K^{-1}\,mol^{-1}}$ |
| $1.98722\ \mathrm{cal\,K^{-1}\,mol^{-1}}$ |

However, a more accurate value can be obtained by measuring the speed of sound in a low-pressure gas and extrapolating its value to zero pressure. The values of $R$ in a variety of units are given in Table 1.2.

The surface in Fig. 1.9 is a plot of the pressure of a fixed amount of perfect gas against its volume and thermodynamic temperature as given by eqn 12. 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 1.5 and 1.8 correspond to the sections through the surface (Fig. 1.10).

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 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 24.790 L 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 L mol$^{-1}$.

## Example 1.3 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 a pressure of 100 atm and a temperature of 300 K, what pressure would it exert at the working temperature if it behaved as a perfect gas?

| | $n$ | $p$ | $V$ | $T$ |
|---|---|---|---|---|
| Initial | Same | 100 | Same | 300 |
| Final | Same | ? | Same | 500 |

2

**Method** The known and unknown data are summarized in (2). We expect the pressure to be greater on account of the increase in temperature. Moreover, because pressure is proportional to temperature, we can anticipate that the pressure will increase by a factor of $T_2/T_1$, where $T_1$ is the initial temperature and $T_2$ is the final temperature. To proceed more formally, we note that, when a problem involves a change in conditions for a constant amount of gas, the perfect gas equation can be developed as follows. First, write eqn 12 for the initial and final sets of conditions:

$$\frac{p_1V_1}{T_1}=nR \qquad \frac{p_2V_2}{T_2}=nR$$

Because $n$ (in this problem) and $R$ are both constant and equal, it follows that

$$\frac{p_1V_1}{T_1}=\frac{p_2V_2}{T_2}$$

Any constant quantities (volume in this example) cancel, and the data may then be substituted into the resulting expression.

Answer Cancellation of the volumes (because $V_1 = V_2$) on each side of this expression 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

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

Comment 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. The expression $p_1V_1/T_1=p_2V_2/T_2$ is commonly called the *combined gas law*.

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

[900 K]

### (c) Mixtures of gases

The kind of question we need to answer when dealing with gaseous mixtures is the contribution that each component gas makes to the total pressure of the sample. In the nineteenth century John Dalton made observations that provide the answer and summarized them in a law:

> **Dalton's law:** The pressure exerted by a mixture of perfect gases is the sum of the partial pressures of the gases.

The **partial pressure** of a perfect gas is the pressure that it would exert if it occupied the container alone. That is, if a certain amount of $H_2$ exerts 25 kPa when present alone in a container, and an amount of $N_2$ exerts 80 kPa when present alone in the same container at the same temperature, then the total pressure when both are present is the sum of these two partial pressures, or 105 kPa (provided the individual gases and the mixture behave perfectly). More generally, if the partial pressure of a perfect gas A is $p_A$, that of a perfect gas B is $p_B$, and so on, then the total pressure when all the gases occupy the same container at the same temperature is

$$p=p_A+p_B+\cdots \qquad (13)^\circ$$

where, for each substance J,

$$p_J = \frac{n_J RT}{V} \qquad (14)^\circ$$

## Example 1.4 Using Dalton's law

A container of volume 10.0 L holds 1.00 mol $N_2$ and 3.00 mol $H_2$ at 298 K. What is the total pressure in atmospheres if each component behaves as a perfect gas?

Method It follows from eqns 13 and 14 that the total pressure when two gases, A and B, occupy a container is

$$p = p_A + p_B = (n_A + n_B)\frac{RT}{V}$$

To obtain the answer expressed in atmospheres, use $R = 8.206 \times 10^{-2}\ \mathrm{L\,atm\,K^{-1}\,mol^{-1}}$.

Answer Under the stated conditions

$$p = (1.00\ \mathrm{mol} + 3.00\ \mathrm{mol}) \times \frac{(8.206 \times 10^{-2}\ \mathrm{L\,atm\,K^{-1}\,mol^{-1}}) \times (298\ \mathrm{K})}{10.0\ \mathrm{L}}$$
$$= 9.78\ \mathrm{atm}$$

Self-test 1.4 Calculate the total pressure when 1.00 mol $N_2$ and 2.00 mol $O_2$ are added to the same container (with the nitrogen and hydrogen still inside) at 298 K.

[17.1 atm]

## (d) Mole fractions and partial pressures

We can take a step closer to the discussion of mixtures of real gases by introducing the mole fraction of each component J. The **mole fraction**, $x_J$, is the amount of J expressed as a fraction of the total amount of molecules, $n$, in the sample:

$$x_J = \frac{n_J}{n} \qquad n = n_A + n_B + \cdots \qquad [15]$$

When no J molecules are present, $x_J = 0$; when only J molecules are present, $x_J = 1$. A mixture of 1.0 mol $N_2$ and 3.0 mol $H_2$, and therefore of 4.0 mol molecules in all, consists of mole fractions 0.25 of $N_2$ and 0.75 of $H_2$. It follows from the definition of $x_J$ that, whatever the composition of the mixture,

$$x_A + x_B + \cdots = 1 \qquad (16)$$

Next, we *define* the partial pressure, $p_J$, of a gas J in a mixture (any gas, not just a perfect gas) as

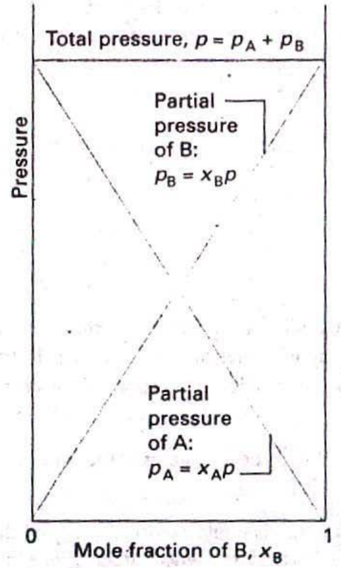
$$p_J = x_J p \qquad [17]$$

where $p$ is the total pressure of the mixture (Fig. 1.11). Only for a mixture of perfect gases can we identify $p_J$ with the pressure that the gas J would exert if it were alone in the container and calculate its value from eqn 14.

It follows from eqns 16 and 17 that the sum of the partial pressures is equal to the total pressure:

$$p_A + p_B + \cdots = (x_A + x_B + \cdots)p = p \qquad (18)$$

This relation is true for both real and perfect gases.



1.11 The partial pressures $p_A$ and $p_B$ of a binary mixture of (real or perfect) gases of total pressure $p$ as the composition changes from pure A to pure B. The sum of the partial pressures is equal to the total pressure. If the gases are perfect, then the partial pressure is also the pressure that each gas would exert if it were present alone in the container.

### Example 1.5 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 17. To use the equation, we need the mole fractions of the components. To calculate mole fractions, which are defined by eqn 15, 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).

Answer The amounts of each type of molecule present in 100 g of air are

$$n(\mathrm{N_2}) = \frac{(100\ \mathrm{g}) \times 0.755}{28.02\ \mathrm{g\,mol^{-1}}} = 2.69\ \mathrm{mol}$$
$$n(\mathrm{O_2}) = \frac{(100\ \mathrm{g}) \times 0.232}{32.00\ \mathrm{g\,mol^{-1}}} = 0.725\ \mathrm{mol}$$
$$n(\mathrm{Ar}) = \frac{(100\ \mathrm{g}) \times 0.013}{39.95\ \mathrm{g\,mol^{-1}}} = 0.033\ \mathrm{mol}$$

Because overall $n = 3.45$ mol, the mole fractions and partial pressures (obtained by multiplying the mole fraction by the total pressure, 1.00 atm) are as follows:

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

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

Self-test 1.5 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?

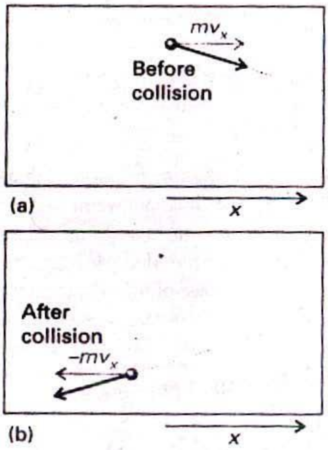
[0.703, 0.189, 0.0084, 0.00027 atm]

## 1.3 The kinetic model of gases

We have seen that properties of a perfect gas can be rationalized qualitatively in terms of a model in which the molecules of the gas are in ceaseless random motion. We shall now see how this interpretation can be expressed quantitatively in terms of the **kinetic model** of gases, in which it is assumed that the only contribution to the energy of the gas is from the kinetic energies of the molecules (that is, the potential energy of the interactions between molecules makes a negligible contribution to the total energy of the gas). The kinetic model is one of the most remarkable—and arguably most beautiful—models in physical chemistry for, from a set of very slender assumptions, powerful quantitative conclusions can be deduced.

The kinetic model of gases 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.



1.12 The pressure of a gas arises from the impact of its molecules on the walls. In an elastic collision of a molecule with a wall perpendicular to the $x$-axis, the $x$-component of velocity is reversed but the $y$- and $z$-components are unchanged.

3. The molecules do not interact, except that they make perfectly elastic collisions when they are in contact.

An elastic collision is one in which no internal modes of motion are excited; that is, the translational energy of the molecules is conserved (remains constant) in a collision.

From these very economical assumptions, it follows that the pressure and volume of the gas are related by the following expression:

$$pV = \tfrac{1}{3}nMc^2 \tag{19}$$°

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:

$$c = \langle v^2 \rangle^{1/2} \qquad [20]$$

The derivation of eqn 19 is set out in the following *Justification*.

### Justification 1.1

Consider the arrangement in Fig. 1.12. When a particle of mass $m$ that is travelling with a component of velocity $v_x$ parallel to the $x$-axis collides with the wall on the right and is reflected, its linear momentum (the product of its mass and its velocity) changes from $mv_x$ before the collision to $-mv_x$ after the collision (when it is travelling in the opposite direction). The momentum therefore changes by $2mv_x$ on each collision (the $y$- and $z$-components are unchanged). Many molecules collide with the wall in an interval $\Delta t$, and the total change of momentum is the product of the change in momentum of each molecule multiplied by the number of molecules that reach the wall during the interval.

Next we calculate the number of molecules that collide with the wall in the interval $\Delta t$. Because a molecule with velocity component $v_x$ can travel a distance $v_x\Delta t$ along the $x$-axis in an interval $\Delta t$, all the molecules within a distance $v_x\Delta t$ of the wall will strike it if they are travelling towards it (Fig. 1.13). It follows that, if the wall has area $A$, then all the particles in a volume $A \times v_x\Delta t$ will reach the wall (if they are travelling towards it). The number density of particles is $nN_A/V$, where $n$ is the total amount of molecules in the container of volume $V$ and $N_A$ is the Avogadro constant, so the number in the volume $Av_x\Delta t$ is $(nN_A/V) \times Av_x\Delta t$.

On average, at any instant half the particles are moving to the right and half are moving to the left. Therefore, the average number of collisions with the wall during the interval $\Delta t$ is $\tfrac{1}{2}nN_A Av_x\Delta t/V$. The total momentum change in that interval is the product of this number and the change $2mv_x$:

$$\begin{aligned}\text{Momentum change} &= \frac{nN_A Av_x\Delta t}{2V} \times 2mv_x = \frac{nmN_A Av_x^2\Delta t}{V}\\ &= \frac{nMAv_x^2\Delta t}{V}\end{aligned}$$

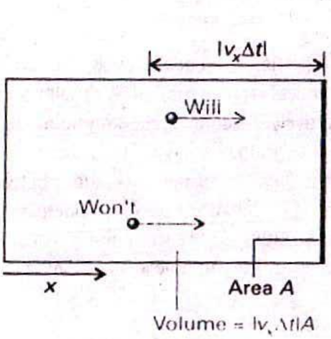
where $M = mN_A$.

Next, to identify the force, we calculate the rate of change of momentum, which is this change of momentum divided by the interval $\Delta t$ during which it occurs:

$$\text{Rate of change of momentum} = \frac{nMAv_x^2}{V}$$

This rate of change of momentum is equal to the force (by Newton's second law of motion). It follows that the pressure, the force divided by the area, is

$$\text{Pressure} = \frac{nMv_x^2}{V}$$



1.13 A molecule will reach the wall on the right within an interval $\Delta t$ if it is within a distance $v_x\Delta t$ of the wall and travelling to the right.

Not all the molecules travel with the same velocity, so the detected pressure, $p$, is the average (denoted $\langle\cdots\rangle$) of the quantity just calculated:

$$p = \frac{nM\langle v_x^2\rangle}{V}$$

This expression already resembles the perfect gas equation of state.

Because the molecules are moving randomly (and there is no net flow in a particular direction), the average speed along $x$ is the same as that in the $y$- and $z$-directions. It follows that

$$c^2 = \langle v_x^2\rangle + \langle v_y^2\rangle + \langle v_z^2\rangle = 3\langle v_x^2\rangle, \qquad \text{implying that } \langle v_x^2\rangle = \tfrac{1}{3}c^2$$

Equation 19 now follows immediately.

---

Equation 19 is one of the key results of the kinetic model. 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.

## (a) Molecular speeds

If eqn 19 is to be precisely 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 given by the expression

$$c = \left(\frac{3RT}{M}\right)^{1/2} \qquad (21)^{\circ}$$

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 faster the molecules travel on average, and, at a given temperature, heavy molecules travel more slowly on average than light molecules. Sound waves are pressure waves, and for them to propagate the molecules of the gas must move to form regions of high and low pressure. Therefore, we should expect the root mean square speeds of molecules to be comparable to the speed of sound in air (340 $\mathrm{m\,s^{-1}}$).

### Illustration

The molar mass of $CO_2$ is 44.01 $\mathrm{g\,mol^{-1}}$. Therefore, it follows from eqn 21 that at 298 K

$$c = \left(\frac{3\times(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})\times(298\ \mathrm{K})}{44.01\times10^{-3}\ \mathrm{kg\,mol^{-1}}}\right)^{1/2} = 411\ \mathrm{m\,s^{-1}}$$

To obtain this result, we have used $R$ in SI units and $1\ \mathrm{J} = 1\ \mathrm{kg\,m^2\,s^{-2}}$.

Equation 21 is an expression for the root mean square speed of molecules. However, in an actual gas the speeds of individual molecules span a wide range, and the collisions in the gas continually redistribute the speeds among the molecules. Before a collision, a particular molecule may be travelling rapidly, but after a collision it may be accelerated to a very high speed, only to be slowed again by the next collision. The fraction of molecules that have speeds in the range $v$ to $v + \mathrm{d}v$ is proportional to the width of the range, and is written

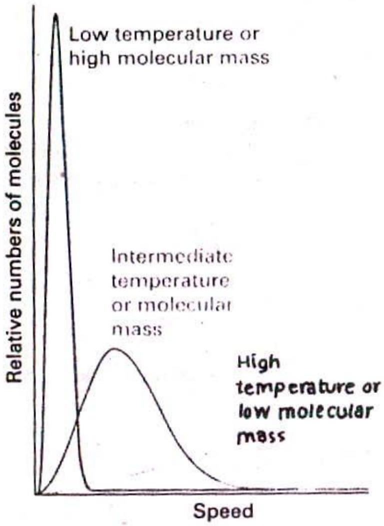
$f(v)\mathrm{d}v$, where $f(v)$, which varies with the speed, $v$, is called the **distribution of speeds**. The precise form of $f$ was derived by J.C. Maxwell, and is

$$f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 \mathrm{e}^{-Mv^2/2RT} \qquad (22)$$

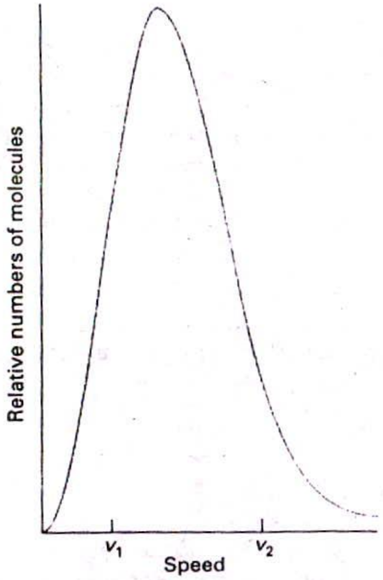
This expression is called the **Maxwell distribution** of speeds, and is derived in the following *Justification*. Its main features are summarized in Fig. 1.14. We see that the range of speeds broadens as the temperature increases. Lighter molecules also have a broader distribution of speeds than heavy molecules. To use eqn 22 quantitatively to calculate the fraction of molecules in a given narrow range of speeds, $\Delta v$, we evaluate $f(v)$ at the speed of interest, then multiply it by the width of the range of speeds of interest (that is, we form $f(v)\Delta v$). To use the distribution to calculate the fraction in a range of speeds that is so wide that it cannot be regarded as almost infinitesimal, we evaluate the integral:

$$\text{Fraction in the range } v_1 \text{ to } v_2 = \int_{v_1}^{v_2} f(v)\,\mathrm{d}v \qquad (23)$$

This integral is the area under the graph of $f$ as a function of $v$, and except in special cases has to be evaluated numerically using mathematical software (Fig. 1.15).



1.14 The distribution of molecular speeds with temperature and molar mass. Note that the most probable speed (corresponding to the peak of the distribution) increases with temperature and with decreasing molar mass and, simultaneously, the distribution becomes broader.



1.15 To calculate the probability that a molecule will have a speed in the range $v_1$ to $v_2$, we integrate the distribution between those two limits; the integral is equal to the area of the curve between the limits, as shown shaded here.

## Justification 1.2

The probability that a molecule has a velocity in the range $v_x$ to $v_x + \mathrm{d}v_x$, $v_y$ to $v_y + \mathrm{d}v_y$, $v_z$ to $v_z + \mathrm{d}v_z$ is proportional to the widths of the ranges and depends on the velocity components, so we write it $f(v_x, v_y, v_z)\,\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z$. The probability that a molecule has a particular velocity parallel to $x$ is independent of the probability that it has a particular velocity parallel to $y$ or $z$, so $f(v_x, v_y, v_z) = f(v_x)f(v_y)f(v_z)$. Moreover, the probability of finding a molecule with a velocity in the range $+|v_x|$ to $+|v_x| + \mathrm{d}v_x$ is the same as finding it in the range $-|v_x|$ to $-|v_x| - \mathrm{d}v_x$, so $f(v_x)$ must depend on the square of $v_x$. Hence, $f(v_x) = f(v_x^2)$, and likewise for $v_y$ and $v_z$. It follows that we can also write $f(v_x, v_y, v_z) = f(v_x^2)f(v_y^2)f(v_z^2)$.

Next, we assume that the probability of a molecule lying in a particular range is independent of its direction of flight. That is, we assume that $f(v_x, v_y, v_z)$ depends only on the speed $v$, with $v^2 = v_x^2 + v_y^2 + v_z^2$, but not on the individual components. For example, we assume that the probability that a molecule has a velocity in an infinitesimal range at the velocity $(1.0, 2.0, 3.0)$ km s$^{-1}$, and speed 3.7 km s$^{-1}$, is the same as the probability that it has a velocity in the same infinitesimal range at the velocity $(2.0, -1.0, -3.0)$ km s$^{-1}$, or any other set of components corresponding to the speed 3.7 km s$^{-1}$. It follows that $f(v_x, v_y, v_z) = f(v_x^2 + v_y^2 + v_z^2)$.

By combining the conclusions of these two paragraphs, we can write

$$f(v_x^2 + v_y^2 + v_z^2) = f(v_x^2)f(v_y^2)f(v_z^2)$$

Only an exponential function satisfies such a relation (because $\mathrm{e}^a\mathrm{e}^b = \mathrm{e}^{a+b}$), so we can conclude that

$$f(v_x) = K\mathrm{e}^{\pm\zeta v_x^2}$$

where $K$ and $\zeta$ (zeta) are constants and $f(v_x) = f(v_x^2)$. The two constants are the same for $f(v_y)$ and $f(v_z)$ because the distributions are independent of direction. Moreover, because the probability is very small that a molecule will have a very high velocity, we can discard the solution with $+\zeta v_x^2$ in the exponent.

To determine the constant $K$, we note that a molecule must have a velocity somewhere in the range $-\infty < v_x < \infty$, so

$$\int_{-\infty}^{\infty} f(v_x)\,\mathrm{d}v_x = 1 \tag{24}$$

Substitution of the expression for $f(v_x)$ then gives

$$1 = K\int_{-\infty}^{\infty} \mathrm{e}^{-\zeta v_x^2}\,\mathrm{d}v_x = K\left(\frac{\pi}{\zeta}\right)^{1/2}$$

Therefore, $K = (\zeta/\pi)^{1/2}$. To determine $\zeta$ we calculate the root mean square speed. The first step is to write

$$\begin{aligned}\langle v_x^2\rangle &= \int_{-\infty}^{\infty} v_x^2 f(v_x)\,\mathrm{d}v_x = \left(\frac{\zeta}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} v_x^2\mathrm{e}^{-\zeta v_x^2}\,\mathrm{d}v_x \\ &= \left(\frac{\zeta}{\pi}\right)^{1/2} \times \tfrac{1}{2}\left(\frac{\pi}{\zeta^3}\right)^{1/2} = \frac{1}{2\zeta}\end{aligned}$$

Therefore,

$$c = (\langle v_x^2\rangle + \langle v_x^2\rangle + \langle v_x^2\rangle)^{1/2} = \left(\frac{3}{2\zeta}\right)^{1/2}$$

However, we already know that $c = (3RT/M)^{1/2}$; therefore $\zeta = M/2RT$. At this stage, therefore, we know that

$$f(v_x) = \left(\frac{M}{2\pi RT}\right)^{1/2} \mathrm{e}^{-Mv_x^2/2RT} \tag{25}$$

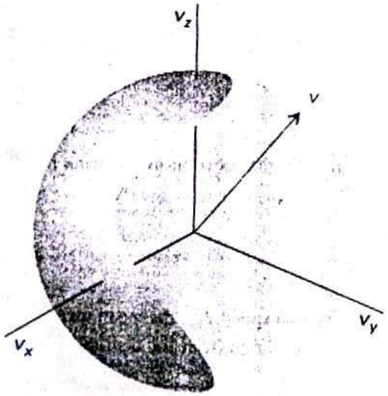
The probability that a molecule has a velocity in the range $v_x$ to $v_x + \mathrm{d}v_x$, $v_y$ to $v_y + \mathrm{d}v_y$, $v_z$ to $v_z + \mathrm{d}v_z$ is

$$\begin{aligned}f(v_x, v_y, v_z)\,\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z &= f(v_x)f(v_y)f(v_z)\,\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z \\ &= \left(\frac{M}{2\pi RT}\right)^{3/2} \mathrm{e}^{-Mv^2/2RT}\,\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z\end{aligned}$$

The probability $f(v)\mathrm{d}v$ that the molecules have a speed in the range $v$ to $v + \mathrm{d}v$ regardless of direction is the sum of the probabilities that the velocity lies in any of the volume elements $\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z$ forming a spherical shell of radius $v$ (Fig. 1.16). The sum of the volume elements on the right-hand side of the last equation is the volume of this shell, $4\pi v^2\,\mathrm{d}v$. Therefore,

$$f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2\mathrm{e}^{-Mv^2/2RT}$$

as given in eqn 22.



1.16 To evaluate the probability that a molecule has a speed in the range $v$ to $v + \mathrm{d}v$, we evaluate the total probability that the molecule will have a speed that is anywhere on the surface of a sphere of radius $v = (v_x^2 + v_y^2 + v_z^2)^{1/2}$ by summing the probabilities that it is in a volume element $\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z$ at a distance $v$ from the origin.

### Example 1.6 Calculating the mean speed of molecules in a gas

What is the mean speed, $\bar{c}$, of $N_2$ molecules in air at 25°C?

**Method** We are asked to calculate the mean speed, not the root mean square speed. A mean value is calculated by multiplying each speed by the fraction of molecules that have that speed, and then adding all the products together. When the speed varies over a continuous range, the sum is replaced by an integral. To employ this approach here, we note that the fraction of molecules with a speed in the range $v$ to $v + \mathrm{d}v$ is $f(v)\,\mathrm{d}v$, so the product of this fraction and the speed is $vf(v)\,\mathrm{d}v$. The mean speed, $\bar{c}$, is obtained by evaluating the integral

$$\bar{c} = \int_0^\infty vf(v)\,\mathrm{d}v$$

with $f$ given in eqn 22.

Answer The integral required is

$$\bar{c} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\int_0^\infty v^3 \mathrm{e}^{-Mv^2/2RT}\,\mathrm{d}v$$

$$= 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} \times \tfrac{1}{2}\left(\frac{2RT}{M}\right)^2 = \left(\frac{8RT}{\pi M}\right)^{1/2}$$

Substitution of the data then gives

$$\bar{c} = \left(\frac{8 \times (8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\ \mathrm{K})}{\pi \times (28.02 \times 10^{-3}\ \mathrm{kg\,mol^{-1}})}\right)^{1/2} = 475\ \mathrm{m\,s^{-1}}$$

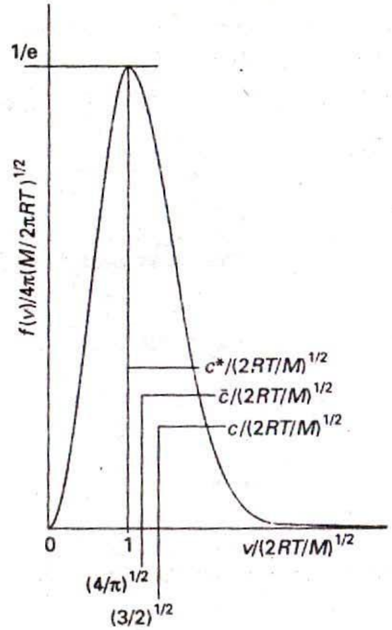
To evaluate the integral we have used the standard result from tables of integrals (or software) that

$$\int_0^\infty x^3 \mathrm{e}^{-ax^2}\,\mathrm{d}x = \frac{1}{2a^2}$$

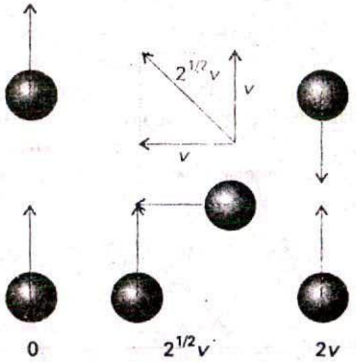
Self-test 1.6 Evaluate the root mean square speed of the molecules by integration. You will need the integral

$$\int_0^\infty x^4 \mathrm{e}^{-ax^4}\,\mathrm{d}x = \tfrac{3}{8}\left(\frac{\pi}{a^5}\right)^{1/2}$$

$[c = (3RT/M)^{1/2}, 515\ \mathrm{m\,s^{-1}}]$



1.17 A summary of the conclusions that can be deduced from the Maxwell distribution for molecules of molar mass $M$ at a temperature $T$: $c^*$ is the most probable speed, $\bar{c}$ is the mean speed, and $c$ is the root mean square speed.



1.18 A simplified version of the argument to show that the relative mean speed of molecules in a gas is related to the mean speed. When the molecules are moving in the same direction, the relative mean speed is zero; it is $2v$ when the molecules are approaching each other. A typical mean direction of approach is from the side, and the mean speed of approach is then $2^{1/2}v$. The last direction of approach is the most characteristic, so the mean speed of approach can be expected to be about $2^{1/2}v$. This value is confirmed by more detailed calculation.

As shown in Example 1.6, the Maxwell distribution may be used to evaluate the mean speed, $\bar{c}$, of the molecules in a gas:

$$\bar{c} = \left(\frac{8RT}{\pi M}\right)^{1/2} \tag{26}$$

The most probable speed, $c^*$, may also be identified from the location of the peak of the distribution:

$$c^* = \left(\frac{2RT}{M}\right)^{1/2} \tag{27}$$

These results are summarized in Fig. 1.17. The **relative mean speed**, $\bar{c}_{\mathrm{rel}}$, the mean speed with which one molecule approaches another, can also be calculated from the distribution:

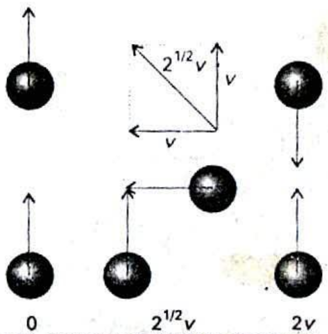
$$\bar{c}_{\mathrm{rel}} = 2^{1/2}\bar{c} \tag{28}$$

This result is much harder to derive, but the diagram in Fig. 1.18 should help to show that it is plausible. The last result can also be generalized to the relative mean speed of two dissimilar molecules of masses $m_A$ and $m_B$:

$$\bar{c}_{\mathrm{rel}} = \left(\frac{8kT}{\pi\mu}\right)^{1/2} \qquad \mu = \frac{m_A m_B}{m_A + m_B} \tag{29}$$

Note that the molecular masses (not the molar masses) and the **Boltzmann constant**, $k = R/N_A$, appear in this expression; the quantity $\mu$ is called the **reduced mass** of the molecules. Equation 29 turns into eqn 28 when the molecules are identical (that is, $m_A = m_B = m$, so $\mu = \frac{1}{2}m$).

The Maxwell distribution has been verified experimentally. For example, molecular speeds can be measured directly with a velocity selector (Fig. 1.19). The spinning disks have slots that permit the passage of only those molecules moving through them at the appropriate speed, and the number of molecules can be determined by collecting them at a detector.



1.19 A velocity selector. The molecules are produced in the source (which may be an oven with a small hole in one wall), and travel in a beam towards the rotating disks. Only if the speed of a molecule is such as to carry it through each slot that rotates into its path will it reach the detector. Thus, the number of slow molecules can be counted by rotating the disks slowly, and the number of fast molecules counted by rotating the disks rapidly.

## (b) The collision frequency

The kinetic model enables us to make more quantitative our picture of the events that take place in a gas. In particular, it enables us to calculate the frequency with which molecular collisions occur and the distance a molecule travels on average between collisions.[2]

We count a 'hit' whenever the centres of two molecules come within a distance $d$ of each other, where $d$, the **collision diameter**, is of the order of the actual diameters of the molecules (for impenetrable hard spheres $d$ is the diameter). As we show in the following *Justification*, kinetic theory can be used to deduce that the **collision frequency**, $z$, the number of collisions made by one molecule divided by the time interval during which the collisions are counted, when there are $N$ molecules in a volume $V$ is

$$z = \sigma \bar{c}_{\text{rel}} \mathcal{N} \qquad \sigma = \pi d^2 \tag{30}^\circ$$

with $\mathcal{N} = N/V$ and $\bar{c}_{\text{rel}}$ given in eqn 28. The area $\sigma$ is called the **collision cross-section** of the molecules. Some typical collision cross-sections are given in Table 1.3 (they are obtained by the techniques described in Section 22.5). In terms of the pressure,

$$z = \frac{\sigma \bar{c}_{\text{rel}} p}{kT} \tag{31}^\circ$$

Table 1.3* Collision cross-sections

| | $\sigma/\text{nm}^2$ |
|---|---|
| Benzene, $C_6H_6$ | 0.88 |
| Carbon dioxide, $CO_2$ | 0.52 |
| Helium, He | 0.21 |
| Nitrogen, $N_2$ | 0.43 |

*More values are given in the *Data section* at the end of this volume.

### Justification 1.3

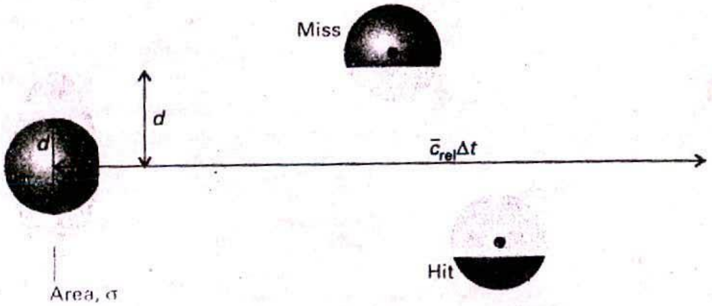
We consider the positions of all the molecules except one to be frozen. Then we note what happens as one mobile molecule travels through the gas with a mean relative speed $\bar{c}_{\text{rel}}$ for a time $\Delta t$. In doing so it sweeps out a 'collision tube' of cross-sectional area $\sigma = \pi d^2$ and length $\bar{c}_{\text{rel}}\Delta t$, and therefore of volume $\sigma\bar{c}_{\text{rel}}\Delta t$ (Fig. 1.20). The number of stationary molecules with centres inside the collision tube is given by the volume of the tube multiplied by the number density $\mathcal{N} = N/V$, and is $\mathcal{N}\sigma\bar{c}_{\text{rel}}\Delta t$. The number of hits scored in the interval $\Delta t$ is equal to this number, so the number of collisions divided by the time interval, is $\mathcal{N}\sigma\bar{c}_{\text{rel}}$. The expression in terms of the pressure of the gas is obtained by using the perfect gas equation to write

$$\frac{N}{V} = \frac{nN_A}{V} = \frac{pN_A}{RT} = \frac{p}{kT}$$

Equation 30 tells us that the collision frequency increases with increasing temperature in a sample held at constant volume. The reason is that the mean relative speed increases with temperature. Equation 31 tells us that, at constant temperature, the collision frequency is proportional to the pressure. Such a proportionality is plausible for, the greater the pressure, the greater the number density of molecules in the sample, and the rate at which they encounter one another is greater even though their average speed remains the same. For an $N_2$ molecule in a sample at 1 atm and 25 °C, $z \approx 7 \times 10^9\ \text{s}^{-1}$, so a given molecule collides

---

[2] The kinetic model also provides a basis for calculating how rapidly physical properties are transported through a gas, Chapter 24, and the rates of chemical reactions, Chapter 27.



1.20 In an interval $\Delta t$, a molecule of diameter $d$ sweeps out a tube of diameter $2d$ and length $\bar{c}_{rel}\Delta t$. As it does so it encounters other molecules with centres that lie within the tube, and each such encounter counts as one collision. In practice, the tube is not straight, but changes direction at each collision. Nevertheless, the volume swept out is the same, and this straightened version of the tube can be used as a basis of the calculation.

about $7 \times 10^9$ times each second. We are beginning to appreciate the timescale of events in gases.

### (c) The mean free path

Once we have the collision frequency, we can calculate the **mean free path**, $\lambda$, the average distance a molecule travels between collisions. If a molecule collides with a frequency $z$, it spends a time $1/z$ in free flight between collisions, and therefore travels a distance $(1/z)\bar{c}$. Therefore, the mean free path is

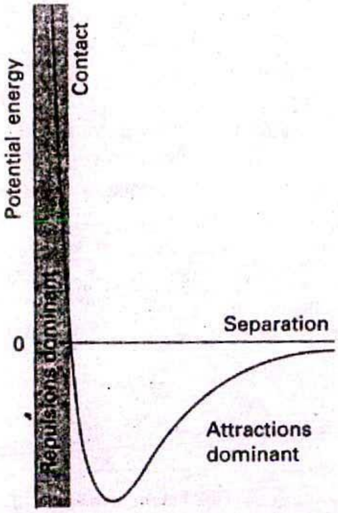
$$\lambda = \frac{\bar{c}}{z} \tag{32}$$

Substitution of the expression for $z$ in eqn 31 gives

$$\lambda = \frac{kT}{2^{1/2}\sigma p} \tag{33}$$

Doubling the pressure reduces the mean free path by half. A typical mean free path in nitrogen gas at 1 atm is 70 nm, or about $10^3$ molecular diameters. Although the temperature appears in eqn 33, in a sample of constant volume, the pressure is proportional to $T$, so $T/p$ remains constant when the temperature is increased. Therefore, the mean free path is independent of the temperature in a sample of gas in a container of fixed volume. The distance between collisions is determined by the number of molecules present in the given volume, not by the speed at which they travel.

In summary, a typical gas ($N_2$ or $O_2$) at 1 atm and 25 °C can be thought of as a collection of molecules travelling with a mean speed of about 350 m s$^{-1}$. Each molecule makes a collision within about 1 ns, and between collisions it travels about $10^2$ to $10^3$ molecular diameters. The kinetic model of gases is valid (and the gas behaves nearly perfectly) if the diameter of the molecules is much smaller than the mean free path ($d \ll \lambda$), for then the molecules spend most of their time far from one another.



1.21 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.

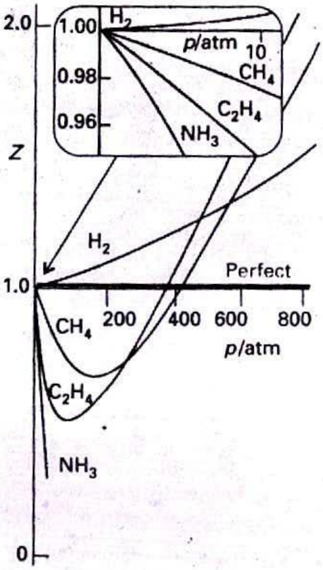
## Real gases

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.

## 1.4 Molecular interactions

Real gases show deviations from the perfect gas law because molecules interact with each other. 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. 1.21). Because they are short-range interactions, repulsions can be expected to be important only when the molecules are close together on average. This is the case at high pressure, when a large number of 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. 1.21). Attractive forces are ineffective when the molecules are far apart (well to the right in Fig. 1.21). Intermolecular forces may also be 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 pressure, 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 perfectly. At moderate pressure, when the molecules are on average only a few molecular diameters apart, 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 are helping to draw the molecules together. At high pressure, when the molecules are on average close together, the repulsive forces dominate and the gas can be expected to be less compressible because now the forces help to drive the molecules apart.



1.22 The variation of the compression factor $Z = pV_m/RT$ 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.

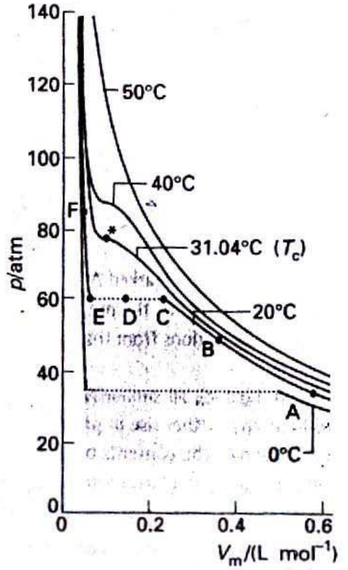
### (a) The compression factor

That real gases reflect the distance dependence of the forces we have described can be demonstrated by plotting the **compression factor**, $Z$, against pressure, where $Z$ is defined as

$$Z = \frac{pV_m}{RT} \tag{34}$$

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. 1.22. 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 are more difficult to compress than a perfect gas (for a given molar volume, the product $pV_m$ is greater than $RT$). Repulsive forces are now dominant. At intermediate pressures, most gases have $Z < 1$, indicating that the attractive forces are dominant and favour compression.



1.23 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.

### (b) Virial coefficients

Some experimental isotherms for carbon dioxide are shown in Fig. 1.23. At large molar volumes and high temperatures the real isotherms do not differ greatly from perfect isotherms. The small differences suggest that the perfect gas law is in fact the first term in an expression of the form

$$pV_m = RT(1 + B'p + C'p^2 + \cdots) \qquad (35)$$

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

| | 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*.

This expression is an example of a common procedure in physical chemistry, in which a simple law (in this case $pV = nRT$) is 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

$$pV_\mathrm{m} = RT\left(1 + \frac{B}{V_\mathrm{m}} + \frac{C}{V_\mathrm{m}^2} + \cdots\right) \tag{36}$$

These two expressions are two versions of the **virial equation of state.**[3] The coefficients $B, C, \ldots$, 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, $C/V_\mathrm{m}^2 \ll B/V_\mathrm{m}$.

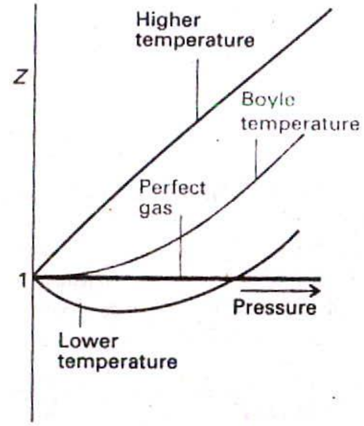
The virial equation can be used to demonstrate the important point that, although the equation of state of a real gas may coincide with the perfect gas law as $p \to 0$, not all its properties necessarily coincide with those of a perfect gas in that limit. Consider, for example, the value of $\mathrm{d}Z/\mathrm{d}p$, 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

$$\frac{\mathrm{d}Z}{\mathrm{d}p} = B' + 2pC' + \cdots \to B' \quad \text{as } p \to 0 \tag{37}$$

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

$$\frac{\mathrm{d}Z}{\mathrm{d}(1/V_\mathrm{m})} \to B \quad \text{as } V_\mathrm{m} \to \infty \text{ corresponding to } p \to 0 \tag{38}$$

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. 1.24). At this temperature, which is called the **Boyle temperature,** $T_\mathrm{B}$, the properties of the real gas do coincide with those of a perfect gas as $p \to 0$. According to the relation above, $Z$ 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 36 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, $B/V_\mathrm{m}$) in the virial equation is zero and $C/V_\mathrm{m}^2$ 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.



1.24 The compression factor 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.

### *(c) Condensation*

Now consider what happens when a sample of gas initially in the state marked A in Fig. 1.23 is compressed 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.

---

[3] The name comes from the Latin word for force.

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 | 22.6 |
| $O_2$ | 50.14 | 78.0 | 154.8 | 0.308 | 405.9 |

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

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).

At and above $T_c$, the sample has a single phase which 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*. At the critical temperature, a surface does not form and the horizontal part of the isotherm has merged to a single point. 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 154.8 K: to liquefy it—to obtain a fluid phase that does not occupy the entire volume—the temperature must first be lowered to below 154.8 K, and then the gas compressed isothermally. The single phase that fills the entire volume at $T > T_c$ may be much denser that we normally consider typical of gases, and the name **supercritical fluid** is preferred.

## 1.5 The van der Waals equation

Conclusions can be drawn 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.H. 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'. Van der Waals himself proposed his equation on the basis of experimental evidence available to him in conjunction with rigorous thermodynamic arguments. The **van der Waals equation** is

$$p = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2 \qquad (39a)$$

Table 1.6* Van der Waals coefficients

| | $a/(\text{atm L}^2\,\text{mol}^{-2})$ | $b/(10^{-2}\,\text{L mol}^{-1})$ |
|---|---|---|
| Ar | 1.363 | 3.219 |
| $CO_2$ | 3.640 | 4.267 |
| He | 0.057 | 2.370 |
| $N_2$ | 1.408 | 3.913 |

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

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

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \tag{39b}$$

The constants $a$ and $b$ are called the **van der Waals coefficients**. They are characteristic of each gas but independent of the temperature; some values are listed in Table 1.6.

## Justification 1.4

The repulsive interactions between molecules are taken into account by supposing that they cause the molecules to behave as small but impenetrable spheres. The nonzero 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 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 39.

In this *Justification* we have built the van der Waals equation using vague arguments about the volumes of molecules and the effects of forces. It 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 1.7 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 39*b* as an equation for the molar volume, we need to rearrange it into

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

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 either with a programmable calculator or with a commercial software package.[4]

---

[4] A procedure is included in the CD that accompanies this text.

Table 1.7 Selected equations of state

| | Equation | Reduced form | Critical constants | | |
|---|---|---|---|---|---|
| | | | $p_c$ | $V_c$ | $T_c$ |
| Perfect gas | $p = \dfrac{RT}{V_m}$ | | | | |
| Van der Waals | $p = \dfrac{RT}{V_m - b} - \dfrac{a}{V_m^2}$ | $p_r = \dfrac{8T_r}{3V_r - 1} - \dfrac{3}{V_r^2}$ | $\dfrac{a}{27b^2}$ | $3b$ | $\dfrac{8a}{27bR}$ |
| Berthelot | $p = \dfrac{RT}{V_m - b} - \dfrac{a}{TV_m^2}$ | $p_r = \dfrac{8T_r}{3V_r - 1} - \dfrac{3}{T_r V_r^2}$ | $\dfrac{1}{12}\left(\dfrac{2aR}{3b^3}\right)^{1/2}$ | $3b$ | $\dfrac{2}{3}\left(\dfrac{2a}{3bR}\right)^{1/2}$ |
| Dieterici | $p = \dfrac{RTe^{-a/RTV_m}}{V_m - b}$ | $p_r = \dfrac{e^2 T_r e^{-2/T_r V_r}}{2V_r - 1}$ | $\dfrac{a}{4e^2 b^2}$ | $2b$ | $\dfrac{a}{4Rb}$ |
| Beattie–Bridgman | $p = \dfrac{(1-\gamma)RT(V_m + \beta) - \alpha}{V_m^2}$ with $\alpha = a_0\left(1 + \dfrac{a}{V_m}\right)$<br>$\beta = b_0\left(1 - \dfrac{b}{V_m}\right)$<br>$\gamma = \dfrac{c_0}{V_m T^3}$ | | | | |
| Virial (Kammerlingh Onnes) | $p = \dfrac{RT}{V_m}\left\{1 + \dfrac{B(T)}{V_m} + \dfrac{C(T)}{V_m^2} + \cdots\right\}$ | | | | |

**Answer** According to Table 1.6, $a = 3.640$ atm $L^2$ $mol^{-2}$ and $b = 4.267 \times 10^{-2}$ $L\,mol^{-1}$. Under the stated conditions, $RT/p = 0.410$ $L\,mol^{-1}$. The coefficients in the equation for $V_m$ are therefore

$$b + RT/p = 0.453\ \mathrm{L\,mol^{-1}}$$
$$a/p = 3.64 \times 10^{-2}\ (\mathrm{L\,mol^{-1}})^2$$
$$ab/p = 1.55 \times 10^{-3}\ (\mathrm{L\,mol^{-1}})^3$$

Therefore, on writing $x = V_m/(\mathrm{L\,mol^{-1}})$, the equation to solve is

$$x^3 - 0.453x^2 + (3.64 \times 10^{-2})x - (1.55 \times 10^{-3}) = 0$$

The acceptable root is $x = 0.366$, which implies that $V_m = 0.370$ $L\,mol^{-1}$.

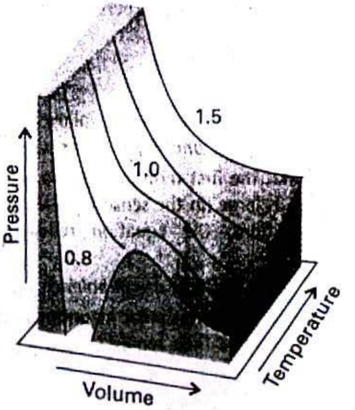
**Comment** For a perfect gas under these conditions, the molar volume is 0.410 $L\,mol^{-1}$.

**Self-test 1.7** Calculate the molar volume of argon at 100°C and 100 atm on the assumption that it is a van der Waals gas.

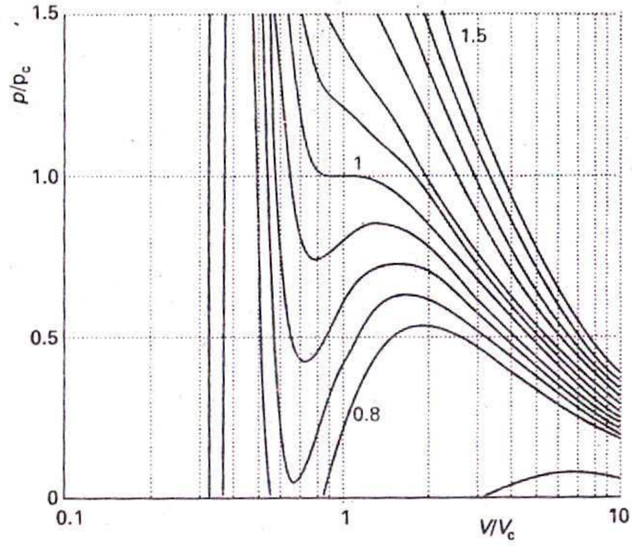
[0.298 $L\,mol^{-1}$]

## (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 is that it is analytical and allows us to draw some general conclusions about real gases. When the equation fails we must use



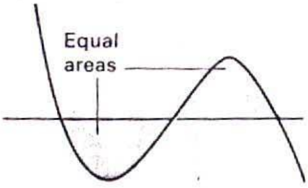
1.25 The surface of possible states allowed by the van der Waals equation. Compare this surface with that shown in Fig. 1.9.



1.26 Van der Waals isotherms at several values of $T/T_c$. Compare these curves with those in Fig.1.23. The van der Waals loops are normally replaced by horizontal straight lines. The critical isotherm is the isotherm for $T/T_c = 1$.

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. 1.23. Some calculated isotherms are shown in Figs 1.25 and 1.26. 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 1.6, are found by fitting the calculated curves to the experimental curves.



**3**

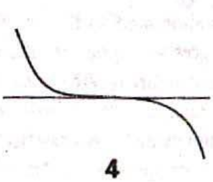
## (b) The features of the equation

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 39*b* 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 39*b* 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.*



**4**

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:

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

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

at the critical point. The solutions of these two equations are

$$V_{\mathrm{c}} = 3b \qquad p_{\mathrm{c}} = \frac{a}{27b^2} \qquad T_{\mathrm{c}} = \frac{8a}{27Rb} \tag{40}$$

These relations can be tested by noting that the **critical compression factor**, $Z_{\mathrm{c}}$, is predicted to be equal to

$$Z_{\mathrm{c}} = \frac{p_{\mathrm{c}}V_{\mathrm{c}}}{RT_{\mathrm{c}}} = \tfrac{3}{8} \tag{41}$$

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

## 1.6 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 **reduced variables** of a gas by dividing the actual variable by the corresponding critical constant:

$$p_{\mathrm{r}} = \frac{p}{p_{\mathrm{c}}} \qquad V_{\mathrm{r}} = \frac{V_{\mathrm{m}}}{V_{\mathrm{c}}} \qquad T_{\mathrm{r}} = \frac{T}{T_{\mathrm{c}}} \tag*{[42]}$$

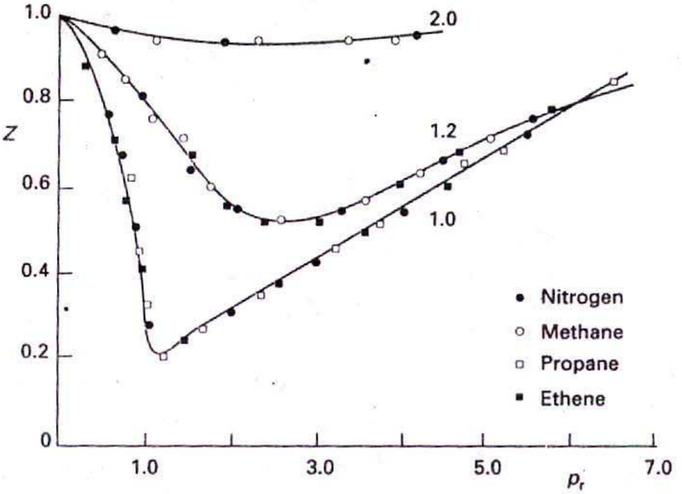
If the reduced pressure of a gas is given, then we can easily calculate its actual pressure by using $p = p_{\mathrm{r}}p_{\mathrm{c}}$, and likewise for the volume and temperature. Van der Waals, who first tried this procedure, hoped that gases confined to the same reduced volume, $V_{\mathrm{r}}$, at the same reduced temperature, $T_{\mathrm{r}}$, would exert the same reduced pressure, $p_{\mathrm{r}}$. The hope was largely fulfilled (Fig. 1.27). 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. 1.22, where similar data are plotted without using reduced variables. The observation that real gases at the same volume and temperature exert the same reduced pressure is called the **principle of corresponding states**. It is only an approximation, and 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 39*b* in terms of the reduced variables, which gives

$$p_{\mathrm{r}}p_{\mathrm{c}} = \frac{RT_{\mathrm{r}}T_{\mathrm{c}}}{V_{\mathrm{r}}V_{\mathrm{c}} - b} - \frac{a}{V_{\mathrm{r}}^2V_{\mathrm{c}}^2}$$

Then we express the critical constants in terms of $a$ and $b$ by using eqn 40:

$$\frac{ap_{\mathrm{r}}}{27b^2} = \frac{8aT_{\mathrm{r}}}{27b(3bV_{\mathrm{r}} - b)} - \frac{a}{9b^2V_{\mathrm{r}}^2}$$



1.27 The compression factors of four gases, including two of those shown in Fig. 1.22, plotted using reduced variables. The use of reduced variables organizes the data on to single curves.

which can be reorganized into

$$p_r = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2} \tag{43}$$

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. 1.26 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, and 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. 1.27 instead of Fig. 1.22).

## Checklist of key ideas

☐ gas

**The perfect gas**

**1.1 The states of gases**

☐ state
☐ equation of state
☐ perfect gas
☐ pressure
☐ standard pressure
☐ mechanical equilibrium
☐ barometer
☐ manometer
☐ temperature
☐ diathermic
☐ adiabatic
☐ thermal equilibrium
☐ Zeroth Law of thermodynamics
☐ thermometer
☐ Celsius scale
☐ perfect-gas temperature scale
☐ thermodynamic temperature scale

**1.2 The gas laws**

☐ Boyle's law (6)
☐ isotherm
☐ limiting law
☐ isobar
☐ Charles's law (9)
☐ Avogadro's principle (11)
☐ gas constant
☐ perfect gas equation (12)
☐ perfect gas
☐ real gas
☐ standard ambient temperature and pressure (SATP)
☐ standard temperature and pressure (STP)
☐ Dalton's law
☐ partial pressure
☐ mole fraction (15)
☐ partial pressure defined (17)

**1.3 The kinetic model of gases**

- ☐ kinetic model of gases
- ☐ elastic collision
- ☐ root mean square speed
- ☐ distribution of speeds
- ☐ Maxwell distribution of speeds (22)
- ☐ relative mean speed (29)
- ☐ Boltzmann constant
- ☐ reduced mass (29)
- ☐ collision diameter
- ☐ collision frequency (30)
- ☐ collision cross-section
- ☐ mean free path (33)

**Real gases**

**1.4 Molecular interactions**

- ☐ attractive and repulsive intermolecular forces
- ☐ compression factor (34)
- ☐ virial equation of state (36)
- ☐ virial coefficient
- ☐ Boyle temperature
- ☐ condensation
- ☐ vapour pressure
- ☐ critical point
- ☐ critical temperature
- ☐ critical pressure
- ☐ critical molar volume
- ☐ critical constants

**1.5 The van der Waals equation**

- ☐ van der Waals equation (39)
- ☐ van der Waals coefficients
- ☐ van der Waals loops
- ☐ Maxwell construction
- ☐ critical compression factor (41)

**1.6 The principle of corresponding states**

- ☐ reduced variables
- ☐ principle of corresponding states

# Further reading

## Articles of general interest

D.B. Clark, The ideal gas law at the center of the sun. *J. Chem. Educ.* **66**, 826 (1989).

J.G. Eberhart, The many faces of van der Waals's equation of state. *J. Chem. Educ.* **66**, 906 (1989).

J.M. Alvaiño, J. Veguillas, and S. Valasco, Equations of state, collisional energy transfer, and chemical equilibrium in gases. *J. Chem. Educ.* **66**, 157 (1989).

G. Rhodes, Does a one-molecule gas obey Boyle's law? *J. Chem. Educ.* **69**, 16 (1992).

J.G. Eberhart, A least-squares technique for determining the van der Waals parameters from the critical constants. *J. Chem. Educ.* **69**, 220 (1992).

J.B. Ott, J.R. Goates, and H.T. Hall, Comparison of equations of state. *J. Chem. Educ.* **48**, 515 (1971).

E.F. Meyer and T.P. Meyer, Supercritical fluid: liquid, gas, both, or neither? A different approach. *J. Chem. Educ.* **63**, 463 (1986).

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).

## Texts and sources of data and information

D. Tabor, *Gases, liquids, and solids.* Cambridge University Press, (1979).

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

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

J.O. Hirschfelder, C.F. Curtiss, and R.B. Bird, *The molecular theory of gases and liquids.* Wiley, New York (1954).

B.W. Rossiter and R.C. Baetzgold (ed.), *Physical methods of chemistry*, VI. Wiley–Interscience, New York (1992).

# Exercises

**1.1 (a)** A sample of air occupies 1.0 L at 25°C and 1.00 atm. What pressure is needed to compress it to 100 $\text{cm}^3$ at this temperature?

**1.1 (b)** A sample of carbon dioxide gas occupies 350 $\text{cm}^3$ at 20°C and 104 kPa. What pressure is needed to compress it to 250 $\text{cm}^3$ at this temperature?

**1.2 (a)** (a) Could 131 g of xenon gas in a vessel of volume 1.0 L 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?

**1.2 (b)** (a) Could 25 g of argon gas in a vessel of volume 1.5 L 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?

**1.3 (a)** A perfect gas undergoes isothermal compression, which reduces its volume by 2.20 L. The final pressure and volume of the gas are $3.78 \times 10^3$ Torr and 4.65 L, respectively. Calculate the original pressure of the gas in (a) Torr, (b) atm.

**1.3 (b)** A perfect gas undergoes isothermal compression, which reduces its volume by 1.80 $\text{dm}^3$. The final pressure and volume of the gas are $1.48 \times 10^3$ Torr and 2.14 $\text{dm}^3$, respectively. Calculate the original pressure of the gas in (a) Torr, (b) bar.

**1.4 (a)** To what temperature must a 1.0 L sample of a perfect gas be cooled from 25 °C in order to reduce its volume to 100 cm$^3$?

**1.4 (b)** To what temperature must a sample of a perfect gas of volume 500 mL be cooled from 35 °C in order to reduce its volume to 150 cm$^3$?

**1.5 (a)** A car tyre (that is, 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?

**1.5 (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?

**1.6 (a)** A sample of 255 mg of neon occupies 3.00 L at 122 K. Use the perfect gas law to calculate the pressure of the gas.

**1.6 (b)** A homeowner uses $4.00 \times 10^3$ 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?

**1.7 (a)** In an attempt to determine an accurate value of the gas constant, $R$, a student heated a 20.000 L container filled with 0.25132 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 0.99707 g cm$^{-3}$.)

**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 |
|---|---|---|---|
| $V_m$/L mol$^{-1}$ | 29.8649 | 44.8090 | 89.6384 |
| $\rho$/(g L$^{-1}$) | 1.07144 | 0.714 110 | 0.356 975 |

**1.8 (a)** At 500 °C and 699 Torr, the mass density of sulfur vapour is 3.71 g L$^{-1}$. What is the molecular formula of sulfur under these conditions?

**1.8 (b)** At 100 °C and 120 Torr, 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 740 Torr and 27 °C is 1.146 g L$^{-1}$, 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 66.5 Torr. 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 g L$^{-1}$ at 330 K and 150 Torr. 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 density of air at −85 °C, 0 °C, and 100 °C is 1.877 g L$^{-1}$, 1.294 g L$^{-1}$, and 0.946 g L$^{-1}$, 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 L at 0 °C and 1.000 atm. A plot of the experimental data of its volume against the Celsius temperature, $\theta$, at constant $p$, gives a straight line of slope 0.0741 L (°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)** Determine the ratios of (a) the mean speeds, (b) the mean kinetic energies of gaseous $H_2$ molecules and Hg atoms at 20 °C.

**1.13 (b)** Determine the ratios of (a) the mean speeds, (b) the mean kinetic energies of He atoms and Hg atoms at 25 °C.

**1.14 (a)** A 1.0 L glass bulb contains $1.0 \times 10^{23}$ $H_2$ molecules. If the pressure exerted by the gas is 100 kPa, what are (a) the temperature of the gas, (b) the root mean square speeds of the molecules? (c) Would the temperature be different if they were $O_2$ molecules?

**1.14 (b)** The best laboratory vacuum pump can generate a vacuum of about 1 nTorr. At 25 °C and assuming that air consists of $N_2$ molecules with a collision diameter of 395 pm, calculate (a) the mean speed of the molecules, (b) the mean free path, (c) the collision frequency in the gas.

**1.15 (a)** At what pressure does the mean free path of argon at 25 °C become comparable to the size of a 1 L vessel that contains it? Take $\sigma = 0.36$ nm$^2$.

**1.15 (b)** At what pressure does the mean free path of argon at 25 °C become comparable to the diameters of the atoms themselves?

**1.16 (a)** At an altitude of 20 km the temperature is 217 K and the pressure 0.050 atm. What is the mean free path of $N_2$ molecules? ($\sigma = 0.43$ nm$^2$.)

**1.16 (b)** At an altitude of 15 km the temperature is 217 K and the pressure 12.1 kPa. What is the mean free path of $N_2$ molecules? ($\sigma = 0.43$ nm$^2$.)

**1.17 (a)** How many collisions does a single Ar atom make in 1.0 s when the temperature is 25 °C and the pressure is (a) 10 atm, (b) 1.0 atm, (c) 1.0 $\mu$atm?

**1.17 (b)** How many collisions per second does an $N_2$ molecule make at an altitude of 15 km? (See Exercise 1.16b for data.)

**1.18 (a)** Calculate the mean free path of molecules in air using $\sigma = 0.43\ \text{nm}^2$ at 25 °C and (a) 10 atm, (b) 1.0 atm, (c) $1.0 \times 10^{-6}$ atm.

**1.18 (b)** Calculate the mean free path of carbon dioxide molecules using $\sigma = 0.52\ \text{nm}^2$ at 25 °C and (a) 15 atm, (b) 1.0 bar, (c) 1.0 Torr.

**1.19 (a)** Use the Maxwell distribution of speeds to estimate the fraction of $N_2$ molecules at 500 K that have speeds in the range 290 to 300 $\text{m s}^{-1}$.

**1.19 (b)** Use the Maxwell distribution of speeds to estimate the fraction of $CO_2$ molecules at 300 K that have speeds in the range 200 to 250 $\text{m s}^{-1}$.

**1.20 (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 L, (ii) at 1000 K in 100 $\text{cm}^3$. Use the data in Table 1.6.

**1.20 (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 L, (ii) at 500 K in 150 $\text{cm}^3$. Use the data in Table 1.6.

**1.21 (a)** Estimate the critical constants of a gas with van der Waals parameters $a = 0.751\ \text{atm L}^2\ \text{mol}^{-2}$ and $b = 0.0226\ \text{L mol}^{-1}$.

**1.21 (b)** Estimate the critical constants of a gas with van der Waals parameters $a = 1.32\ \text{atm L}^2\ \text{mol}^{-2}$ and $b = 0.0436\ \text{L mol}^{-1}$.

**1.22 (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?

**1.22 (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?

**1.23 (a)** In an industrial process, nitrogen is heated to 500 K at a constant volume of 1.000 $\text{m}^3$. 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, $a = 1.408\ \text{L}^2\ \text{atm mol}^{-2}$, $b = 0.0391\ \text{L mol}^{-1}$.

**1.23 (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, $a = 1.378\ \text{L}^2\ \text{atm mol}^{-2}$, $b = 3.183 \times 10^{-2}\ \text{L mol}^{-1}$.

**1.24 (a)** The density of water vapour at 327.6 atm and 776.4 K is 133.2 $\text{g dm}^{-3}$. (a) Determine the molar volume, $V_m$, of water and the compression factor, $Z$, from these data. (b) Calculate $Z$ from the van der Waals equation with $a = 5.536\ \text{L}^2\ \text{atm mol}^{-2}$ and $b = 0.03049\ \text{L mol}^{-1}$.

**1.24 (b)** The density of water vapour at 1.00 bar and 383 K is 0.5678 $\text{kg m}^{-3}$. (a) Determine the molar volume, $V_m$, of water and the compression factor, $Z$, from these data. (b) Calculate $Z$ from the van der Waals equation with $a = 5.536\ \text{L}^2\ \text{atm mol}^{-2}$ and $b = 0.03049\ \text{L mol}^{-1}$.

**1.25 (a)** Suppose that 10.0 mol $C_2H_6(g)$ is confined to 4.860 L 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, $a = 5.562\ \text{L}^2\ \text{atm mol}^{-2}$, $b = 0.06380\ \text{L mol}^{-1}$.

**1.25 (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.

**1.26 (a)** A vessel of volume 22.4 L 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.

**1.26 (b)** A vessel of volume 22.4 L 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.

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

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

**1.28 (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.

**1.28 (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.

**1.29 (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.

**1.29 (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.

**1.30 (a)** A certain gas obeys the van der Waals equation with $a = 0.50\ \text{m}^6\ \text{Pa mol}^{-2}$. Its volume is found to be $5.00 \times 10^{-4}\ \text{m}^3\ \text{mol}^{-1}$ 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?

**1.30 (b)** A certain gas obeys the van der Waals equation with $a = 0.76\ \text{m}^6\ \text{Pa mol}^{-2}$. Its volume is found to be $4.00 \times 10^{-4}\ \text{m}^3\ \text{mol}^{-1}$ 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** 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.

**1.2** 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 $g\,cm^{-3}$?

**1.3** Recent communications 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 L atm at 0°N and 40 L atm at 100°N. What is the value of the absolute zero of temperature on their temperature scale?

**1.4** A meterological balloon had a radius of 1.0 m when released at sea level at 20°C and expanded to a radius of 3.0 m when it had risen to its maximum altitude where the temperature was $-20$°C. What is the pressure inside the balloon at that altitude?

**1.5** Deduce the relation between the pressure and mass density, $\rho$, 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.

| $p$/Torr | 91.74 | 188.98 | 277.3 | 452.8 | 639.3 | 760.0 |
|---|---|---|---|---|---|---|
| $\rho/(g\,L^{-1})$ | 0.232 | 0.489 | 0.733 | 1.25 | 1.87 | 2.30 |

**1.6** Charles's law is sometimes expressed in the form $V = V_0(1 + \alpha\theta)$, where $\theta$ is the Celsius temperature, $\alpha$ is a constant, and $V_0$ is the volume of the sample at 0°C. The following values for $\alpha$ 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 |

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

**1.7** Investigate some of the technicalities of ballooning 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 $H_2$?

**1.8** 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.

**1.9** A constant-volume perfect gas thermometer indicates a pressure of 50.2 Torr 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?

**1.10** A vessel of volume 22.4 L 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.

**1.11** In an experiment to measure the speed of molecules by a rotating slotted-disk experiment, the apparatus consisted of five coaxial 5.0 cm diameter disks separated by 1.0 cm, the slots in their rims being displaced by 2.0° between neighbours. The relative intensities, $\mathcal{I}$, of the detected beam of Kr atoms for two different temperatures and at a series of rotation rates were as follows:

| $\nu$/Hz | 20 | 40 | 80 | 100 | 120 |
|---|---|---|---|---|---|
| $\mathcal{I}$(40 K) | 0.846 | 0.513 | 0.069 | 0.015 | 0.002 |
| $\mathcal{I}$(100 K) | 0.592 | 0.485 | 0.217 | 0.119 | 0.057 |

Find the distributions of molecular velocities, $f(v_x)$, at these temperatures, and check that they conform to the theoretical prediction for a one-dimensional system.

**1.12** Cars were timed by police radar as they passed in both directions below a bridge. Their velocities (kilometres per hour, numbers of cars in parentheses) to the east and west were as follows: 80 E (40), 85 E (62), 90 E (53), 95 E (12), 100 E (2); 80 W (38), 85 W (59), 90 W (60), 100 W (2). What are (a) the mean velocity, (b) the mean speed, (c) the root mean square speed?

**1.13** A population consists of people of the following heights (in metres, numbers of individuals in parentheses): 1.80 (1), 1.82 (2), 1.84 (4), 1.86 (7), 1.88 (10), 1.90 (15), 1.92 (9), 1.94 (4), 1.96 (0), 1.98 (1). What are (a) the mean height, (b) the root mean square height of the population?

**1.14** Calculate the escape velocity (the minimum initial velocity that will take an object to infinity) from the surface of a planet of radius $R$. What are the values for (a) the Earth, $R = 6.37 \times 10^6$ m, $g = 9.81\ m\,s^{-2}$, (b) Mars, $R = 3.38 \times 10^6$ m, $m_{Mars}/m_{Earth} = 0.108$? At what temperatures do $H_2$, He, and $O_2$ molecules have mean speeds equal to their escape speeds? What proportion of the molecules have enough speed to escape when the temperature is (a) 240 K, (b) 1500 K? Calculations of this kind are very important in considering the composition of planetary atmospheres.

**1.15** 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).

**1.16** At 273 K, measurements on argon gave $B = -21.7\ \mathrm{cm^3\,mol^{-1}}$ and $C = 1200\ \mathrm{cm^6\,mol^{-2}}$, 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.

**1.17** 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. 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, $a = 1.408\ \mathrm{atm\,L^2\,mol^{-2}}$, $b = 0.0391\ \mathrm{L\,mol^{-1}}$.

**1.18** The mass density of water vapour at 327.6 atm and 776.4 K is $1.332 \times 10^2\ \mathrm{g\,L^{-1}}$. Given that for water $T_c = 647.4$ K, $p_c = 218.3$ atm, $a = 5.536\ \mathrm{atm\,L^2\,mol^{-2}}$, $b = 0.03049\ \mathrm{L\,mol^{-1}}$, and $M = 18.02\ \mathrm{g\,mol^{-1}}$, 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.

**1.19** The critical volume and critical pressure of a certain gas are $160\ \mathrm{cm^3\,mol^{-1}}$ 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.

**1.20** 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 L at 25°C.

## Theoretical problems

**1.21** The Maxwell distribution of speeds was derived from arguments about probability, but it can also be derived from the Boltzmann distribution; see the *Introduction*. Do so.

**1.22** Start from the Maxwell-Boltzmann distribution and derive an expression for the most probable speed of a gas of molecules at a temperature $T$. Go on to demonstrate the validity of the equipartition conclusion (see the *Introduction*) that the average translational kinetic energy of molecules free to move in three dimensions is $\frac{3}{2}kT$.

**1.23** Consider molecules that are confined to move in a plane (a two-dimensional gas). Calculate the distribution of speeds and determine the mean speed of the molecules at a temperature $T$.

**1.24** A specially constructed velocity-selector accepts a beam of molecules from an oven at a temperature $T$ but blocks the passage of molecules with a speed greater than the mean. What is the mean speed of the emerging beam, relative to the initial value, treated as a one-dimensional problem?

**1.25** What is the proportion of gas molecules having (a) more than, (b) less than the root mean square speed? (c) What are the proportions having speeds greater and smaller than the mean speed?

**1.26** Calculate the fractions of molecules in a gas that have a speed in a range $\Delta v$ at the speed $nc^*$ relative to those in the same range at $c^*$ itself. This calculation can be used to estimate the fraction of very energetic molecules (which is important for reactions). Evaluate the ratio for $n = 3$ and $n = 4$.

**1.27** 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.

**1.28** 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 $B = -21.7\ \mathrm{cm^3\,mol^{-1}}$ and $C = 1200\ \mathrm{cm^6\,mol^{-2}}$ for the virial coefficients at 273 K. What are the values of $a$ and $b$ in the corresponding van der Waals equation of state?

**1.29** 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.

**1.30** Equations 35 and 36 are expansions in $p$ and $1/V_m$, respectively. Find the relation between $B, C$ and $B', C'$.

**1.31** The second virial coefficient $B'$ can be obtained from measurements of the density $\rho$ of a gas at a series of pressures. Show that the graph of $p/\rho$ against $p$ should be a straight line with slope proportional to $B'$. Use the data on dimethyl ether in Problem 1.5 to find the values of $B'$ and $B$ at 25°C.

**1.32** 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 $(\partial V/\partial T)_p$.

**1.33** 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.

**1.34** 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?

**1.35** The barometric formula

$$p = p_0 e^{-Mgh/RT}$$

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 $\rho$ is $dp = -\rho g\,dh$. Remember that $\rho$ depends on the pressure. Evaluate the pressure difference between the top and bottom of (a) a laboratory vessel of height 15 cm, and (b) the World Trade Center, 1350 ft. Ignore temperature variations.

## Additional problems supplied by Carmen Giunta and Charles Trapp

**1.36** Amedeo Avogadro (*Journal de Physique* (1811)) noted that two volumes of hydrogen combine with one volume of oxygen to form two volumes of water vapour. He also gave the density of water vapour relative to that of air as 0.625 and that of hydrogen as 0.0732. Use this information and Avogadro's principle to compute the molar masses of water vapour and oxygen relative to that of hydrogen.

**1.37** 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.

**1.38** 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)) which included the following 300 K isotherm.

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

(a) Compute the second virial coefficient, $B$, at this temperature. (b) If you have access to nonlinear curve-fitting software, compute the third virial coefficient, $C$, at this temperature.

**1.39** Ozone is a trace atmospheric gas which plays an important role in screening the Earth from harmful ultraviolet light, 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 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 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?

**1.40** 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).

**1.41** In the *standard model* of stellar structure (I. Nicholson, *The sun*, Rand McNally, New York (1982)), the interior of the Sun is thought to consist of 36 per cent H and 64 per cent He by mass, at a density of 158 g cm$^{-3}$. Both atoms are completely ionized. The approximate dimensions of the nuclei can be calculated from the formula $r_{\text{nucleus}} = 1.4\times10^{-15}A^{1/3}$ m, where $A$ is the mass number. The size of the free electron, $r_e \approx 10^{-18}$ m, is negligible compared to the size of the nuclei. (a) Calculate the excluded volume in 1.0 cm$^3$ of the stellar interior and on that basis decide upon the applicability of the perfect gas law to this system. (b) The standard model suggests that the pressure in the stellar interior is $2.5\times10^{11}$ atm. Calculate the temperature of the Sun's interior based on the perfect gas model. The generally accepted standard model value is $1.6\times10^{7}$ K. (c) Would a van der Waals type of equation (with $a = 0$) give a better value for $T$?

**1.42** Problem 1.7 on ballooning is most readily solved (see the *Solutions manual*) with the use of 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 Archimedes' principle for the atmosphere from the barometric formula (see Problem 1.35). *Hint.* Assume a simple shape for the balloon, perhaps a right circular cylinder of cross-sectional area $A$ and height $h$.

**1.43** The composition of the atmosphere is roughly 80 per cent nitrogen and 20 per cent oxygen by mass. At what height above the surface of the Earth would the atmosphere become 90 per cent nitrogen and 10 per cent oxygen by mass? Assume that the temperature of the atmosphere is constant at 25°C. What is the pressure of the atmosphere at that height?

**1.44** Show that the compression factor, $Z$, of a van der Waals gas can be expressed as $Z = V_r'/(V_r' - \frac{1}{8}) - 27/64T_rV_r'$, where $V_r' = p_cV_m/RT_c$ is the 'pseudoreduced volume', or alternatively as the solution of the cubic equation $Z^3 - \{(p_r/8T_r) + 1\}Z^2 + (27p_r/64T_r^2)Z - 27p_r^2/512T_r^3 = 0$. Solve this equation for $Z$ for nitrogen, methane, propane, and ethene at $T_r = 1.2$ and $p_r = 3.0$ and compare to the value given in Fig. 1.27.

# 2

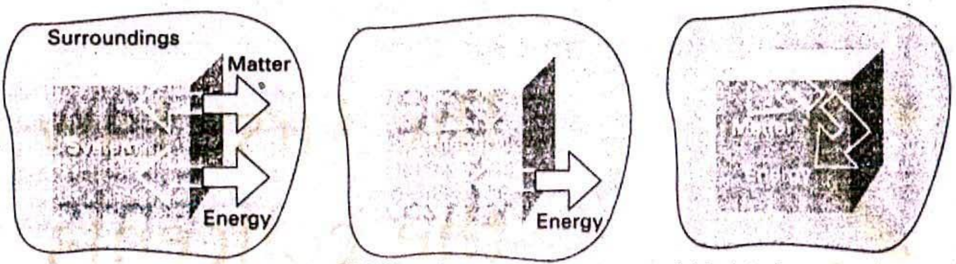
# The First Law: the concepts

*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 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.*

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 produce 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

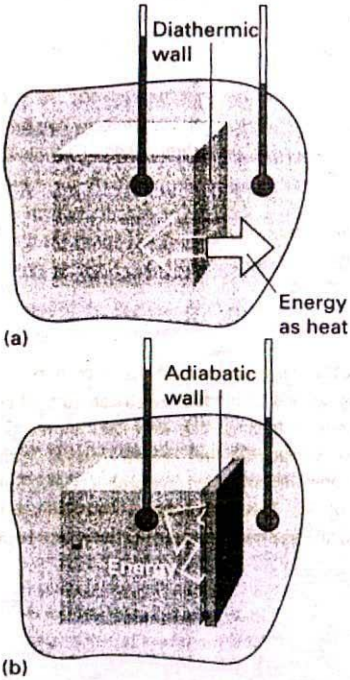
For the purposes of physical chemistry, the universe is divided into two parts, the system and its surroundings. The **system** is the part of the world in which we have a special interest. It may be a reaction vessel, an engine, an electrochemical cell, a biological cell, and so on. The **surroundings** are where we make our measurements. The type of system depends on the characteristics of the boundary that divides it from the surroundings (Fig. 1.1). 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



(a) Open (b) Closed (c) Isolated

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.

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, and 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.



2.2 (a) A diathermic system is one that allows energy to escape as heat through its boundary if there is a difference in temperature between the system and its surroundings. (b) An adiabatic system is one that does not permit the passage of energy as heat through its boundary even if there is a temperature difference between the system and its surroundings.

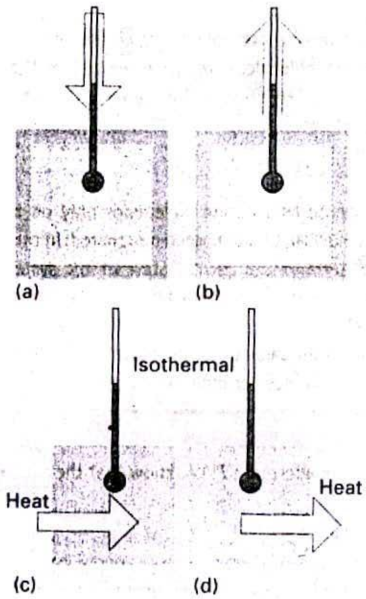
## 2.1 Work, heat, and energy

The fundamental physical property in thermodynamics is work: **work** is done when an object is moved against an opposing force. It is equivalent to a change in the height of 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), its capacity to do work is increased, so the energy of the system is increased. When the system does work (when the piston moves out or the spring unwinds), its energy is reduced because it can do less work than before.

Experiments have shown that the energy of a system (its capacity to do work) may be changed by means other than work itself. When the energy of a system changes as a result of a temperature difference between it 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 cold water. Not all boundaries permit the transfer of energy even though there is a temperature difference between the system and its surroundings. A boundary that does permit energy transfer as heat (such as steel and glass) is called **diathermic**. A boundary that does not permit energy transfer as heat is called **adiabatic** (Fig. 2.2).

A process that releases energy as heat is called **exothermic**. All combustion reactions are exothermic. Processes that absorb energy as heat are called **endothermic**. An example of an endothermic process is the vaporization of water. 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. 2.3.



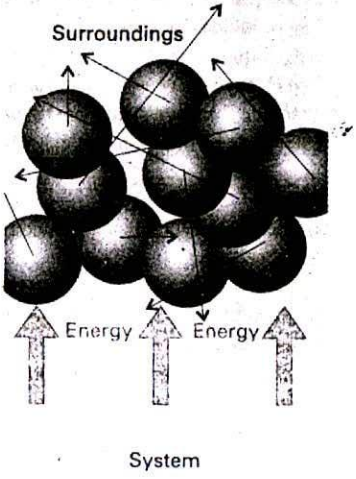
2.3 (a) When an endothermic process occurs in an adiabatic system, the temperature falls; (b) if the process is exothermic, then the temperature rises. (c) When an endothermic process occurs in a diathermic container, energy enters as heat from the surroundings, and the system remains at the same temperature;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

Molecular interpretation 2.1

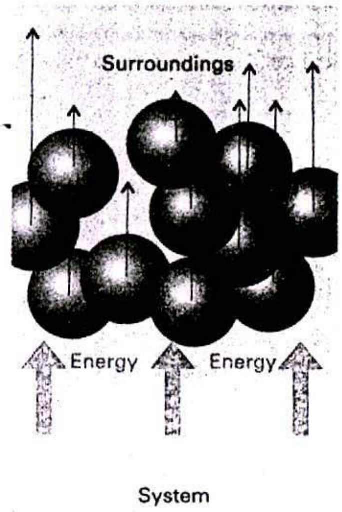
In molecular terms, *heat is the transfer of energy that makes use of chaotic molecular motion.* The chaotic motion of molecules is called **thermal motion.** The thermal motion of the molecules in the hot surroundings stimulates the molecules in the cooler system to move more vigorously and, as a result, 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. 2.4).

In contrast, *work is the transfer of energy that makes use of organized motion* (Fig. 2.5). When a weight is raised or lowered, its atoms move in an organized way. The atoms in a spring move in an orderly way when it is wound; the 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 particles 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.



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



2.5 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.

## 2.2 The First Law

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 composing the system. We denote by $\Delta U$ 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 $U_f$:

$$\Delta U = U_f - U_i \qquad [1]$$

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.

Internal energy, heat, and work are all measured in the same units, the joule (J). Changes in molar internal energy are typically expressed in kilojoules per mole (kJ mol$^{-1}$).

---

**Molecular interpretation 2.2**

Consider the case of a monatomic perfect gas at a temperature $T$. We know that the kinetic energy of one atom, of mass $m$, is

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

According to the equipartition theorem (see the *Introduction*), the average energy of each term is $\tfrac{1}{2}kT$, where $k$ is the Boltzmann constant. 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 $\tfrac{3}{2}NkT$, or $\tfrac{3}{2}nRT$. 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.

When the gas consists of polyatomic molecules that can rotate around three axes as well as translate in three dimensions, there is an additional contribution of $\tfrac{3}{2}RT$ arising from the kinetic energy of rotation. In this case, therefore,

$$U_m = U_m(0) + 3RT$$

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

Energy is also taken up by the vibrations of molecules. However, these modes cannot be treated classically because the separations between their energy levels are so wide. The expression for the mean energy of an oscillator of frequency $\nu$ is worked out by using the quantum mechanical expression for the energy levels (which form a uniform ladder like that illustrated in Fig. 0.7) and the Boltzmann distribution. The resulting expression (which is derived in Section 19.1b) is

$$U_m = U_m(0) + \frac{N_A h\nu}{e^{h\nu/kT} - 1}$$

It may be verified that the second term on the right increases with temperature and approaches $RT$, the classical expression, when $kT \gg h\nu$.

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.

### (a) The conservation of energy

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. We cannot use a system to do work, leave it isolated for a month, and then come back expecting to finding 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 of the first kind (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 $\Delta U$ for the resulting change in internal energy, then it follows that

$$\Delta U = q + w \tag{2}$$

Equation 2 is the mathematical statement of the First Law of thermodynamics, 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.

**Illustration**

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 was

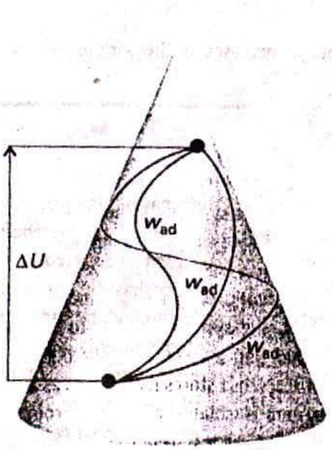
$$\Delta U = +100\ \text{kJ} - 15\ \text{kJ} = +85\ \text{kJ}$$

### (b) The formal statement of the First Law

The expression of the First Law that we have given is adequate for most purposes in thermodynamics. However, there are several unsatisfactory features about it, such as how we define and measure 'heat'. This section gives a more sophisticated version of the law, and shows how eqn 2 can be put on a firmer foundation. As the remainder of the text does not depend on this material, it is possible to omit it and go immediately to the following section ('Work and heat').

We begin by pretending that we do not know what we mean by 'energy'. We pretend that we know only what is meant by work, because we can observe a weight being raised or lowered in the surroundings. We also know how to measure work by noting the height through which the weight is raised. Throughout this section, work will be the fundamental, measurable quantity, and we define energy, heat, and the First Law in terms of work alone. We shall employ terms that have been established by the Zeroth Law of thermodynamics (Section 1.1), namely, state and temperature and the concepts of adiabatic and diathermic walls.

In an adiabatic system of a particular composition, it is known experimentally that the same increase in temperature is brought about by the same quantity of any kind of work we do on the system. Thus, if 1 kJ of mechanical work is done on the system (by stirring it with rotating paddles, for instance), or 1 kJ of electrical work is done (by passing an electric current through a heater), and so on, then the same rise in temperature is produced. The following statement of the First Law of thermodynamics is a summary of a large number of observations of this kind:



2.6 It is found that the same quantity of work must be done on an adiabatic system to achieve the same change of state even though different means of achieving that work may be used. This path independence implies the existence of a state function, the internal energy. The change in internal energy is like the change in altitude when climbing a mountain: its value is independent of path.

**The work needed to change an adiabatic system from one specified state to another specified state is the same however the work is done.**

This form of the law looks completely different from the form we gave before, but we shall now see how it implies eqn 2.

Suppose we do work $w_{ad}$ on an adiabatic system to change it from an initial state i to a final state f. The work may be of any kind (mechanical or electrical) and may take the system through different intermediate states (different temperatures and pressures, for instance). We might (in ignorance of the First Law) think that we need to label $w_{ad}$ with the path and to write $w_{ad}$(mechanical) or $w_{ad}$(electrical). However, the First Law tells us that $w_{ad}$ is the same for all paths and depends only on the initial and final states. This conclusion is analogous to climbing a mountain: the height we must climb between any two points is independent of the path we take (Fig. 2.6). In mountain climbing we can attach a number, the altitude, $A$, to each point on the mountain and express the height, $h$, of the climb as a difference in altitudes:

$$h = A_f - A_i = \Delta A$$

That is, in mountain climbing, the observation that $h$ is independent of the path taken implies the existence of the state function $A$. The First Law has exactly the same implication. The fact that $w_{ad}$ is independent of the path implies that to each state of the system we can attach a value of a quantity—we call it the 'internal energy', $U$—and express the work as a difference in internal energies:

$$w_{ad} = U_f - U_i = \Delta U \qquad [3]$$

This equation also shows that we can measure the change in the internal energy of a system by measuring the work needed to bring about the change in an adiabatic system.

## (c) The mechanical definition of heat

Suppose we strip away the thermal insulation around the system and make it diathermic. The system is now in thermal contact with its surroundings as we drive it from the same initial state to the same final state. The change in internal energy is the same as before, because $U$ is a state function, but we might find that the work we must do is not the same as before. Thus, whereas we might have needed to do 42 kJ of work when the system was in an adiabatic container, to achieve the same change of state we might now have to do 50 kJ of work. The difference between the work done in the two cases is *defined* as the heat absorbed by the system in the process:

$$q = w_{\mathrm{ad}} - w \qquad [4]$$

In the present case, we would conclude that $q = 42\ \mathrm{kJ} - 50\ \mathrm{kJ} = -8\ \mathrm{kJ}$, and report that 8 kJ of energy had left the system as heat. We see that we now have a purely mechanical definition of heat in terms of work. We know how to measure work in terms of the height through which a weight falls, so we now also have a method for measuring heat in terms of work.

Finally, we can express eqn 4 in a more familiar way. Because we already know that $\Delta U$ is (by definition) equal to $w_{\mathrm{ad}}$, the expression for the energy transferred to the system as heat is $q = \Delta U - w$. However, this expression is equivalent to eqn 2, the mathematical form of the First Law that we saw earlier.

## Work and heat

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 $\mathrm{d}U$. Then, if the work done on a system is $\mathrm{d}w$ and the energy supplied to it as heat is $\mathrm{d}q$, in place of eqn 2 we have

$$\mathrm{d}U = \mathrm{d}q + \mathrm{d}w \qquad (5)$$

To use eqn 5 we must be able to relate $\mathrm{d}q$ and $\mathrm{d}w$ to events taking place in the surroundings.

### 2.3 Expansion work

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.

### *(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 $\mathrm{d}z$ against an opposing force of magnitude $F$ is

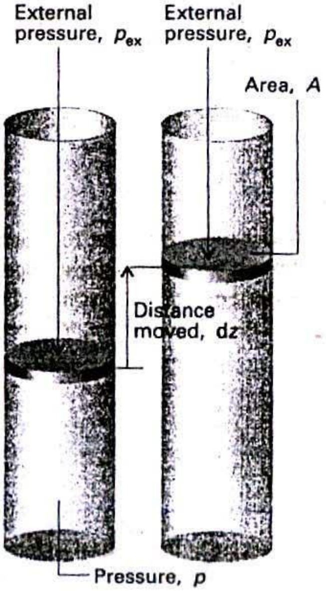
$$\mathrm{d}w = -F\,\mathrm{d}z \qquad [6]$$

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. 2.7, in which one wall of a system is a massless, frictionless, rigid, perfectly fitting piston of area $A$. If the external pressure is $p_{\mathrm{ex}}$, the force on the outer face of the piston is $F = p_{\mathrm{ex}}A$. When the system expands through a distance $\mathrm{d}z$ against an external pressure $p_{\mathrm{ex}}$, it follows that the work done is $\mathrm{d}w = -p_{\mathrm{ex}}A\,\mathrm{d}z$. But $A\,\mathrm{d}z$ is the change in volume, $\mathrm{d}V$, in the course of the expansion. Therefore, the work done when the system expands by $\mathrm{d}V$ against a pressure $p_{\mathrm{ex}}$ is

$$\mathrm{d}w = -p_{\mathrm{ex}}\,\mathrm{d}V \qquad (7)$$

To obtain the total work done when the volume changes from $V_{\mathrm{i}}$ to $V_{\mathrm{f}}$ we integrate this expression between the initial and final volumes:

$$w = -\int_{V_{\mathrm{i}}}^{V_{\mathrm{f}}} p_{\mathrm{ex}}\,\mathrm{d}V \qquad (8)$$



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

Table 2.1 Varieties of work*

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

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

† For work in joules (J). Note that $1\ \mathrm{N\,m} = 1\ \mathrm{J}$ and $1\ \mathrm{V\,C} = 1\ \mathrm{J}$.

The force acting on the piston, $p_{\mathrm{ex}}A$, 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 8 can still be used, but now $V_{\mathrm{f}} < V_{\mathrm{i}}$. It is important to note that it is still the external pressure that determines the magnitude of the work.

Other types of work (for example, electrical 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 eqn 7.

### (b) Free expansion

By **free expansion** we mean expansion against zero opposing force. It occurs when $p_{\mathrm{ex}} = 0$. According to eqn 7, $\mathrm{d}w = 0$ for each stage of the expansion. Hence, overall:

$$w = 0 \tag{9}$$

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

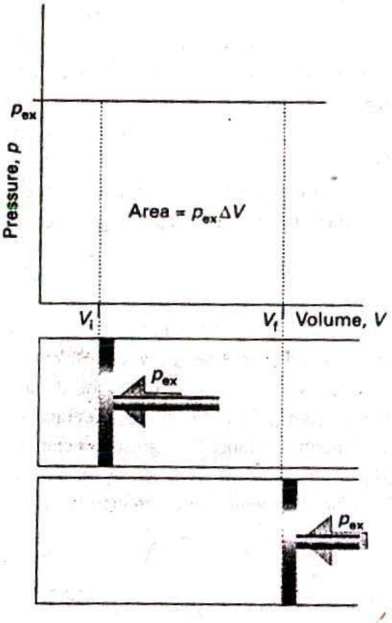
Now suppose that the external pressure is constant throughout the expansion. For example, the piston may be pressed on by the atmosphere, which exerts the same pressure throughout the expansion. A chemical example of this condition is the expansion of a gas formed in a chemical reaction. Equation 8 may now be evaluated by taking the constant $p_{\mathrm{ex}}$ 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 $\Delta V = V_{\mathrm{f}} - V_{\mathrm{i}}$,

$$w = -p_{\mathrm{ex}}\Delta V \tag{10}$$

This result is illustrated graphically in Fig. 2.8, which makes use of the fact that an integral can be interpreted as an area.[1] The magnitude of $w$, which is 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.



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

---

[1] Specifically, 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 $x = b$.

### (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 and 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 $p_{ex} = p$, eqn 7 becomes

$$\mathrm{d}w = -p_{ex}\,\mathrm{d}V = -p\,\mathrm{d}V \qquad (11)_{\mathrm{rev}}$$

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

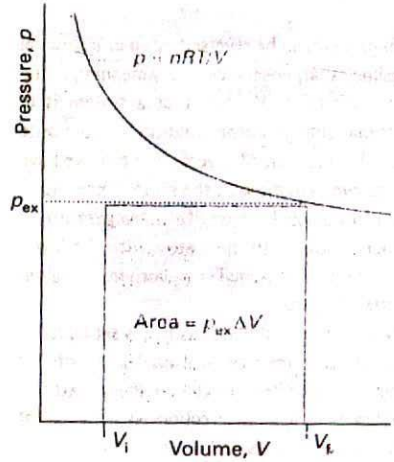
$$w = -\int_{V_i}^{V_f} p\,\mathrm{d}V \qquad (12)_{\mathrm{rev}}$$

The integral can be evaluated once we know how the pressure of the confined gas depends on its volume. Equation 12 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

$$w = -nRT\int_{V_i}^{V_f} \frac{\mathrm{d}V}{V} = -nRT \ln\left(\frac{V_f}{V_i}\right) \qquad (13)^{\circ}_{\mathrm{rev}}$$



2.9 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.

When the final volume is greater than the initial volume, as in an expansion, the logarithm in eqn 13 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 of the work it has done. The equation also shows 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.

The result of the calculation can be expressed as an indicator diagram, for the magnitude of the work done is equal to the area under the isotherm $p = nRT/V$ (Fig. 2.9). 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 4.6b) 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.

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 10. 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 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

$$\mathrm{Fe(s)} + \mathrm{2HCl(aq)} \longrightarrow \mathrm{FeCl_2(aq)} + \mathrm{H_2(g)}$$

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 $\mathrm{g\,mol^{-1}}$, it follows that

$$w \approx -\frac{50\ \mathrm{g}}{55.85\ \mathrm{g\,mol^{-1}}} \times (8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (298.15\ \mathrm{K})$$
$$\approx -2.2\ \mathrm{kJ}$$

The system (the reaction mixture) does 2.2 kJ of work driving back the atmosphere.

**Comment** Note that (for this perfect gas system) 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 2.3** 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

$$dU = dq + dw_{\text{exp}} + dw_{\text{e}} \tag{14}$$

where $dw_e$ is work in addition (e for 'extra') to the expansion work, $dw_{\text{exp}}$. 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 $dw_{\text{exp}} = 0$. 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:

$$dU = dq \qquad \text{(at constant volume, no additional work)} \tag{15}$$

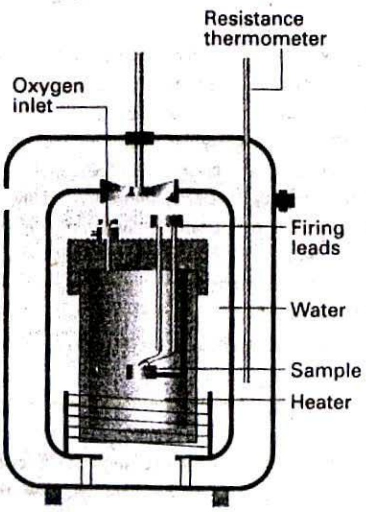
We express this relation by writing $dU = dq_V$, where the subscript implies a change at constant volume. For a measurable change,

$$\Delta U = q_V \tag{16}$$

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.

### (a) Calorimetry

The most common device for measuring $\Delta U$ is the **adiabatic bomb calorimeter** (Fig. 2.10). 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 that 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.



2.10 A constant-volume bomb calorimeter. The 'bomb' is the central vessel, which is massive 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.

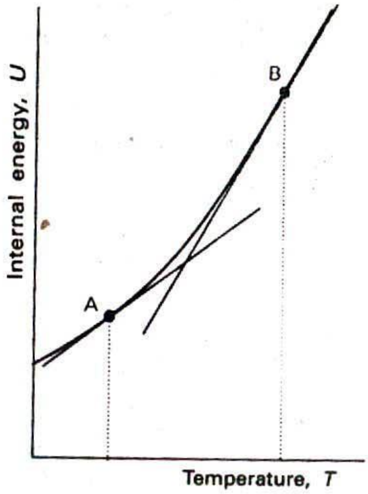
The change in temperature, $\Delta T$, of the calorimeter is proportional to the heat that the reaction releases or absorbs. Therefore, by measuring $\Delta T$ we can determine $q_V$ and hence find $\Delta U$. The conversion of $\Delta T$ to $q_V$ is best achieved by calibrating the calorimeter using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

$$q = C\Delta T \tag{17}$$

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

$$q = I\mathcal{V}t \tag{18}$$

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.



2.11 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 graph at any temperature (as shown by the tangents at A and B) 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.

## Illustration

If we pass a current of 10.0 A from a 12 V supply for 300 s, then from eqn 18 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 $C = (36\text{ kJ})/(5.5\text{ K}) = 6.5\text{ kJ K}^{-1}$.

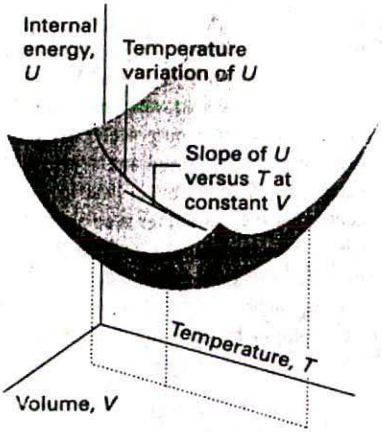
### (b) Heat capacity

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 shall suppose that the sample is confined to a constant volume. For example, it 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. 2.11 may be obtained. The slope of 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[2]

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad [19]$$

The notation is that of a 'partial derivative'. A partial derivative is a slope calculated with all except one variables held constant.[3] 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. 2.12).

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 heat to bring about the same rise in temperature). The **molar heat capacity at constant volume**, $C_{V,\text{m}}$, is the heat capacity per mole of material, and is an intensive property (all molar quantities are intensive). Typical values of $C_{V,\text{m}}$ for polyatomic gases are close to 25 $\text{J K}^{-1}\text{ mol}^{-1}$. 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. The specific heat capacity of water at room temperature is close to 4 $\text{J K}^{-1}\text{ g}^{-1}$. 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.



2.12 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 $(\partial U/\partial T)_V$.

**Molecular interpretation 2.3**

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 $U_\text{m} = U_\text{m}(0) + \frac{3}{2}RT$, so from eqn 19

$$C_{V,\text{m}} = \left(\frac{\partial U_\text{m}}{\partial T}\right)_V = \tfrac{3}{2}R$$

---

[2] 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.

[3] Partial derivatives are reviewed in *Further information 1*.

The numerical value is 12.47 J K$^{-1}$ mol$^{-1}$. Similarly, for a gas composed of nonlinear polyatomic molecules

$$C_{V,\mathrm{m}} = 3R \tag{20}$$

or 24.94 J K$^{-1}$ mol$^{-1}$. These values are both independent of temperature.

The heat capacity arising from vibration is obtained by evaluating the derivative of the expression derived using quantum mechanics, and for a vibrational frequency $\nu$ is

$$C_{V,\mathrm{m}} = Rf^2 \qquad f = \left(\frac{h\nu}{kT}\right)\frac{\mathrm{e}^{-h\nu/2kT}}{1-\mathrm{e}^{-h\nu/kT}} \tag{21}$$

The factor $f = 0$ at $T = 0$ and $f \approx 1$ when $kT \gg h\nu$. That is, the contribution of the vibration of a molecule to the molar heat capacity is zero at $T = 0$ and climbs towards its classical value ($R$) as the temperature is raised. Physically, at low temperatures the gap between the energy levels is so great that the vibrations cannot be excited, so energy cannot be absorbed. As the temperature is raised, more and more energy levels become accessible, and the molecule begins to behave as though its vibrations were not quantized.

---

The heat capacity can be used to relate a change in internal energy to a change in temperature of a constant-volume system. It follows from eqn 19 that

$$\mathrm{d}U = C_V\,\mathrm{d}T \qquad \text{(at constant volume)} \tag{22a}$$

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

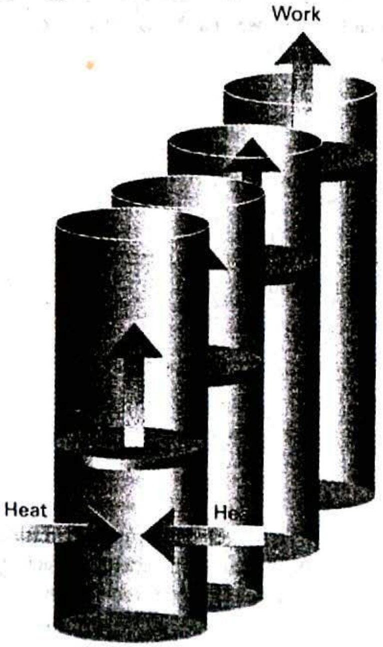
$$\Delta U = C_V\Delta T \qquad \text{(at constant volume)} \tag{22b}$$

Because a change in internal energy can be identified with the heat supplied at constant volume (eqn 16), the last equation can be written

$$q_V = C_V\Delta T \tag{22c}$$

This relation provides a simple way of measuring the heat capacity of a sample: a measured quantity of heat is supplied to the sample (electrically, for example), and the resulting increase in temperature is monitored. The ratio of the heat supplied to the temperature rise it causes is the heat capacity of the sample.

A large heat capacity implies that, for a given quantity of 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 heat is supplied. At a phase transition (such as at the boiling point of water), the temperature of a substance does not rise as heat is supplied (the energy is used to drive the endothermic phase transition, in this case to vaporize the water, rather than to increase its temperature), so, 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 6.7.



2.13 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.

## 2.5 Enthalpy

The change in internal energy is not equal to the heat supplied 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. 2.13), so $\mathrm{d}U$ is less than $\mathrm{d}q$. However, we shall now show that in this case the heat supplied at constant pressure is equal to the change in another thermodynamic property of the system, the **enthalpy, $H$**.

## (a) The definition of enthalpy

The enthalpy is defined as

$$H = U + pV \qquad [23]$$

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. As is true of any state function, the change in enthalpy, $\Delta H$, between any pair of initial and final states is independent of the path between them.

The change in enthalpy is equal to the heat supplied at constant pressure to a system (so long as the system does no additional work):

$$\mathrm{d}H = \mathrm{d}q \qquad \text{(at constant pressure, no additional work)} \qquad (24a)$$

For a measurable change,

$$\Delta H = q_p \qquad (24b)$$

### Justification 2.1

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 $H$ 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 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

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

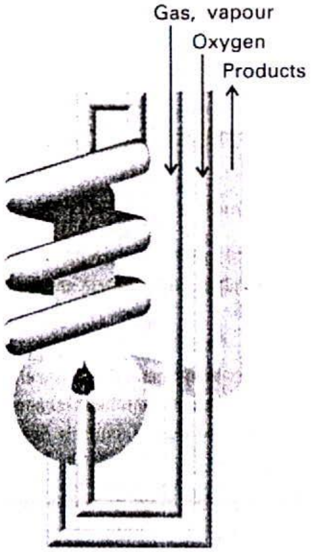
as in eqn 24*a*.

---

The result expressed in eqn 24 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. For a combustion reaction an adiabatic flame calorimeter may be used to measure $\Delta T$ when a



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

given amount of substance burns in a supply of oxygen (Fig. 2.14). Another route to $\Delta H$ is to measure the internal energy change by using a bomb calorimeter, and then to convert $\Delta U$ to $\Delta H$. 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 $\Delta H$ and $\Delta U$ 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.

### Example 2.2 Relating $\Delta H$ and $\Delta U$

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 $\mathrm{g\,cm^{-3}}$ and 2.93 $\mathrm{g\,cm^{-3}}$, respectively.

**Method** The starting point for the calculation is the relation between the enthalpy of a substance and its internal energy (eqn 23). 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, $\rho$, by using $\rho = M/V_m$.

**Answer** The change in enthalpy when the transformation 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 $\mathrm{cm^3}$, and that of 1.0 mol $CaCO_3$ as calcite is 37 $\mathrm{cm^3}$. Therefore,

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

(because $1\ \mathrm{Pa\,m^3} = 1\ \mathrm{J}$). Hence,

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

which is only 0.1 per cent of the value of $\Delta U$.

**Comment** 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 $\Delta H$ and $\Delta U$ when 1.0 mol of grey tin (density 5.75 $\mathrm{g\,cm^{-3}}$) changes to white tin (density 7.31 $\mathrm{g\,cm^{-3}}$) 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 $H$:

$$H = U + pV = U + nRT \qquad (25)^\circ$$

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

$$\Delta H = \Delta U + \Delta n_g RT \qquad (26)^\circ$$

where $\Delta n_g$ is the change in the amount of gas molecules in the reaction. For example, in the reaction

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) \qquad \Delta n_g = -3 \text{ mol}$$

because 3 mol of gas-phase molecules is replaced by 2 mol of liquid-phase molecules, and at 298 K the enthalpy and internal energy changes taking place in the system are related by

$$\Delta H - \Delta U = (-3 \text{ mol}) \times RT \approx -7.5 \text{ kJ}$$

Note that the difference is expressed in kilojoules, not joules as in Example 2.2. The enthalpy change is smaller 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 heat supplied (from $q = IVt$), 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 26.

**Answer** The enthalpy change is

$$\Delta H = q_p = (0.50 \text{ A}) \times (12 \text{ V}) \times (300 \text{ s}) = +1.8 \text{ kJ}$$

Because 0.798 g of water is 0.0443 mol $H_2O$, the enthalpy of vaporization per mole of $H_2O$ is

$$\Delta H_m = +\frac{1.8 \text{ kJ}}{0.0443 \text{ mol}} = +41 \text{ kJ mol}^{-1}$$

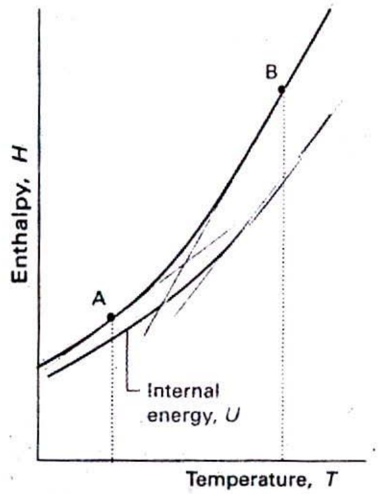
In the process $H_2O(l) \rightarrow H_2O(g)$ the change in the amount of gas molecules is $\Delta n_g = +1$ mol, so

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

**Comment** 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$^{-1}$, 6.6 × 10$^2$ s]



**2.15** The slope of a graph of the enthalpy of a system subjected to a constant pressure plotted against temperature is the constant-pressure heat capacity. The slope of the graph 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, the slope of the graph of enthalpy versus temperature is steeper than that of the graph of internal energy versus temperature, and $C_{p,m}$ is larger than $C_{V,m}$.

Enthalpy and internal energy changes may also be measured by noncalorimetric methods (see Chapters 9 and 10).

## (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 a graph of enthalpy against temperature at constant pressure is called the **heat capacity at constant pressure,** $C_p$ (Fig. 2.15). More formally:

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \qquad [27]$$

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,** $C_{p,m}$, 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,

$$\mathrm{d}H = C_p\,\mathrm{d}T \qquad \text{(at constant pressure)} \qquad (28a)$$

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

$$\Delta H = C_p \Delta T \qquad \text{(at constant pressure)} \qquad (28b)$$

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

$$q_p = C_p \Delta T \qquad (29)$$

This expression shows us how to measure the heat capacity of a sample: a measured quantity of heat is supplied 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 (one of the noble gases). However, when it is necessary to take the variation into account, a convenient approximate empirical expression is

$$C_{p,\mathrm{m}} = a + bT + \frac{c}{T^2} \qquad (30)$$

The empirical parameters $a$, $b$, and $c$ are independent of temperature. Some typical values are given in Table 2.2.

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

| | $a$ | $b/(10^{-3}\,\mathrm{K}^{-1})$ | $c/(10^5\,\mathrm{K}^2)$ |
|---|---|---|---|
| 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* at the end

### 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.

---

[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.

**Method** The heat capacity of $N_2$ changes with temperature, so we cannot use eqn 28*b* (which assumes that the heat capacity of the substance is constant). Therefore, we must use eqn 28*a*, substitute eqn 30 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

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

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 30 at 25 °C), we would have found that the two enthalpies differed by 2.19 $\mathrm{kJ\,mol^{-1}}$.

**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)?

[$\Delta H = \tfrac{1}{4}aT^4$]

### (d) The relation between heat capacities

Most systems expand when heated at constant pressure. Such systems do work on the surroundings and 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.*

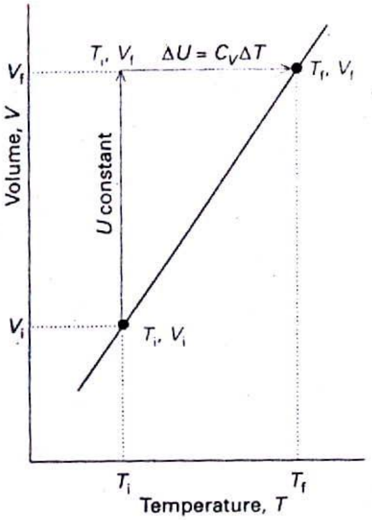
There is a simple relation between the two heat capacities of a perfect gas:

$$C_p - C_V = nR \qquad (31)^{\circ}$$

(This relation is derived in Section 3.3a.) It follows that the molar heat capacity of a perfect gas is about 8 $\mathrm{J\,K^{-1}\,mol^{-1}}$ larger at constant pressure than at constant volume. Because the heat capacity at constant volume of a nonlinear polyatomic gas is about 25 $\mathrm{J\,K^{-1}\,mol^{-1}}$, the difference is highly significant and must be taken into account.

## 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, the



2.16 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 increased at constant volume. The overall change in internal energy is the sum of the changes for the two steps.

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.

## (a) The work of adiabatic change

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. 2.16). 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 arises solely from the kinetic energies of the molecules, 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

$$\Delta U = C_V(T_f - T_i) = C_V\Delta T \tag{32}$$

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

$$w_{ad} = C_V\Delta T \tag*{(33)°}$$

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 $\Delta T$.

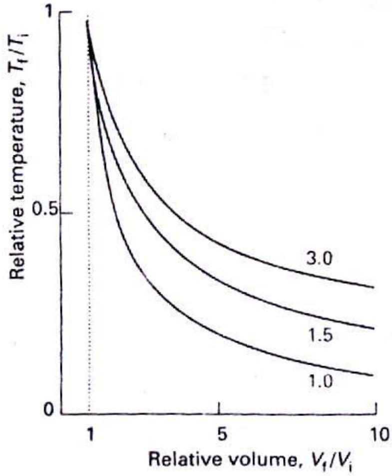
To use eqn 33, we need to relate the change in temperature to the change in volume (which we know). The most important type of adiabatic expansion (and the only kind that we need for later) is *reversible* adiabatic expansion, in which the external pressure is matched to the internal pressure throughout. For adiabatic, reversible expansion the initial and final temperatures are related by

$$V_f T_f^c = V_i T_i^c \qquad c = \frac{C_{V,m}}{R} \tag*{$(34)^{\circ}_{rev}$}$$

This expression is derived in the following *Justification* and the temperature dependence it implies is shown in Fig. 2.17. All we need do at this stage to find the work done by the system is to solve this relation for $T_f$,

$$T_f = T_i\left(\frac{V_i}{V_f}\right)^{1/c} \tag*{$(35)^{\circ}_{rev}$}$$

calculate $\Delta T$, and substitute into eqn 33.



2.17 The variation of temperature as a perfect gas is expanded reversibly and adiabatically. The curves are labelled with different values of $c = C_{V,m}/R$. Note that the temperature falls most steeply for gases with low molar heat capacity.

### Justification 2.2

Consider a stage in the expansion when the pressure inside and out is $p$ (the expansion is reversible, so the internal and external pressures are equal at all stages). The work done when the gas expands by $dV$ is $-p\,dV$. However, for a perfect gas, $dU = C_V\,dT$ (by the same argument as in the text for a macroscopic change). Therefore, because $dU = dw$ for an adiabatic change, we can write

$$C_V\,dT = -p\,dV$$

We are dealing with a perfect gas, so we can replace $p$ by $nRT/V$ and obtain

$$C_V\frac{dT}{T} = -nR\frac{dV}{V}$$

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,

$$C_V \int_{T_i}^{T_f} \frac{dT}{T} = -nR \int_{V_i}^{V_f} \frac{dV}{V}$$

(We are taking $C_V$ to be independent of temperature.) Then, because $\int dx/x = \ln x$, we obtain

$$C_V \ln\left(\frac{T_f}{T_i}\right) = -nR \ln\left(\frac{V_f}{V_i}\right)$$

With $c = C_V/nR$ and by using $a \ln x = \ln x^a$ and $-\ln(x/y) = \ln(y/x)$ we obtain

$$\ln\left(\frac{T_f}{T_i}\right)^c = \ln\left(\frac{V_i}{V_f}\right)$$

which implies eqn 34.

---

## Illustration

Consider the adiabatic, reversible expansion of 0.020 mol Ar, initially at 25°C, from 0.50 L to 1.00 L. The molar heat capacity of argon at constant volume is 12.48 $\text{J K}^{-1}\,\text{mol}^{-1}$, so $c = 1.501$. Therefore, from eqn 35,

$$T_f = (298\ \text{K}) \times \left(\frac{0.50\ \text{L}}{1.00\ \text{L}}\right)^{1/1.501} = 188\ \text{K}$$

It follows that $\Delta T = -110$ K, and therefore, from eqn 33, that

$$\begin{aligned} w = C_V\Delta T &= (0.020\ \text{mol}) \times (12.48\ \text{J K}^{-1}\,\text{mol}^{-1}) \times (-110\ \text{K}) \\ &= -27\ \text{J} \end{aligned}$$

Note that the temperature change is independent of the mass 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 L to 2.00 L, the other initial conditions being the same.

[194 K, −56 J, −56 J]

---

### *(b) Heat capacity ratio and adiabats*

Now we consider the change in pressure that results from an adiabatic, reversible expansion of a perfect gas. We show in the *Justification* below that

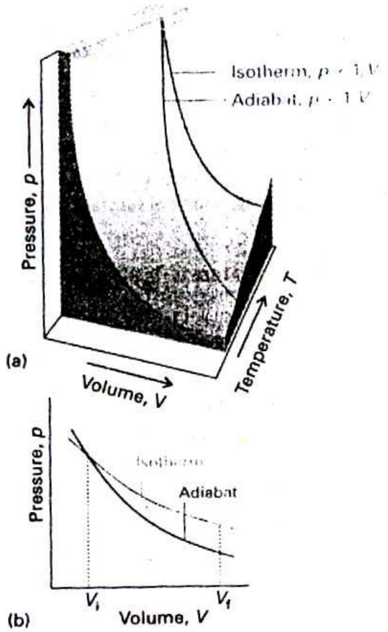
$$pV^{\gamma} = \text{constant} \qquad (36)^{\circ}_{\text{rev}}$$

where the **heat capacity ratio**, $\gamma$, of a substance is defined as

$$\gamma = \frac{C_{p,\text{m}}}{C_{V,\text{m}}} \qquad [37]$$

Because the heat capacity at constant pressure is greater than the heat capacity at constant volume, $\gamma > 1$. For a perfect gas, it follows from eqn 31 that

$$\gamma = \frac{C_{V,\text{m}} + R}{C_{V,\text{m}}} \qquad (38)^{\circ}$$



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

For a monatomic perfect gas, $C_{V,\mathrm{m}} = \frac{3}{2}R$ (see *Molecular interpretation* 2.3), 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 $\gamma = \frac{4}{3}$.

### Justification 2.3

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 established (eqn 35) that for a reversible adiabatic change the temperature changes so as to satisfy

$$\frac{T_\mathrm{i}}{T_\mathrm{f}} = \left(\frac{V_\mathrm{f}}{V_\mathrm{i}}\right)^{1/c}$$

Then we combine the two expressions, to obtain

$$p_\mathrm{i}V_\mathrm{i}^{\gamma} = p_\mathrm{f}V_\mathrm{f}^{\gamma}$$

It follows that $pV^{\gamma} = \text{constant}$ as used in the text.

The curves of pressure versus volume for adiabatic, reversible change are known as adiabats, and one 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.

### Illustration

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

$$p_\mathrm{f} = p_\mathrm{i}\left(\frac{V_\mathrm{i}}{V_\mathrm{f}}\right)^{\gamma} = (100\ \mathrm{kPa}) \times \left(\tfrac{1}{2}\right)^{5/3} = 31.5\ \mathrm{kPa}$$

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

## Thermochemistry

The study of the heat produced or required by 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 heat produced or absorbed 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 the $\Delta U$ or $\Delta H$ for a reaction, we can predict the heat the reaction can produce.

We have already remarked that a process that releases heat is classified as exothermic and one that absorbs heat is classified as endothermic. Because the release of heat 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 heat 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.**

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 enthalpy of 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

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

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) 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 $\Delta_{\text{trs}}H^\ominus$ (Table 2.3). The standard enthalpy of vaporization, $\Delta_{\text{vap}}H^\ominus$, is one example. Another is the standard enthalpy of fusion $\Delta_{\text{fus}}H^\ominus$, the enthalpy change accompanying the conversion of a solid to a liquid, as in

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

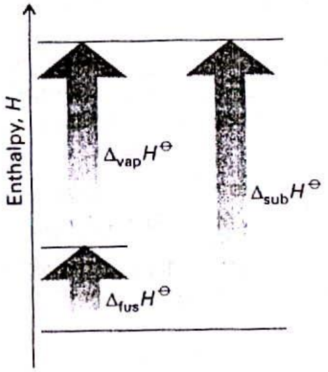
As in this case, it is sometimes convenient to know the standard enthalpy change at the transition temperature as well as at the conventional temperature.

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 (so long as the initial and final states are the same). For example, we can picture the conversion of a

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

| | $T_f/\text{K}$ | Fusion | $T_b/\text{K}$ | 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<br>44.016 at 298 K |
| He | 3.5 | 0.021 | 4.22 | 0.084 |

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



1

solid to a vapour either as occurring by sublimation (the direct conversion from solid to vapour),

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

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

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

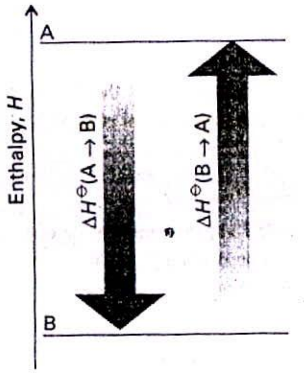
Because the overall result of the indirect path is the same as that of the direct path, the overall enthalpy change is the same in each case (1), and we can conclude that (for processes occurring at the same temperature)

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

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 must differ only in sign (2):

$$\Delta H^\ominus(A \rightarrow B) = -\Delta H^\ominus(A \leftarrow B)$$



2

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$^{-1}$.

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. Broadly speaking, the **standard reaction enthalpy**, $\Delta_rH^\ominus$, is the change in enthalpy when reactants in their standard states change to products in their standard states, as in

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

Table 2.4 Enthalpies of transition

| Transition | Process | Symbol* |
|---|---|---|
| Transition | Phase $\alpha \longrightarrow$ phase $\beta$ | $\Delta_{trs}H$ |
| Fusion | $s \longrightarrow l$ | $\Delta_{fus}H$ |
| Vaporization | $l \longrightarrow g$ | $\Delta_{vap}H$ |
| Sublimation | $s \longrightarrow g$ | $\Delta_{sub}H$ |
| Mixing of fluids | Pure $\longrightarrow$ mixture | $\Delta_{mix}H$ |
| Solution | Solute $\longrightarrow$ solution | $\Delta_{sol}H$ |
| Hydration | $X^\pm(g) \longrightarrow X^\pm(aq)$ | $\Delta_{hyd}H$ |
| Atomization | Species(s, l, g) $\longrightarrow$ atoms(g) | $\Delta_{at}H$ |
| Ionization | $X(g) \longrightarrow X^+(g) + e^-(g)$ | $\Delta_{ion}H$ |
| Electron gain | $X(g) + e^-(g) \longrightarrow X^-(g)$ | $\Delta_{eg}H$ |
| Reaction | Reactants $\longrightarrow$ products | $\Delta_rH$ |
| Combustion | Compound(s, l, g) + $O_2(g) \longrightarrow CO_2(g)$, $H_2O(l, g)$ | $\Delta_cH$ |
| Formation | Elements $\longrightarrow$ compound | $\Delta_fH$ |
| Activation | Reactants $\longrightarrow$ activated complex | $\Delta^\ddagger H$ |

* IUPAC recommendations. In common usage, the transition subscript is often attached to $\Delta H$, as in $\Delta H_{trs}$

This 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. The combination of a chemical equation and a standard reaction enthalpy is called a **thermochemical equation**. A standard reaction enthalpy refers to the overall process

Pure, unmixed reactants in their standard states
$\longrightarrow$ pure, separated 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.

We said 'broadly speaking' above, because the precise specification of the standard reaction enthalpy is more specific about the significance of the 'per mole' that appears in the value of $\Delta_r H^\ominus$. To establish this precise definition, consider the reaction

$$2\text{A} + \text{B} \longrightarrow 3\text{C} + \text{D}$$

The standard enthalpy of this reaction is based on the expression

$$\Delta_r H^\ominus = \sum_{\text{Products}} \nu H_m^\ominus - \sum_{\text{Reactants}} \nu H_m^\ominus \qquad (39)$$

where the terms on the right are the standard molar enthalpies of the products and reactants weighted by the stoichiometric coefficients, $\nu$, in the chemical equation. For our reaction,

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

where $H_m^\ominus(\text{J})$ is the standard molar enthalpy of species J at the temperature of interest.

A somewhat more sophisticated way of expressing the definition, which is useful for some of the formal expressions we shall derive (but less so in practice), is obtained by writing the reaction in the symbolic form

$$0 = 3\text{C} + \text{D} - 2\text{A} - \text{B}$$

by subtracting the reactants from both sides (and replacing the arrow by an equals sign). This equation has the form

$$0 = \sum_{\text{J}} \nu_{\text{J}}\text{J} \qquad (40)$$

where J denotes the substances and the $\nu_{\text{J}}$ are the corresponding **stoichiometric numbers** in the chemical equation. These numbers have the values

$$\nu_{\text{A}} = -2 \qquad \nu_{\text{B}} = -1 \qquad \nu_{\text{C}} = +3 \qquad \nu_{\text{D}} = +1$$

Note that, in the convention we shall adopt, the stoichiometric numbers of the products are positive and those of the reactants are negative. The standard reaction enthalpy is then defined as

$$\Delta_r H^\ominus = \sum_{\text{J}} \nu_{\text{J}} H_m^\ominus(\text{J}) \qquad [41]$$

as may be verified by substituting the values of the stoichiometric numbers given above.

## Illustration

For the reaction

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

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

| | $\Delta_f H^\ominus/(\mathrm{kJ\,mol^{-1}})$ | $\Delta_c H^\ominus/(\mathrm{kJ\,mol^{-1}})$ |
|---|---|---|
| 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 | −726 |

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

the stoichiometric numbers are

$$\nu(N_2) = -1 \qquad \nu(H_2) = -3 \qquad \nu(NH_3) = +2$$

so the standard reaction enthalpy is

$$\Delta_r H^\ominus = 2H_m^\ominus(NH_3) - \{H_m^\ominus(N_2) + 3H_m^\ominus(H_2)\}$$

……

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

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

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.

### (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,

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

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

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

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

Method Add and subtract the reactions given, together with any others needed, so as to reproduce the reaction required. Then add and subtract the reaction enthalpies in the same way. Additional data are in Table 2.5.

Answer The combustion reaction we require is

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

This reaction can be recreated from the following sum:

$$\begin{array}{ll} & \Delta_r H^{\ominus}/\text{kJ mol}^{-1} \\ C_3H_6(g) + H_2(g) \longrightarrow C_3H_8(g) & -124 \\ C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l) & -2220 \\ H_2O(l) \longrightarrow H_2(g) + \tfrac{1}{2}O_2(l) & +286 \\ \hline C_3H_6(g) + \tfrac{9}{2}O_2(g) \longrightarrow 3CO_2(g) + 3H_2O(l) & -2058 \end{array}$$

Comment The skill to develop is the ability to assemble a given thermochemical equation from others.

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$^{-1}$]

## 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 most reproducible form of the element. Standard enthalpies of formation are expressed as enthalpies per mole of the compound. The standard enthalpy of formation of liquid benzene at 298 K, for example, refers to the reaction

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

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

$$N_2(g) \longrightarrow N_2(g)$$

Some enthalpies of formation are listed in Tables 2.5 and 2.6.

Table 2.6* Standard enthalpies of formation of inorganic compounds, $\Delta_f H^{\ominus}/(\text{kJ mol}^{-1})$, at 298 K

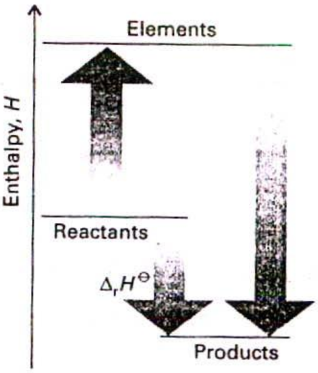
| | | | |
|---|---|---|---|
| $H_2O(l)$ | $-285.83$ | $H_2O_2(l)$ | $-187.78$ |
| $NH_3(g)$ | $-46.11$ | $N_2H_4(l)$ | $+50.63$ |
| $NO_2(g)$ | $+33.18$ | $N_2O_4(g)$ | $+9.16$ |
| NaCl(s) | $-411.15$ | KCl(s) | $-436.75$ |

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

### (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 (3). Hence, in the enthalpies of formation of substances, we have enough information to calculate the enthalpy of any reaction by using

$$\Delta_r H^{\ominus} = \sum_{\text{Products}} \nu \Delta_f H^{\ominus} - \sum_{\text{Reactants}} \nu \Delta_f H^{\ominus} \qquad (42)$$



3

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

## Illustration

The standard reaction enthalpy of

$$2HN_3(l) + 2NO(g) \longrightarrow H_2O_2(l) + 4N_2(g)$$

is calculated as follows:

$$\begin{aligned}\Delta_r H^\ominus &= \{\Delta_f H^\ominus(H_2O_2, l) + 4\Delta_f H^\ominus(N_2, g)\} \\ &\quad - \{2\Delta_f H^\ominus(HN_3, l) + 2\Delta_f H^\ominus(NO, g)\} \\ &= \{-187.78 + 4(0)\} - \{2(264.0) + 2(90.25)\}\ \text{kJ mol}^{-1} \\ &= -892.3\ \text{kJ mol}^{-1}\end{aligned}$$

The formal expression for eqn 42 in terms of a reaction written as in eqn 40 is

$$\Delta_r H^\ominus = \sum_J \nu_J \Delta_f H^\ominus(J) \qquad [43]$$

It may be verified that this expression reproduces the value calculated in the *Illustration*.

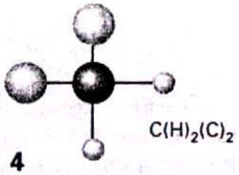
### *(b) Group contributions*

We have seen that standard reaction enthalpies may be constructed 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 composition of the species. The short answer is that there is no *thermodynamically* exact way of breaking enthalpies of formation down into contributions from individual atoms and bonds. In the past, approximate procedures based on **mean bond enthalpies**, $\Delta H$(A—B), the enthalpy change associated with the breaking of a specific A—B bond,

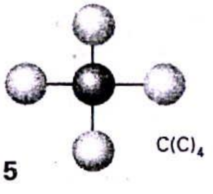
$$\text{A—B(g)} \longrightarrow \text{A(g)} + \text{B(g)} \qquad \Delta H(\text{A—B})$$

have been used. However, this procedure is notoriously unreliable, in part because the $\Delta H$(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.

Somewhat more reliable is an approach in which a molecule is regarded as being built up of **thermochemical groups**, an atom or physical group of atoms bound to at least two other atoms: two examples are shown as (4) and (5). The enthalpy of formation of the compound is then expressed (approximately, at least) as the sum of the contributions associated with all the thermochemical groups into which the molecule can be divided. A list of the appropriate values is given in Table 2.7 and the method is illustrated in the following example. Table 2.7 also contains information on heat capacity, which is approximately additive in a similar sense.



4



5

**Table 2.7*** Benson thermochemical groups

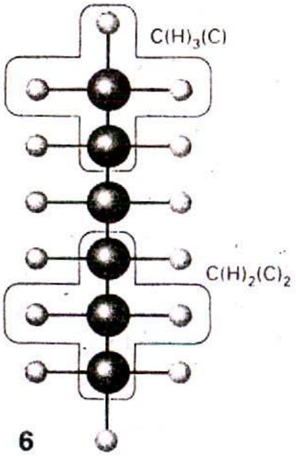
| Group | $\Delta_f H^\ominus$/ (kJ mol$^{-1}$) | $C^\ominus_{p,m}$/ (J K$^{-1}$ mol$^{-1}$) |
|---|---|---|
| C(H)$_3$(C) | −42.17 | 25.9 |
| C(H)$_2$(C)$_2$ | −20.7 | 22.8 |
| C(H)(C)$_3$ | −6.19 | 18.7 |
| C(C)$_4$ | +8.16 | 18.2 |

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

### **Example 2.6** Using the thermochemical group approach

Estimate the standard enthalpy of formation at 298 K of hexane in (a) the gas phase, (b) the liquid phase.

Method First, identify the thermochemical groups present in the molecule. Then add together the appropriate values in Table 2.7. To obtain the enthalpy of formation of the



6

liquid, include the enthalpy of condensation of the vapour, that is the negative of the enthalpy of vaporization of the liquid (Table 2.3).

Answer The decomposition of the molecule into groups is depicted in (6). There are two C(H)$_3$(C) groups and four C(H)$_2$(C)$_2$ groups; therefore

$$\begin{aligned}\Delta_f H^{\ominus}(\mathrm{C_6H_{14}}, \mathrm{g}) &= 2(-42.17\ \mathrm{kJ\,mol^{-1}}) + 4(-20.7\ \mathrm{kJ\,mol^{-1}})\\ &= -167.1\ \mathrm{kJ\,mol^{-1}}\end{aligned}$$

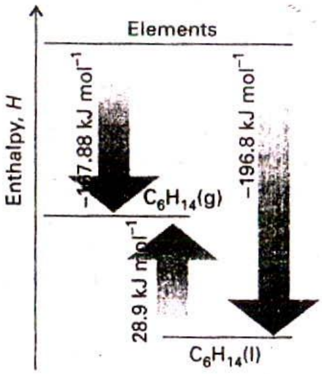
The enthalpy of vaporization of hexane is 28.9 kJ mol$^{-1}$ (Table 2.3); therefore (7),

$$\Delta_f H^{\ominus}(\mathrm{C_6H_{14}}, \mathrm{l}) = (-167.1\ \mathrm{kJ\,mol^{-1}}) - (28.9\ \mathrm{kJ\,mol^{-1}}) = -196.0\ \mathrm{kJ\,mol^{-1}}$$

The experimental value is $-198.7\ \mathrm{kJ\,mol^{-1}}$.

Self-test 2.7 Estimate the standard enthalpy of formation of gaseous 2,2-dimethylpropane.

[$-160.52\ \mathrm{kJ\,mol^{-1}}$]



7

## 2.9 The temperature dependence of reaction enthalpies

The standard enthalpies of many important reactions have been measured at different temperatures, and for serious work these accurate data must be used. However, in the absence of this information, standard reaction enthalpies at different temperatures may be estimated from heat capacities and the reaction enthalpy at some other temperature.

It follows from eqn 27 that, when a substance is heated from $T_1$ to $T_2$, its enthalpy changes from $H(T_1)$ to

$$H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_p\,\mathrm{d}T \tag{44}$$

(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

$$\Delta_r H^{\ominus}(T_2) = \Delta_r H^{\ominus}(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^{\ominus}\,\mathrm{d}T \tag{45}$$

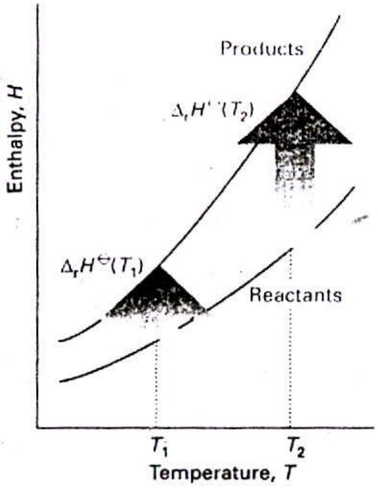
where $\Delta_r C_p^{\ominus}$ is the difference of the molar heat capacities of products and reactants under standard conditions weighted by the stoichiometric coefficients that appear in the chemical equation:

$$\Delta_r C_p^{\ominus} = \sum_{\text{Products}} \nu C_{p,\mathrm{m}}^{\ominus} - \sum_{\text{Reactants}} \nu C_{p,\mathrm{m}}^{\ominus} \tag{46}$$

More formally,

$$\Delta_r C_p^{\ominus} = \sum_{\mathrm{J}} \nu_{\mathrm{J}} C_{p,\mathrm{m}}^{\ominus}(\mathrm{J}) \tag*{[47]}$$

Equation 45 is known as **Kirchhoff's law** (Fig. 2.19). It is normally a good approximation to assume that $\Delta_r C_p^{\ominus}$ 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 30.



2.19 An illustration of the content of Kirchhoff's law. When the temperature is increased, the enthalpies 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.

### Example 2.7 Using Kirchhoff's law

The standard enthalpy of formation of gaseous $H_2O$ at 298 K is $-241.82\ \mathrm{kJ\,mol^{-1}}$. Estimate its value at 100°C given the following values of the molar heat capacities at constant pressure: $H_2O(g)$ : $33.58\ \mathrm{J\,K^{-1}\,mol^{-1}}$; $H_2(g)$ : $28.84\ \mathrm{J\,K^{-1}\,mol^{-1}}$; $O_2(g)$ : $29.37\ \mathrm{J\,K^{-1}\,mol^{-1}}$. 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 45 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

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(g)$$

so

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

It then follows that

$$\begin{aligned}\Delta_f H^{\ominus}(373\ \mathrm{K}) &= -241.82\ \mathrm{kJ\,mol^{-1}} + (75\ \mathrm{K}) \times (-9.94\ \mathrm{J\,K^{-1}\,mol^{-1}})\\ &= -242.6\ \mathrm{kJ\,mol^{-1}}\end{aligned}$$

**Self-test 2.8** Estimate the standard enthalpy of formation of liquid cyclohexane at 400 K from the data in Table 2.5 in the *Data section* at the end of this volume.

$[-163\ \mathrm{kJ\,mol^{-1}}]$

## Checklist of key ideas

☐ thermodynamics

**The basic concepts**

☐ system
☐ surroundings
☐ open system
☐ closed system
☐ isolated system

**2.1 Work, heat, and energy**

☐ work
☐ energy
☐ heat
☐ diathermic boundary
☐ adiabatic boundary
☐ exothermic processes
☐ endothermic processes
☐ the molecular interpretation of heat and work
☐ thermal motion

**2.2 The First Law**

☐ internal energy
☐ state function
☐ First Law of thermodynamics
☐ alternative statement of First Law
☐ definition of heat

**Work and heat**

**2.3 Expansion work**

☐ expansion work
☐ work defined
☐ free expansion
☐ expansion against constant pressure
☐ indicator diagram
☐ reversible change
☐ equilibrium
☐ work of reversible expansion (12)
☐ work of isothermal reversible expansion (13)
☐ maximum work and reversible change

**2.4 Heat transactions**

☐ internal energy change and heat transfer at constant volume
☐ adiabatic bomb calorimeter
☐ calorimeter constant
☐ heat capacity
☐ heat capacity at constant volume
☐ molar heat capacity at constant volume
☐ specific heat capacity
☐ internal energy change and temperature rise (22)

**2.5 Enthalpy**

☐ enthalpy
☐ enthalpy change and heat transfer at constant pressure
☐ relation between $\Delta U$ and $\Delta H$ (26)

- ☐ heat capacity at constant pressure
- ☐ molar heat capacity at constant pressure
- ☐ empirical temperature variation (30)
- ☐ relation between heat capacities (31)

**2.6 Adiabatic changes**

- ☐ work of adiabatic change
- ☐ temperature change accompanying adiabatic change
- ☐ heat capacity ratio
- ☐ pressure–volume relation for adiabatic change
- ☐ adiabat

**Thermochemistry**

- ☐ thermochemistry

**2.7 Standard enthalpy changes**

- ☐ standard enthalpy change
- ☐ standard state
- ☐ standard enthalpy of vaporization
- ☐ standard enthalpy of transition $(\Delta_{trs}H^{\ominus})$
- ☐ addition of enthalpy changes
- ☐ enthalpy change for reverse process
- ☐ standard reaction enthalpy $(\Delta_r H^{\ominus}_r)$
- ☐ thermochemical equation
- ☐ writing a chemical equation formally
- ☐ stoichiometric numbers
- ☐ standard enthalpy of combustion
- ☐ Hess's law

**2.8 Standard enthalpies of formation**

- ☐ standard enthalpy of formation $(\Delta_f H^{\ominus})$
- ☐ reference state
- ☐ combining enthalpies of formation
- ☐ mean bond enthalpy
- ☐ thermochemical group

**2.9 The temperature dependence of reaction enthalpies**

- ☐ Kirchhoff's law for the temperature dependence of reaction enthalpies

---

## Further reading

### Articles of general interest

E.A. Gislason and N.C. Craig, General definitions of work and heat in thermodynamic processes. *J. Chem. Educ.* **64**, 670 (1987).

E.R. Boyko and J.F. Belliveau, Simplification of some thermochemical equations. *J. Chem. Educ.* **67**, 743 (1990).

T. Solomon, Standard enthalpies of formation of ions in solution. *J. Chem. Educ.* **68**, 41 (1991).

R.S. Treptow, Bond energies and enthalpies: an often neglected difference. *J. Chem. Educ.* **72**, 497 (1995).

J. Güèmez, S. Velasco, and M.A. Matías, Thermal coefficients and heat capacities in systems with chemical reaction: the Le Chatelier–Braun principle. *J. Chem. Educ.* **72**, 199 (1995).

R.D. Freeman, Conversion of standard (1 atm) thermodynamic data to the new standard-state pressure, 1 bar ($10^5$ Pa). *Bull. Chem. Thermodynamics* **25**, 523 (1982).

I.H. Segel and L.D. Segel, Energetics of biological processes. In *Encyclopedia of applied physics* (ed. G.L. Trigg) **6**, 207. VCH, New York (1993).

### Texts and sources of data and information

B.W. Rossiter and R.C. Baetzgold (ed.), *Physical methods of chemistry*, **VI**. Wiley–Interscience, New York (1992).

M.L. McGlashan, *Chemical thermodynamics*. Academic Press, London (1979).

W.E. Dasent, *Inorganic energetics*. Cambridge University Press (1982).

D.A. Johnson, *Some thermodynamic aspects of inorganic chemistry*. Cambridge University Press (1982).

S.W. Benson, *Thermochemical kinetics*. Wiley, New York (1976).

J.D. Cox and G. Pilcher, *Thermochemistry of organic and organometallic compounds*. Academic Press, New York (1970).

D.R Stull, E.F. Westrum, and G.C. Sinke, *The chemical thermodynamics of organic compounds*. Wiley–Interscience, New York (1969).

D.B. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, I. Halow, S.M. Bailey, K.L. Churney, and R.L. Nuttall, *The NBS tables of chemical thermodynamic properties*. Published as *J. Phys. Chem. Reference Data* **11** (Supplement 2), 1982.

M.W. Chase, Jr, C.A. Davies, J.R. Downey, Jr, D.J. Frurip, R.A. McDonald, and A.N. Syverud, *JANAF thermochemical tables. The NBS tables of chemical thermodynamic properties*. Published as *J. Phys. Chem. Reference Data* **14** (Supplement 1), 1985.

J.B. Pedley, R.D. Naylor, and S.P. Kirby, *Thermochemical data of organic compounds*. Chapman & Hall, London (1986).

J.A. Dean (ed.), *Handbook of organic chemistry*. McGraw–Hill, New York (1987).

R.C. Weast (ed.), *Handbook of chemistry and physics*, Vol. 78. CRC Press, Boca Raton (1997).

A.M. James and M.P. Lord (ed.), *Macmillan's chemical and physical data*. Macmillan, London (1992).

J. Emsley, *The elements*. Oxford University Press (1996).

E.F.G. Harrington, Thermodynamic data and their uses. *Chemical thermodynamics: Specialist Periodical Reports*. **1**, 31 (1973).

D.R. Stull and G.C. Sinke, *Thermodynamic properties of the elements*. American Chemical Society, Washington (1956).

CODATA Bulletin 28: Recommended key values of thermodynamics. *J. Chem. Thermo.* **10**, 903 (1978).

## Exercises

Assume all gases are perfect unless stated otherwise. Note that 1 bar = 1.01325 atm exactly. Unless otherwise stated, thermochemical data are for 298.15 K.

**2.1 (a)** Calculate the work done to raise a mass of 1.0 kg through 10 m on the surface of (a) the Earth ($g = 9.81\ \mathrm{m\,s^{-2}}$) and (b) the moon ($g = 1.60\ \mathrm{m\,s^{-2}}$).

**2.1 (b)** Calculate the work done to raise a mass of 5.0 kg through 100 m on the surface of (a) the Earth ($g = 9.81\ \mathrm{m\,s^{-2}}$) and (b) Mars ($g = 3.73\ \mathrm{m\,s^{-2}}$).

**2.2 (a)** Calculate the work needed for a 65 kg person to climb through 4.0 m on the surface of the Earth.

**2.2 (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.

**2.3 (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.

**2.3 (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.

**2.4 (a)** A sample consisting of 1.00 mol Ar is expanded isothermally at 0°C from 22.4 L to 44.8 L (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 $q$, $w$, $\Delta U$, and $\Delta H$.

**2.4 (b)** A sample consisting of 2.00 mol He is expanded isothermally at 22°C from 22.8 L to 31.7 L (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 $q$, $w$, $\Delta U$, and $\Delta H$.

**2.5 (a)** A sample consisting of 1.00 mol of monatomic perfect gas, 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, $\Delta U$, $q$, and $w$.

**2.5 (b)** A sample consisting of 2.00 mol of a perfect gas, 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, $\Delta U$, $q$, and $w$.

**2.6 (a)** A sample of 4.50 g of methane gas occupies 12.7 L 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 L. (b) Calculate the work that would be done if the same expansion occurred reversibly.

**2.6 (b)** A sample of argon of mass 6.56 g occupies 18.5 L 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 L. (b) Calculate the work that would be done if the same expansion occurred reversibly.

**2.7 (a)** In the isothermal reversible compression of 52.0 mmol of a perfect gas at 260 K, the volume of the gas is reduced to one-third its initial value. Calculate $w$ for this process.

**2.7 (b)** In the isothermal reversible compression of 1.77 mmol of a perfect gas at 273 K, the volume of the gas is reduced to 0.224 of its initial value. Calculate $w$ for this process.

**2.8 (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 $w$, $q$, $\Delta U$, and $\Delta H$ for this process.

**2.8 (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 $w$, $q$, $\Delta U$, and $\Delta H$ for this process.

**2.9 (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.

**2.9 (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.

**2.10 (a)** Calculate the heat required to melt 750 kg of sodium metal at 371 K.

**2.10 (b)** Calculate the heat required to melt 500 kg of potassium metal at 336 K. The enthalpy of fusion of potassium is 2.40 kJ mol$^{-1}$.

**2.11 (a)** The value of $C_{p,\mathrm{m}}$ for a sample of a perfect gas was found to vary with temperature according to the expression $C_{p,\mathrm{m}}/(\mathrm{J\,K^{-1}}) = 20.17 + 0.3665(T/\mathrm{K})$. Calculate $q$, $w$, $\Delta U$, and $\Delta H$ for 1.00 mol when the temperature of 1.00 mol of gas is raised from 25°C to 200°C (a) at constant pressure, (b) at constant volume.

**2.11 (b)** The constant-pressure heat capacity of a sample of a perfect gas was found to vary with temperature according to the expression $C_{p,\mathrm{m}}/(\mathrm{J\,K^{-1}}) = 20.17 + 0.4001(T/\mathrm{K})$. Calculate $q$, $w$, $\Delta U$, and $\Delta H$ for 1.00 mol when the temperature of 1.00 mol of gas is raised from 0°C to 100°C (a) at constant pressure, (b) at constant volume.

**2.12 (a)** Calculate the final temperature of a sample of argon of mass 12.0 g that is expanded reversibly and adiabatically from 1.0 L at 273.15 K to 3.0 L.

**2.12 (b)** Calculate the final temperature of a sample of carbon dioxide of mass 16.0 g that is expanded reversibly and adiabatically from 500 mL at 298.15 K to 2.00 L.

**2.13 (a)** A sample of carbon dioxide of mass 2.45 g at 27.0°C is allowed to expand reversibly and adiabatically from 500 mL to 3.00 L. What is the work done by the gas?

**2.13 (b)** A sample of nitrogen of mass 3.12 g at 23.0°C is allowed to expand reversibly and adiabatically from 400 mL to 2.00 L. What is the work done by the gas?

**2.14 (a)** Calculate the final pressure of a sample of carbon dioxide that expands reversibly and adiabatically from 57.4 kPa and 1.0 L to a final volume of 2.0 L. Take $\gamma = 1.4$.

**2.14 (b)** Calculate the final pressure of a sample of water vapour that expands reversibly and adiabatically from 87.3 Torr and 500 mL to a final volume of 3.0 L. Take $\gamma = 1.3$.

**2.15 (a)** Calculate the final pressure of a sample of carbon dioxide of mass 2.4 g that expands reversibly and adiabatically from an initial temperature of 278 K and volume 1.0 L to a final volume of 2.0 L. Take $\gamma = 1.4$.

**2.15 (b)** Calculate the final pressure of a sample of water vapour of mass 1.4 g that expands reversibly and adiabatically from an initial temperature of 300 K and volume 1.0 L to a final volume of 3.0 L. Take $\gamma = 1.3$.

**2.16 (a)** Calculate the standard enthalpy of formation of butane at 25°C from its standard enthalpy of combustion.

**2.16 (b)** Calculate the standard enthalpy of formation of hexane at 25°C from its standard enthalpy of combustion.

**2.17 (a)** When 229 J of energy is supplied as heat at constant pressure 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.

**2.17 (b)** When 178 J of energy is supplied as heat at constant pressure to 1.9 mol of a gas, the temperature of the sample increases by 1.78 K. Calculate the molar heat capacities at constant volume and constant pressure of the gas.

**2.18 (a)** A sample of a liquid of mass 25 g is cooled from 290 K to 275 K at constant pressure by the extraction of 1.2 kJ of energy as heat. Calculate $q$ and $\Delta H$ and estimate the heat capacity of the sample.

**2.18 (b)** A sample of a liquid of mass 30.5 g is cooled from 288 K to 275 K at constant pressure by the extraction of 2.3 kJ of energy as heat. Calculate $q$ and $\Delta H$ and estimate the heat capacity of the sample.

**2.19 (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 $\mathrm{J\,K^{-1}\,mol^{-1}}$, calculate $q$, $\Delta H$, and $\Delta U$.

**2.19 (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 $\mathrm{J\,K^{-1}\,mol^{-1}}$, calculate $q$, $\Delta H$, and $\Delta U$.

**2.20 (a)** A sample of 4.0 mol $O_2$ is originally confined in 20 L 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 $q$, $w$, $\Delta T$, $\Delta U$, and $\Delta H$. (The final pressure of the gas is not necessarily 600 Torr.)

**2.20 (b)** A sample of 5.0 mol $CO_2$ is originally confined in 15 L 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 $q$, $w$, $\Delta T$, $\Delta U$, and $\Delta H$. (The final pressure of the gas is not necessarily 78.5 kPa.)

**2.21 (a)** A sample consisting of 3.0 mol of perfect gas at 200 K and 2.00 atm is compressed reversibly and adiabatically until the temperature reaches 250 K. Given that its molar constant-volume heat capacity is 27.5 $\mathrm{J\,K^{-1}\,mol^{-1}}$, calculate $q$, $w$, $\Delta U$, $\Delta H$, and the final pressure and volume.

**2.21 (b)** A sample consisting of 2.5 mol of perfect gas at 220 K and 200 kPa is compressed reversibly and adiabatically until the temperature reaches 255 K. Given that its molar constant-volume heat capacity is 27.6 $\mathrm{J\,K^{-1}\,mol^{-1}}$, calculate $q$, $w$, $\Delta U$, $\Delta H$, and the final pressure and volume.

**2.22 (a)** A sample consisting of 1.0 mol of perfect gas with $C_V = 20.8\ \mathrm{J\,K^{-1}}$ 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.

**2.22 (b)** A sample consisting of 1.5 mol of perfect gas with $C_{p,\mathrm{m}} = 20.8\ \mathrm{J\,K^{-1}\,mol^{-1}}$ 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.

**2.23 (a)** Estimate the change in volume that occurs when a sample of mercury of volume 1.0 $\mathrm{cm^3}$ is heated through 5.0 K at room temperature.

**2.23 (b)** Estimate the change in volume that occurs when a sample of iron of volume 5.0 $\mathrm{cm^3}$ is heated through 10.0 K at room temperature.

**2.24 (a)** Consider a system consisting of 2.0 mol $CO_2$ (assumed to be a perfect gas) at 25°C confined to a cylinder of cross-section 10 $\mathrm{cm^2}$ at 10 atm. The gas is allowed to expand adiabatically and irreversibly against a constant pressure of 1.0 atm. Calculate $w$, $q$, $\Delta U$, $\Delta H$, and $\Delta T$ when the piston has moved 20 cm.

**2.24 (b)** Consider a system consisting of 3.0 mol $O_2$ (assumed to be a perfect gas) at 25°C confined to a cylinder of cross-section 22 $\mathrm{cm^2}$ at 820 kPa. The gas is allowed to expand adiabatically and irreversibly against a constant pressure of 110 kPa. Calculate $w$, $q$, $\Delta U$, $\Delta H$, and $\Delta T$ when the piston has moved 15 cm.

**2.25 (a)** A sample consisting of 65.0 g of xenon is confined in a container at 2.00 atm and 298 K and then allowed to expand adiabatically (a) reversibly to 1.00 atm, (b) against a constant pressure of 1.00 atm. Calculate the final temperature in each case.

**2.25 (b)** A sample consisting of 15.0 g of nitrogen is confined in a container at 220 kPa and 200 K and then allowed to expand adiabatically (a) reversibly to 110 kPa, (b) against a constant pressure of 110 kPa. Calculate the final temperature in each case.

**2.26 (a)** A certain liquid has $\Delta_{\mathrm{vap}}H^{\ominus} = 26.0\ \mathrm{kJ\,mol^{-1}}$. Calculate $q$, $w$, $\Delta H$, and $\Delta U$ when 0.50 mol is vaporized at 250 K and 750 Torr.

**2.26 (b)** A certain liquid has $\Delta_{\mathrm{vap}}H^{\ominus} = 32.0\ \mathrm{kJ\,mol^{-1}}$. Calculate $q$, $w$, $\Delta H$, and $\Delta U$ when 0.75 mol is vaporized at 260 K and 765 Torr.

**2.27 (a)** The standard enthalpy of formation of ethylbenzene is $-12.5\ \mathrm{kJ\,mol^{-1}}$. Calculate its standard enthalpy of combustion.

**2.27 (b)** The standard enthalpy of formation of phenol is $-165.0\ \mathrm{kJ\,mol^{-1}}$. Calculate its standard enthalpy of combustion.

**2.28 (a)** Calculate the standard enthalpy of hydrogenation of 1-hexene to hexane given that the standard enthalpy of combustion of 1-hexene is $-4003\ \text{kJ mol}^{-1}$.

**2.28 (b)** Calculate the standard enthalpy of hydrogenation of 1-butene to butane given that the standard enthalpy of combustion of 1-butene is $-2717\ \text{kJ mol}^{-1}$.

**2.29 (a)** The standard enthalpy of combustion of cyclopropane is $-2091\ \text{kJ mol}^{-1}$ 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 $+20.42\ \text{kJ mol}^{-1}$. Calculate the enthalpy of isomerization of cyclopropane to propene.

**2.29 (b)** From the following data, determine $\Delta_f H^{\ominus}$ for diborane, $B_2H_6(g)$, at 298 K:

(1) $B_2H_6(g) + 3O_2(g) \longrightarrow B_2O_3(s) + 3H_2O(g)$ $\quad \Delta_r H^{\ominus} = -1941\ \text{kJ mol}^{-1}$

(2) $2B(s) + \frac{3}{2}O_2(g) \longrightarrow B_2O_3(s)$ $\quad \Delta_r H^{\ominus} = -2368\ \text{kJ mol}^{-1}$

(3) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$ $\quad \Delta_r H^{\ominus} = -241.8\ \text{kJ mol}^{-1}$

**2.30 (a)** Calculate the standard internal energy of formation of liquid methyl acetate from its standard enthalpy of formation, which is $-442\ \text{kJ mol}^{-1}$.

**2.30 (b)** Calculate the standard internal energy of formation of urea from its standard enthalpy of formation, which is $-333.51\ \text{kJ mol}^{-1}$.

**2.31 (a)** The temperature of a bomb calorimeter rose by 1.617 K when a current of 3.20 A was passed for 27.0 s from a 12.0 V source. Calculate the calorimeter constant.

**2.31 (b)** The temperature of a bomb calorimeter rose by 1.712 K when a current of 2.86 A was passed for 22.5 s from a 12.0 V source. Calculate the calorimeter constant.

**2.32 (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 100 mg of phenol, $C_6H_5OH(s)$, is burned in the calorimeter under the same conditions?

**2.32 (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?

**2.33 (a)** When 0.3212 g of glucose was burned in a bomb calorimeter of calorimeter constant $641\ \text{J K}^{-1}$ the temperature rose by 7.793 K. Calculate (a) the standard molar enthalpy of combustion, (b) the standard internal energy of combustion, and (c) the standard enthalpy of formation of glucose.

**2.33 (b)** When 0.2715 g of fructose was burned in a bomb calorimeter of calorimeter constant $437\ \text{J K}^{-1}$ the temperature rose by 9.69 K. Calculate (a) the standard molar enthalpy of combustion, (b) the standard internal energy of combustion, and (c) the standard enthalpy of formation of fructose.

**2.34 (a)** Calculate the standard enthalpy of solution of AgCl(s) in water from the enthalpies of formation of the solid and the aqueous ions.

**2.34 (b)** Calculate the standard enthalpy of solution of AgBr(s) in water from the enthalpies of formation of the solid and the aqueous ions.

**2.35 (a)** The standard enthalpy of decomposition of the yellow complex $H_3NSO_2$ into $NH_3$ and $SO_2$ is $+40\ \text{kJ mol}^{-1}$. Calculate the standard enthalpy of formation of $H_3NSO_2$.

**2.35 (b)** Given that the standard enthalpy of combustion of graphite is $-393.51\ \text{kJ mol}^{-1}$ and that of diamond is $-395.41\ \text{kJ mol}^{-1}$, calculate the enthalpy of the graphite → diamond transition.

**2.36 (a)** The mass of a typical (sucrose) sugar cube is 1.5 g. Calculate the energy released as heat when a cube is burned in air. To what height could a 65 kg person climb on the energy a cube provides assuming 25 per cent of the energy is available for work?

**2.36 (b)** The mass of a typical glucose tablet is 2.5 g. Calculate the energy released as heat when a tablet is burned in air. To what height could a 65 kg person climb on the energy a cube provides assuming 25 per cent of the energy is available for work?

**2.37 (a)** The standard enthalpy of combustion of propane gas is $-2220\ \text{kJ mol}^{-1}$ and the standard enthalpy of vaporization of propane liquid is $+15\ \text{kJ mol}^{-1}$. Calculate (a) the standard enthalpy and (b) the standard internal energy of combustion of liquid propane.

**2.37 (b)** The standard enthalpy of combustion of butane gas is $-2878\ \text{kJ mol}^{-1}$ and the standard enthalpy of vaporization of butane liquid is $+21.0\ \text{kJ mol}^{-1}$. Calculate (a) the standard enthalpy and (b) the standard internal energy of combustion of liquid butane.

**2.38 (a)** Express the following reactions in the form $0 = \sum_J \nu_J J$, identify the stoichiometric numbers, and classify the reactions as exothermic or endothermic.

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

(b) $2C(s) + H_2(g) \longrightarrow C_2H_2(g)$ $\quad \Delta_r H^{\ominus} = +227\ \text{kJ mol}^{-1}$

(c) $NaCl(s) \longrightarrow NaCl(aq)$ $\quad \Delta_r H^{\ominus} = +3.9\ \text{kJ mol}^{-1}$

**2.38 (b)** Express the following reactions in the form $0 = \sum_J \nu_J J$, identify the stoichiometric numbers, and classify the reactions as exothermic or endothermic.

(a) $C(s, \text{diamond}) \longrightarrow C(s, \text{graphite})$ $\quad \Delta_r H^{\ominus} = -1.9\ \text{kJ mol}^{-1}$

(b) $Fe_3O_4(s) + CO(g) \longrightarrow 3FeO(s) + CO_2(g)$ $\quad \Delta_r H^{\ominus} = +35.9\ \text{kJ mol}^{-1}$

(c) $3FeO(s) + CO_2(g) \longrightarrow Fe_3O_4(s) + CO(g)$ $\quad \Delta_r H^{\ominus} = -35.9\ \text{kJ mol}^{-1}$

**2.39 (a)** Use standard enthalpies of formation to calculate the standard enthalpies of the following reactions:

(a) $2NO_2(g) \longrightarrow N_2O_4(g)$

(b) $NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$

**2.39 (b)** Use standard enthalpies of formation to calculate the standard enthalpies of the following reactions:

(a) Cyclopropane(g) ⟶ propene(g)

(b) $HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$

**2.40 (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. Assume all gases are perfect.

(1) $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$ $\quad \Delta_r H^\ominus = -184.62\ \text{kJ mol}^{-1}$
(2) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$ $\quad \Delta_r H^\ominus = -483.64\ \text{kJ mol}^{-1}$
(3) $4HCl(g) + O_2(g) \longrightarrow Cl_2(g) + 2H_2O(g)$

**2.40 (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 HI(g) and $H_2O(g)$ all at 298 K. Assume all gases are perfect.

(1) $H_2(g) + I_2(s) \longrightarrow 2HI(g)$ $\quad \Delta_r H^\ominus = +52.96\ \text{kJ mol}^{-1}$
(2) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$ $\quad \Delta_r H^\ominus = -483.64\ \text{kJ mol}^{-1}$
(3) $4HI(g) + O_2(g) \longrightarrow I_2(s) + 2H_2O(g)$

**2.41 (a)** For the reaction $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$, $\Delta_r U^\ominus = -1373\ \text{kJ mol}^{-1}$ at 298 K. Calculate $\Delta_r H^\ominus$.

**2.41 (b)** For the reaction $2C_6H_5COOH(s) + 13O_2(g) \rightarrow 12CO_2(g) + 6H_2O(g)$, $\Delta_r U^\ominus = -772.7\ \text{kJ mol}^{-1}$ at 298 K. Calculate $\Delta_r H^\ominus$.

**2.42 (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:

$2KClO_3(s) \longrightarrow 2KCl(s) + 3O_2(g)$ $\quad \Delta_r H^\ominus = -89.4\ \text{kJ mol}^{-1}$
$NaOH(s) + CO_2(g) \longrightarrow NaCO_3(s)$ $\quad \Delta_r H^\ominus = -127.5\ \text{kJ mol}^{-1}$

**2.42 (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:

$2NOCl(g) \longrightarrow 2NO(g) + Cl_2(g)$ $\quad \Delta_r H^\ominus = +75.5\ \text{kJ mol}^{-1}$

**2.43 (a)** Use the information in Table 2.5 to predict the standard reaction enthalpy of $2NO_2(g) \rightarrow N_2O_4(g)$ at 100°C from its value at 25°C.

**2.43 (b)** Use the information in Table 2.5 to predict the standard reaction enthalpy of $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ at 100°C from its value at 25°C.

**2.44 (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.

**2.44 (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 2.6. Assume the heat capacities to be constant over the temperature range involved.

**2.45 (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 $Cl^-(g)$, $-383.7\ \text{kJ mol}^{-1}$.

**2.45 (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 $Br^-(g)$, $-337\ \text{kJ mol}^{-1}$.

**2.46 (a)** Use the thermochemical groups in Table 2.7 to estimate the standard enthalpy of formation in the gas phase of (a) cyclohexane, (b) 2,4-dimethylhexane.

**2.46 (b)** Use the thermochemical groups in Table 2.7 to estimate the standard enthalpy of formation of gaseous (a) 2,2,4-trimethylpentane, (b) 2,2-dimethylpropane.

# 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** Calculate the heat needed to raise the temperature of the air in a house from 20°C to 25°C. Assume that the house contains 600 m$^3$ of air, which should be taken to be a perfect diatomic gas. The density of air is $1.21\ \text{kg m}^{-3}$ at 20°C. Calculate $\Delta U$ and $\Delta H$ for the heating of the air.

**2.2** 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?

**2.3** Consider a perfect gas contained in a cylinder and separated by a frictionless adiabatic piston into two sections, A and B; Section B is in contact with a water bath that maintains it at constant temperature. Initially $T_A = T_B = 300$ K, $V_A = V_B = 2.00$ L, and $n_A = n_B = 2.00$ mol. Heat is supplied to Section A and the piston moves to the right reversibly until the final volume of Section B is 1.00 L. Calculate (a) the work done by the gas in Section A, (b) $\Delta U$ for the gas in Section B, (c) $q$ for the gas in B, (d) $\Delta U$ for the gas in A, and (e) $q$ for the gas in A. Assume $C_{V,m} = 20.0\ \text{J K}^{-1}\ \text{mol}^{-1}$.

**2.4** A sample consisting of 1 mol of a monatomic perfect gas (for which $C_{V,m} = \frac{3}{2}R$) is taken through the cycle shown in Fig. 2.20. (a) Determine the temperature at 1,2, and 3. (b) Calculate $q$, $w$, $\Delta U$, and $\Delta H$ 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.

**2.5** A 5.0 g block of solid carbon dioxide is allowed to evaporate in a vessel of volume 100 cm$^3$ maintained at 25°C. Calculate the work done when the system expands (a) isothermally against a pressure of

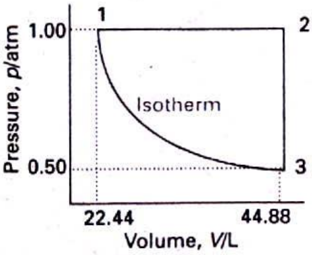


Fig. 2.20

1.0 atm, and (b) isothermally and reversibly to the same volume as in (a).

**2.6** 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 which 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 were open to the atmosphere?

**2.7** A new fluorocarbon of molar mass 102 $g\,mol^{-1}$ was placed in an electrically heated vessel. When the pressure was 650 Torr, the liquid boiled at 78°C. After the boiling point had been reached, it was found that a current of 0.232 A from a 12.0 V supply passed for 650 s vaporized 1.871 g of the sample. Calculate the (molar) enthalpy and internal energy of vaporization.

**2.8** An object is cooled by the evaporation of liquid methane at its normal boiling point (112 K). What volume of gas at 1.00 atm pressure must be formed from the liquid in order to remove 32.5 kJ of energy as heat from the object?

**2.9** The molar heat capacity of ethane is represented in the temperature range 298 K to 400 K by the empirical expression $C_{p,m}/(J\,K^{-1}\,mol^{-1}) = 14.73 + 0.1272(T/K)$. 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.

**2.10** 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 $-3251\ kJ\,mol^{-1}$, gave a temperature rise of 1.940 K. Calculate the internal energy of combustion of D-ribose and its enthalpy of formation.

**2.11** The standard enthalpy of formation of the metallocene bis-(benzene)chromium was measured in a calorimeter. It was found for the reaction $Cr(C_6H_6)_2(s) \rightarrow Cr(s) + 2C_6H_6(g)$ that $\Delta_r U^\ominus(583\ K) = +8.0\ kJ\,mol^{-1}$. 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 140 $J\,K^{-1}\,mol^{-1}$ in its liquid range and 28 $J\,K^{-1}\,mol^{-1}$ as a gas.

**2.12** The standard enthalpy of combustion of sucrose is $-5645\ kJ\,mol^{-1}$. What is the advantage (in kilojoules per mole of energy released as heat) of complete aerobic oxidation compared with anaerobic hydrolysis of sucrose to lactic acid?

## Theoretical problems

**2.13** With reference to Fig. 2.21, and assuming perfect gas behaviour, calculate: (a) the amount of gas molecules (in moles) in this system and its volume in states B and C, (b) the work done on the gas along the paths ACB and ADB, (c) the work done on the gas along the isotherm AB, (d) $q$ and $\Delta U$ for each of the three paths. Take $C_{V,m} = \frac{3}{2}R$ and $T = 313$ K.

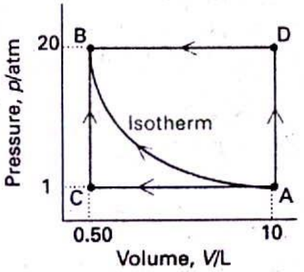


Fig. 2.21

**2.14** When a system is taken from state A to state B along the path ACB in Fig. 2.22, 80 J of heat flows into the system and the system does 30 J of work. (a) How much heat flows into the system along path ADB if the work done is 10 J? (b) When the system is returned from state B to A along the curved path, the work done on the system is 20 J. Does the system absorb or liberate heat, and how much? (c) If $U_D - U_A = +40$ J, find the heat absorbed in the processes AD and DB.

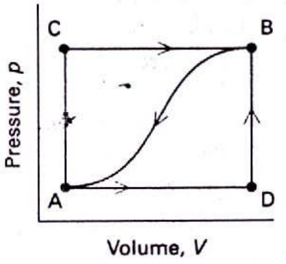


Fig. 2.22

**2.15** Show that the value of $\Delta H$ for the adiabatic expansion of a perfect gas may be calculated by integration of $dH = V\,dp$, and evaluate the integral for reversible adiabatic expansion.

**2.16** 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 $xV_c$.

## Additional problems supplied by Carmen Giunta and Charles Trapp

**2.17** Since their discovery in 1985, fullerenes have received the attention of many chemical researchers. Kolesov *et al.* have recently 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 $\Delta_c H^\ominus$ and $\Delta_f H^\ominus$ of $C_{60}$.

**2.18** 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) $DyCl_3(s) \longrightarrow DyCl_3(aq, \text{in } 4.0\ \mathrm{M\,HCl})$
$\Delta_r H^\ominus = -180.06\ \mathrm{kJ\,mol^{-1}}$

(2-
) $Dy(s) + 3HCl(aq, 4.0\ \mathrm{M}) \longrightarrow DyCl_3(aq, \text{in } 4.0\ \mathrm{M\,HCl}) + \frac{3}{2}H_2(g)$
$\Delta_r H^\ominus = -699.43\ \mathrm{kJ\,mol^{-1}}$

(3) $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow HCl(aq, 4.0\ \mathrm{M})$
$\Delta_r H^\ominus = -158.31\ \mathrm{kJ\,mol^{-1}}$

Determine $\Delta_f H^\ominus(DyCl_3, s)$ from these data.

**2.19** 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 which is applicable to studies of pyrolysis and the 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*-$C_4H_9 \longrightarrow$ *sec*-$C_4H_9$, (b) *tert*-$C_4H_9 \longrightarrow C_3H_6 + CH_3$, (c) *tert*-$C_4H_9 \longrightarrow C_2H_4 + C_2H_5$.

| 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 |

**2.20** Alkyl radicals are important intermediates in the combustion and atmospheric chemistry of hydrocarbons. N. Cohen has reported group additivity tables for the thermochemistry of alkyl radicals in the gas phase (N. Cohen, *J. Phys. Chem.* **96**, 9052 (1992)). He suggests computing enthalpies of formation based on the following bond-dissociation energies ($\Delta U^\ominus$) for C–H bonds: primary (–(H)C(H)–H), $420.5\ \mathrm{kJ\,mol^{-1}}$; secondary (–(C)C(H)–H), $410.5\ \mathrm{kJ\,mol^{-1}}$; tertiary (–(C)C(C)–H), $398.3\ \mathrm{kJ\,mol^{-1}}$. Estimate $\Delta_f H^\ominus$ of (a) $C_2H_5$, (b) *sec*-$C_4H_9$, and (c) *tert*-$C_4H_9$. ($\Delta_f H^\ominus$(2-methylpropane, g) $= -134.2\ \mathrm{kJ\,mol^{-1}}$.)

**2.21** 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* (1995)), compute the standard enthalpies of the following reactions:

(a) $SiH_4(g) \longrightarrow SiH_2(g) + H_2(g)$

(b) $Si_2H_6(g) \longrightarrow SiH_2(g) + SiH_4(g)$

**2.22** 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. Darling and Schlegel (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) $SiH_4(g) + \frac{1}{2}O_2(g) \longrightarrow SiH_3OH(g)$

(b) $SiH_4(g) + O_2(g) \longrightarrow SiH_2O(g) + H_2O(l)$

(c) $SiH_3OH(g) \longrightarrow SiH_2O(g) + H_2(g)$

Note that $\Delta_f H^\ominus(SiH_4, g) = +34.3\ \mathrm{kJ\,mol^{-1}}$ (*CRC Handbook* (1995)).

**2.23** *Polytropic processes* are defined as those that satisfy the condition $pV^n = C$, where $C$ is a constant. In one experiment, 1.00 mol of 'air molecules' is compressed from 1.00 bar to 10.0 bar at 25°C by two different combinations of reversible polytropic processes: (1) heating at constant volume to the final pressure, followed by cooling at constant pressure, (2) adiabatic compression to the final volume, followed by cooling at constant volume. (a) Sketch these processes on a $pV$ diagram and identify the value of $n$ for each step in each process. (b) Calculate $q$, $w$, $\Delta U$, and $\Delta H$ for each step in the processes and for the overall process. Note that the overall process can be accomplished in one isothermal reversible step. Assume air is a perfect diatomic gas with $C_{p,\mathrm{m}} = \frac{7}{2}R$.

**2.24** For reversible polytropic processes described by the general relation $pV^n = C$, derive the following expressions for work and heat

$$w = \frac{RT_1}{n-1}\left\{\left(\frac{p_2}{p_1}\right)^{(n-1)/n} - 1\right\}$$

$$q = \frac{(n-\gamma)RT_1}{(n-1)(\gamma-1)}\left\{\left(\frac{p_2}{p_1}\right)^{(n-1)/n} - 1\right\}$$

Show that these expressions reduce to already familiar expressions for $n = 0, 1, \gamma$, and $\infty$.

**2.25** From the enthalpy of combustion data in Table 2.5 for the alkanes methane through octane, test the extent to which the relation $\Delta_c H^\ominus = k(M/\mathrm{g\,mol^{-1}})^n$ holds and find the numerical values for $k$ and $n$. Predict $\Delta_c H^\ominus$ for decane and compare to the known value.

**2.26** Ammonia is compressed in a piston-cylinder apparatus from an initial state of 30°C and 500 kPa to a final pressure of 1400 kPa. The following data were obtained during the process.

| $p$/kPa | 500 | 653 | 802 | 945 | 1100 | 1248 | 1400 |
|---|---|---|---|---|---|---|---|
| $V$/L | 1.25 | 1.08 | 0.96 | 0.84 | 0.72 | 0.60 | 0.50 |

(a) Is this a polytropic process? (See Problem 2.23 for the definition of a polytropic process.) If so, what is $n$? (b) Calculate the work done on the ammonia. (c) What is the final temperature?

# 3

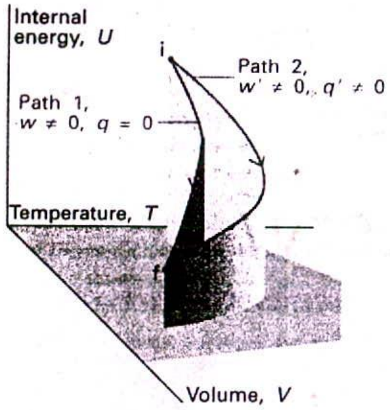
# The First Law: the machinery

*In this chapter we begin to unfold some of the power of thermodynamics by showing how to establish relations between different properties of a system. The procedure we use is based on the experimental fact that the internal energy and the enthalpy are state functions, and we derive a number of relations between observables by exploring the mathematical consequences of these facts. 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 a quantitative relation between the heat capacities of a substance at constant pressure and constant volume.*

We saw in Section 2.2 that properties that are independent of how a sample is prepared are called **state functions**. Such properties can be regarded as functions of variables, such as pressure and temperature, that define the current state of the system. 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. Properties that relate to the preparation of the state are called **path functions**. Examples of path functions are the work that is done in preparing a state and the energy transferred as heat. 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, not to the current state itself.

## State functions and exact differentials

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.



3.1 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 $\Delta U$.

## 3.1 State functions

Consider a system undergoing the changes depicted in Fig. 3.1. 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 but in which the expansion is not adiabatic. The internal energies 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 introduced 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.

### (a) Exact and inexact differentials

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:

$$\Delta U = \int_i^f \mathrm{d}U \tag{1}$$

The value of $\Delta U$ 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 which, 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:

$$q = \int_{i,\,\text{path}}^{f} \mathrm{d}q \tag{2}$$

Notice the difference between this equation and eqn 1. First, we do not write $\Delta q$, because $q$ is not a state function and the energy supplied as heat cannot be expressed as $q_f - q_i$. Secondly, it is necessary to 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 $\text{đ}q$ to emphasize that it is inexact.

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, it is different if the change takes place adiabatically from if it takes place nonadiabatically. It follows that $\mathrm{d}w$ is an inexact differential. It is often written $\text{đ}w$.

### Example 3.1 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 $\Delta U$ 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. Because the internal energy of a perfect gas arises only from the kinetic energy of its molecules, it is independent of volume; therefore, 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. We derived a number of expressions for the work done in a variety of processes in Chapter 2, 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 2.13, so $w = -nRT \ln(V_f/V_i)$ and consequently $q = nRT \ln(V_f/V_i)$.

**Self-test 3.1** Calculate the values of $q$, $w$, and $\Delta U$ for an irreversible isothermal expansion of a perfect gas against a constant nonzero external pressure.

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

## (b) Changes in internal energy

We shall now begin to unfold the consequences of $dU$ being an exact differential by noting that, for a closed system of constant composition (the only type of system considered in this chapter), $U$ is a function of volume and temperature.[1] 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[2] of $U$ with respect to $V$. If, instead, $T$ changes to $T + dT$ at constant volume, the internal energy changes to

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

Now suppose that $V$ and $T$ both change infinitesimally. The new internal energy, neglecting second-order infinitesimals (those proportional to $dVdT$), is

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

As a result of the infinitesimal changes in conditions, the internal energy $U'$ differs from $U$ by the infinitesimal amount $dU$. Therefore, from the last equation we obtain the very important result that

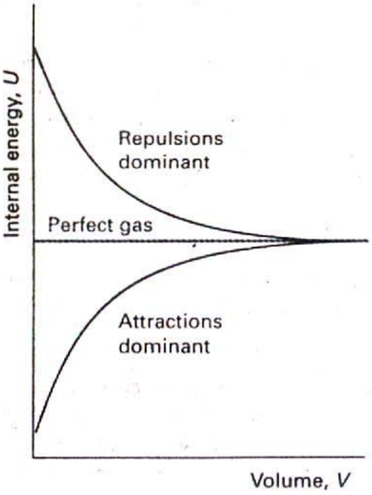
$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT \qquad (3)$$

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 partial derivatives.

---

[1] $U$ could be regarded as a function of $V$, $T$, and $p$ but, because there is an equation of state, it is possible to express $p$ in terms of $V$ and $T$, so $p$ is not an independent variable. We could have chosen $p$, $T$ or $p$, $V$ as independent variables, but $V$, $T$ fit our purpose.

[2] Partial derivatives are reviewed in *Further information 1*.



3.2 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 further apart on average. If repulsions are dominant, the internal energy decreases as the gas expands.

In every case, a partial derivative is the slope of a graph of the property of interest against *one* of the variables on which it depends (recall Fig. 2.12), all the other variables being held constant. In many cases the slopes have a straightforward physical interpretation, and thermodynamics gets shapeless and difficult only when that meaning is not kept in sight. In the present case, we have already met $(\partial U/\partial T)_V$ in eqn 2.19, where we saw that it is the constant-volume heat capacity, $C_V$. Therefore, we can write

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + C_V\, dT \qquad (4)$$

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 the volume it occupies is changed at constant temperature. We shall denote it $\pi_T$ (because it has the same dimensions as pressure), and call it the **internal pressure**:

$$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T \qquad [5]$$

We shall see that the internal pressure is a measure of the strength of the cohesive forces in the sample. Then

$$dU = \pi_T\, dV + C_V\, dT \qquad (6)$$

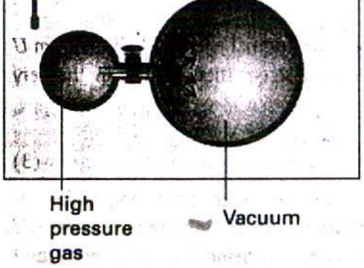
If the internal energy increases ($dU > 0$) as the volume of the sample expands isothermally ($dV > 0$), which is the case when there are attractive forces between the particles, a graph of internal energy against volume slopes upwards and $\pi_T > 0$ (Fig. 3.2). When there are no interactions between the molecules, the internal energy is independent of their separation and hence independent of the volume the sample occupies; hence $\pi_T = 0$ for a perfect gas. 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 $pV = nRT$.

## (c) The Joule experiment

James Joule thought that he could measure $\pi_T$ 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. 3.3). 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.

The thermodynamic implications of the experiment are as follows. No work was done in the expansion into a vacuum, so $w = 0$. No heat entered or left the system (the gas) 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. His experiment was on a par with Boyle's: he extracted an essential limiting property of a gas, a property of a perfect gas, without detecting the small deviations characteristic of real gases.



3.3 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.

### Illustration

For ammonia, $\pi_T = 840$ Pa at 300 K and 1.0 bar, and $C_{V,m} = 27.32\ \mathrm{J\,K^{-1}\,mol^{-1}}$. The change in molar internal energy of ammonia when it is heated through 2.0 K and compressed through 100 $\mathrm{cm}^3$ is approximately

$$\begin{aligned}\Delta U_{\mathrm{m}} &\approx (840\ \mathrm{J\,m^{-3}\,mol^{-1}}) \times (-100 \times 10^{-6}\ \mathrm{m^3}) \\ &\quad + (27.32\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (2.0\ \mathrm{K}) \\ &\approx -0.084\ \mathrm{J\,mol^{-1}} + 55\ \mathrm{J\,mol^{-1}} = +55\ \mathrm{J\,mol^{-1}}\end{aligned}$$

Note that the contribution of the heating term greatly dominates that of the compression term for this gas.

### (d) Changes in internal energy at constant pressure

Partial derivatives have many useful properties and some that we shall draw on frequently are reviewed in *Further information 1.* 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 6 by $dT$ and impose the condition of constant pressure on the resulting differentials, so that $dU/dT$ 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 differential coefficient on the right in this expression is the slope of the plot of volume against temperature (at constant pressure). This property is normally tabulated as the **expansion coefficient**, $\alpha$, of a substance,[3] which is defined as

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \qquad [7]$$

A large value of $\alpha$ means that the volume of the sample responds strongly to changes in temperature. Some experimental values are given in Table 3.1.

**Table 3.1*** Expansion coefficients ($\alpha$) and isothermal compressibilities ($\kappa_T$)

| Substance | $\alpha/(10^{-4}\,\mathrm{K^{-1}})$ | $\kappa_T/(10^{-6}\,\mathrm{atm^{-1}})$ |
|---|---|---|
| Benzene | 12.4 | 92.1 |
| Diamond | 0.030 | 0.187 |
| Lead | 0.861 | 2.21 |
| Water | 2.1 | 49.6 |

* More values are given in the *Data section* at the end of this volume.

### **Example 3.2** Using the expansion coefficient of a gas

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

**Method** The expansion coefficient is defined in eqn 7. To use this expression, we simply substitute the expression for $V$ in terms of $T$ obtained from the equation of state for the gas. As implied by eqn 7, the pressure, $p$, is treated as a constant.

**Answer** (a) Because $pV = nRT$, we can write

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

The higher the temperature, the less responsive is its volume to a change in temperature.

**Self-test 3.2** Evaluate $\alpha$ for a gas for which the equation of state is $p = nRT/(V - nb)$.

$[\alpha = (1 - b/V_{\mathrm{m}})/T]$

---

[3] As for heat capacities, the expansion coefficients of a mixture depend 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.

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

$$\left(\frac{\partial U}{\partial T}\right)_p = \alpha\pi_T V + C_V \tag{8}$$

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 $\alpha$, which can be measured in another, and in terms of the quantity $\pi_T$. For a perfect gas, $\pi_T = 0$, so

$$\left(\frac{\partial U}{\partial T}\right)_p = C_V \tag*{(9)°}$$

That is, the constant-volume heat capacity of a perfect gas is equal to the slope of a plot of internal energy against temperature at constant pressure as well as (by definition) to the slope at constant volume.

At this stage we know the slope of $U$ with respect to $T$ at constant volume (the constant-volume heat capacity) and the slope of $U$ with respect to $T$ at constant pressure, eqn 8. The fact that the former expression is so simple strongly suggests that it is sensible to treat $U$ as a function of the volume, and to use it in thermodynamics when $V$ is under our control. We saw a hint of that simplicity earlier in the expression $\Delta U = q_V$.

## 3.2 The temperature dependence of the enthalpy

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 hence d$H$ is an exact differential.

### *(a) Changes in the enthalpy at constant volume*

The variation of enthalpy with temperature at constant pressure is simply the constant-pressure heat capacity, $C_p$. The simplicity of this relation strongly suggests that $H$ will prove to be 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 2.24). We shall therefore regard $H$ as a function of $p$ and $T$, and adapt the argument in Section 3.1 to find an expression for the one temperature variation we currently lack, the variation of $H$ with temperature at constant volume. This relation will prove useful for relating the heat capacities at constant pressure and volume and for a discussion of the liquefaction of gases.

By the same argument as for $U$ (but with $p$ in place of $V$) we find that, for a closed system of constant composition,

$$\mathrm{d}H = \left(\frac{\partial H}{\partial p}\right)_T \mathrm{d}p + \left(\frac{\partial H}{\partial T}\right)_p \mathrm{d}T \tag{10}$$

We recognize the second coefficient as the definition of the constant-pressure heat capacity, $C_p$, so

$$\mathrm{d}H = \left(\frac{\partial H}{\partial p}\right)_T \mathrm{d}p + C_p\,\mathrm{d}T \tag{11}$$

The manipulation of this expression is slightly more involved than before, but we show in the *Justification* below that it implies that

$$\left(\frac{\partial H}{\partial T}\right)_V = \left(1 - \frac{\alpha\mu}{\kappa_T}\right)C_p \tag{12}$$

where the isothermal compressibility, $\kappa_T$, is defined as

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \qquad [13]$$

and the Joule–Thomson coefficient, $\mu$, is defined as

$$\mu = \left(\frac{\partial T}{\partial p}\right)_H \qquad [14]$$

Equation 12 applies to any substance. Because all the quantities that appear in it can be measured in suitable experiments, we now know how $H$ varies with $T$ when the volume of the sample is held constant.

## Justification 3.1

First, divide eqn 11 through by $dT$ and impose constant volume:

$$\left(\frac{\partial H}{\partial T}\right)_V = \left(\frac{\partial H}{\partial p}\right)_T\left(\frac{\partial p}{\partial T}\right)_V + C_p$$

The third differential coefficient looks like something we ought to recognize, and is perhaps related to $(\partial V/\partial T)_p$, the expansion coefficient. It follows from the chain relation in *Further information 1* that

$$\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_p\left(\frac{\partial V}{\partial p}\right)_T = -1$$

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, another relation between partial differentials (see *Further information 1*) allows us to invert partial derivatives and to write $(\partial y/\partial x)_z = 1/(\partial x/\partial y)_z$, and leads to

$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{(\partial V/\partial T)_p}{(\partial V/\partial p)_T} = \frac{\alpha}{\kappa_T}$$

Next, we must change $(\partial H/\partial p)_T$ into something recognizable. The chain relation lets us write this partial derivative as

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

Both derivatives may be brought up into the numerator:

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

and we can recognize both the constant-pressure heat capacity, $C_p$, and the Joule–Thomson coefficient $\mu$ as defined in the text. Therefore,

$$\left(\frac{\partial H}{\partial p}\right)_T = -\mu C_p \qquad (15)$$

When we use this expression in the first equation in this *Justification*, we obtain eqn 12.

### (b) The isothermal compressibility

The negative sign in the definition of $\kappa_T$, eqn 13, ensures that it is positive, because an increase of pressure, implying a positive $dp$, brings about a reduction of volume, a negative d$V$. The isothermal compressibility is obtained from the slope of the plot of volume against pressure at constant temperature (that is, it is proportional to the slope of an isotherm). Some values of $\kappa_T$ are listed in Table 3.1. Its value for a perfect gas is obtained by substitution of the perfect gas equation of state into eqn 13, which gives

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial(nRT/p)}{\partial p}\right)_T = -\frac{nRT}{V}\left(-\frac{1}{p^2}\right) = \frac{1}{p} \qquad (16)^{\circ}$$

This expression shows that, the higher the pressure of the gas, the lower its compressibility.

## Example 3.3 Using the isothermal compressibility

The isothermal compressibility of water at 20°C and 1 atm is $4.94 \times 10^{-6}$ atm$^{-1}$. What change of volume occurs when a sample of volume 50 cm$^3$ is subjected to an additional 1000 atm at constant temperature?

**Method** We know from the definition of $\kappa_T$ that, for an infinitesimal change of pressure at constant temperature, the volume changes by

$$\mathrm{d}V = \left(\frac{\partial V}{\partial p}\right)_T \mathrm{d}p = -\kappa_T V\,\mathrm{d}p$$

Therefore, for a finite change in pressure, we need to integrate both sides. When confronted by an integration, it is often a useful first approximation (for substances other than gases) to suppose that the integrand is constant over the range of integration.

**Answer** The integral we need to evaluate is

$$\int_{V_i}^{V_f} \mathrm{d}V = -\int_{p_i}^{p_f} \kappa_T V\,\mathrm{d}p$$

The integral on the left is $\Delta V$. If we suppose that $\kappa_T$ and $V$ are approximately constant over the range of pressures of interest, we can write

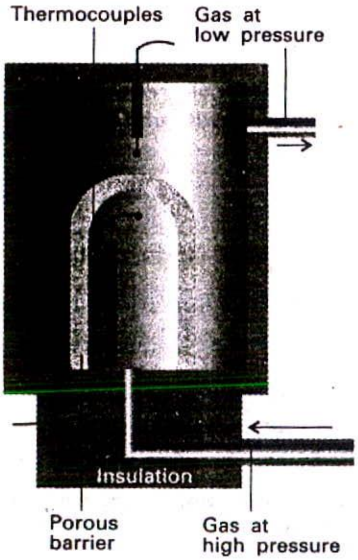
$$\Delta V = -\kappa_T V \int_{p_i}^{p_f} \mathrm{d}p = -\kappa_T V \Delta p$$

Substitution of the data into the last expression then gives

$$\Delta V = -(4.94 \times 10^{-6}\ \mathrm{atm}^{-1}) \times (50\ \mathrm{cm}^3) \times (1000\ \mathrm{atm}) = -0.25\ \mathrm{cm}^3$$

**Comment** Because the compression results in a decrease in volume of only 0.5 per cent, the assumption of constant $V$ and $\kappa_T$ is probably acceptable as a first approximation. Note that very high pressures are needed to bring about significant changes of volume.

**Self-test 3.3** A sample of copper of volume 50 cm$^3$ is subjected to an additional pressure of 100 atm and a temperature increase of 5.0 K. Estimate the total change in volume. [8.8 mm$^3$]



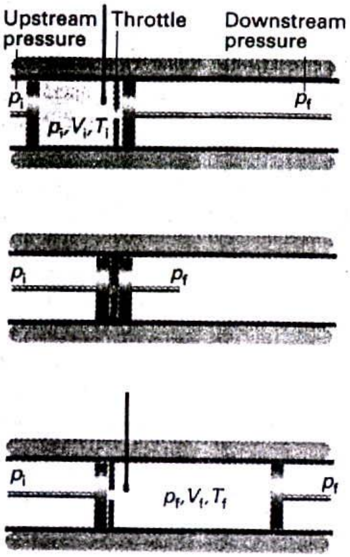
3.4 A diagram of the apparatus used for measuring the Joule–Thomson effect. The gas expands through the porous barrier, which acts as a throttle, and the whole apparatus is thermally insulated. As explained in the text, this arrangement corresponds to an isenthalpic expansion (expansion at constant enthalpy).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

### (c) The Joule–Thomson effect

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.

The cunning required to impose the constraint of constant enthalpy on a change of state 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. 3.4). 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 adiabatic expansion is now called the **Joule–Thomson effect**.

The thermodynamic analysis of the experiment takes as the system a sample of fixed amount of gas. Because all changes to the gas occur adiabatically, $q = 0$. To calculate the work done as the gas passes through the throttle, we consider 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. 3.5). 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 $-p_i(0 - V_i)$, or $p_iV_i$. The gas expands isothermally on the right of the throttle (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 $-p_f(V_f - 0)$, or $-p_fV_f$. The total work done on the gas is the sum of these two quantities, or $p_iV_i - p_fV_f$. It follows that the change of internal energy of the gas as it moves from one side of the throttle to the other is



3.5 A diagram representing 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.

$$U_f - U_i = w = p_iV_i - p_fV_f$$

Reorganization of this expression gives

$$U_f + p_fV_f = U_i + p_iV_i, \qquad \text{or } H_f = H_i \tag{17}$$

Therefore, the expansion occurs without change of enthalpy: it is an **isenthalpic process, a** process at constant 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 $\Delta p$ implies that the thermodynamic quantity measured is $(\partial T/\partial p)_H$, which is the Joule–Thomson coefficient, $\mu$. In other words, the physical interpretation of $\mu$ is that it is the ratio of the change in temperature to the change in pressure when a gas expands under adiabatic conditions.

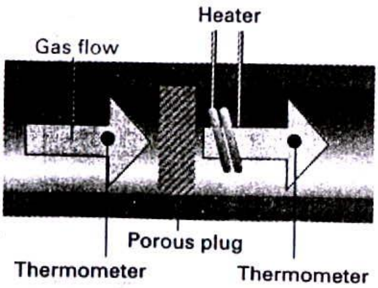
The modern method of measuring $\mu$ is indirect, and involves measuring the **isothermal Joule–Thomson coefficient**, the quantity

$$\mu_T = \left(\frac{\partial H}{\partial p}\right)_T \qquad [18]$$

The two coefficients are related by eqn 15:

$$\mu_T = -C_p\mu \tag{19}$$

To measure $\mu_T$, 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. 3.6). The energy provided by the heater is monitored. Because the heat can be identified with the value of $\Delta H$ for the gas (because $\Delta H = q_p$), and the pressure change $\Delta p$ is known, the value of $\mu_T$ can be obtained from the limiting value of $\Delta H/\Delta p$ as $\Delta p \to 0$, and then converted to $\mu$. Some values obtained in this way are listed in Table 3.2.



3.6 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 $\Delta H$ and used to calculate $(\partial H/\partial p)_T$, which is then converted to $\mu$ as explained in the text.

Real gases have nonzero Joule–Thomson coefficients and, depending on the identity of the gas, the pressure, the relative magnitudes of the attractive and repulsive intermolecular forces, and the temperature, the sign of the coefficient may be either positive or negative

(Fig. 3.7). 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 3.2, Fig. 3.8). As indicated in Fig. 3.8, a gas typically has two inversion temperatures, one at high temperature and the other at low.

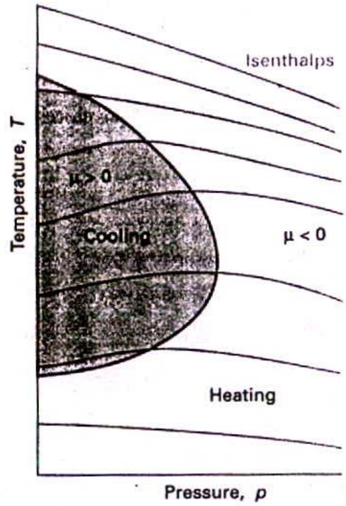
The 'Linde refrigerator' makes use of Joule–Thomson expansion to liquefy gases (Fig. 3.9). The gas at high pressure is allowed to expand through a throttle; it cools and is circulated past the incoming gas. That gas is cooled, and its subsequent expansion cools it still further. There comes a stage when 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.[4] 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 is an example of a property mentioned in Section 1.4b that depends on derivatives and not on $p$, $V$, and $T$ themselves.

**Table 3.2*** Inversion temperatures ($T_I$), normal freezing ($T_f$) and boiling ($T_b$) points, and Joule–Thomson coefficients ($\mu$) at 1 atm and 298 K

| | $T_I$/K | $T_f$/K | $T_b$/K | $\mu$/(K atm$^{-1}$) |
|---|---|---|---|---|
| Ar | 723 | 83.8 | 87.3 | |
| $CO_2$ | 1500 | | 194.7 | 1.11 |
| He | 40 | | 4.2 | −0.060 |
| $N_2$ | 621 | 63.3 | 77.4 | 0.25 |

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



3.7 The sign of the Joule–Thomson coefficient, $\mu$, 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 slopes change from negative to positive.

## 3.3 The relation between $C_V$ and $C_p$

The constant-pressure heat capacity $C_p$ differs from the constant-volume heat capacity $C_V$ by the work needed to change the volume of the system to maintain constant pressure. This work arises in two ways. One is the work of driving back the atmosphere; the other is the work of stretching the bonds in the material, including any weak intermolecular interactions. In the case of a perfect gas, the second makes no contribution. We shall now derive a general relation between the two heat capacities, and show that it reduces to the perfect gas result in the absence of intermolecular forces.

### (a) The relation for a perfect gas

First, we carry through the calculation for a perfect gas. In this special case, we can use eqn 9 to express both heat capacities in terms of derivatives at constant pressure:

$$C_p - C_V = \left(\frac{\partial H}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_p \tag{20}$$

Then we introduce

$$H = U + pV = U + nRT$$

into the first term, which results in

$$C_p - C_V = \left(\frac{\partial U}{\partial T}\right)_p + nR - \left(\frac{\partial U}{\partial T}\right)_p = nR \qquad (21)^\circ$$

This is the formal derivation of eqn 2.31.

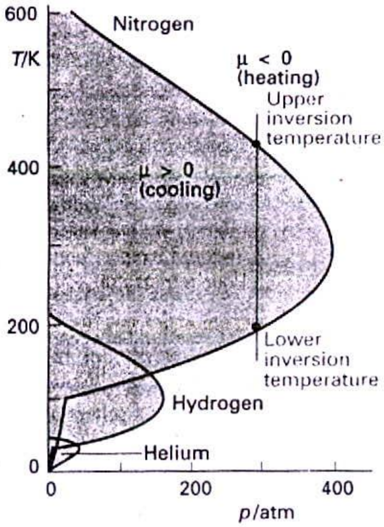
### (b) The general case

We shall now demonstrate that the general relation between the two heat capacities for any pure substance is

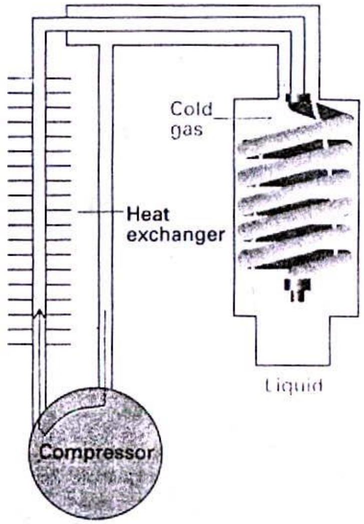
$$C_p - C_V = \frac{\alpha^2 TV}{\kappa_T} \tag{22}$$

---

[4] Simple adiabatic expansion does cool a perfect gas, because the gas does work; recall Section 2.6.



3.8 The inversion temperatures for three real gases, nitrogen, hydrogen, and helium.



3.9 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.

This formula is a thermodynamic expression, which means that it applies to any substance (that is, it is 'universally true'). It reduces to eqn 21 for a perfect gas when we set $\alpha = 1/T$ and $\kappa_T = 1/p$.

### Justification 3.2

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 8 lets us write this difference as $\alpha\pi_T V$. The factor $\alpha V$ 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

$$C_p - C_V = \alpha(p + \pi_T)V$$

As just remarked, the first term on the right ($\alpha pV$) is a measure of the work needed to push back the atmosphere; the second term on the right, $\alpha\pi_T V$, 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 5.1 that

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

When this expression is inserted in the last equation we obtain

$$C_p - C_V = \alpha TV\left(\frac{\partial p}{\partial T}\right)_V$$

The same coefficient as appears here was encountered in *Justification* 3.1, where we saw that it is equal to $\alpha/\kappa_T$. Therefore, this expression turns into eqn 22.

---

Because thermal expansivities, $\alpha$, of liquids and solids are small, it is tempting to deduce from eqn 22 that for them $C_p \approx C_V$. But this is not always so, because the compressibility $\kappa_T$ might also be small, so $\alpha^2/\kappa_T$ 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 22 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.

## Checklist of key ideas

- ☐ state functions
- ☐ path functions

**State functions and exact differentials**

**3.1 State functions**

- ☐ exact differential
- ☐ inexact differential
- ☐ change in internal energy arising from changes in volume and temperature
- ☐ internal pressure ($\pi_T$, 5)
- ☐ Joule experiment to show $\pi_T = 0$
- ☐ expansion coefficient ($\alpha$, 7)

**3.2 The temperature dependence of the enthalpy**

- ☐ variation of enthalpy with temperature at constant volume
- ☐ isothermal compressibility ($\kappa_T$, 13)
- ☐ Joule–Thomson coefficient ($\mu$, 14)
- ☐ isothermal compressibility of a perfect gas
- ☐ Joule–Thomson effect
- ☐ isenthalpic process
- ☐ isothermal Joule–Thomson coefficient ($\mu_T$, 18)
- ☐ inversion temperature
- ☐ Linde refrigerator

**3.3 The relation between $C_V$ and $C_p$**

- ☐ the relation between $C_p$ and $C_V$ for a perfect gas
- ☐ the relation between $C_p$ and $C_V$ for a general substance

## Further reading

### Articles of general interest

S.M. Blinder, Mathematical methods in elementary thermodynamics. *J. Chem. Educ.* **43**, 85 (1966).

E.W. Anacker, S.E. Anacker, and W.J. Swartz, Some comments on partial derivatives in thermodynamics. *J. Chem. Educ.* **64**, 674 (1987).

G.A. Estèvez, K. Yang, and B.B. Dasgupta, Thermodynamic partial derivatives and experimentally measurable quantities. *J. Chem. Educ.* **66**, 890 (1989).

R.A. Alberty, Legendre transforms in chemical thermodynamics. *Chem. Rev.* **94**, 1457 (1994).

### Texts and sources of data and information

M.L. McGlashan, *Chemical thermodynamics*. Academic Press, London (1979).

D.M. Hirst, *Mathematics for chemists*. Macmillan, London (1983).

E. Steiner, *The chemistry maths book*. Oxford University Press (1996).

## Exercises

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

**3.1 (a)** Show that the following functions have exact differentials: (a) $x^2y + 3y^2$, (b) $x \cos xy$.

**3.1 (b)** Show that the following functions have exact differentials: (a) $x^3y^2$, (b) $t(t + e^s) + s$.

**3.2 (a)** Let $z = ax^2y^3$. Find d$z$.

**3.2 (b)** Let $z = x/(1 + y)^2$. Find d$z$.

**3.3 (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.

**3.3 (b)** (a) What is the total differential of $z = x^3 - 2xy^2 + 15$? (b) Show that $\partial^2 z/\partial y \partial x = \partial^2 z/\partial x \partial y$ for this function.

**3.4 (a)** Let $z = xy - y + \ln x + 2$. Find d$z$ and show that it is exact.

**3.4 (b)** Let $z = x^2y + xy^2$. Find d$z$ and show that it is exact.

**3.5 (a)** Express $(\partial C_V/\partial V)_T$ as a second-derivative of $U$ and find its relation to $(\partial U/\partial V)_T$. From this relation show that $(\partial C_V/\partial V)_T = 0$ for a perfect gas.

**3.5 (b)** Express $(\partial C_p/\partial p)_T$ as a second-derivative of $H$ and find its relation to $(\partial H/\partial p)_T$. From this relation show that $(\partial C_p/\partial p)_T = 0$ for a perfect gas.

**3.6 (a)** By direct differentiation of $H = U + pV$, obtain a relation between $(\partial H/\partial U)_p$ and $(\partial U/\partial V)_p$.

**3.6 (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.

**3.7 (a)** Write an expression for $\mathrm{d}V$ given that $V$ is a function of $p$ and $T$. Deduce an expression for $\mathrm{d}\ln V$ in terms of the expansion coefficient and the isothermal compressibility.

**3.7 (b)** Write an expression for $\mathrm{d}p$ given that $p$ is a function of $V$ and $T$. Deduce an expression for $\mathrm{d}\ln p$ in terms of the expansion coefficient and the isothermal compressibility.

**3.8 (a)** The internal energy of a perfect monatomic gas relative to its value at $T = 0$ is $\frac{3}{2}nRT$. Calculate $(\partial U/\partial V)_T$ and $(\partial H/\partial V)_T$ for the gas.

**3.8 (b)** The internal energy of a perfect monatomic gas relative to its value at $T = 0$ is $\frac{3}{2}nRT$. Calculate $(\partial H/\partial p)_T$ and $(\partial U/\partial p)_T$ for the gas.

**3.9 (a)** The coefficient of thermal expansion, $\alpha$, is defined in eqn 7 and the isothermal compressibility, $\kappa_T$, is defined in eqn 13. Starting from the expression for the total differential $\mathrm{d}V$ in terms of $T$ and $p$, show that $(\partial p/\partial T)_V = \alpha/\kappa_T$.

**3.9 (b)** Evaluate $\alpha$ and $\kappa_T$ for a perfect gas.

**3.10 (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, $\mu$, at 0°C, assuming it remains constant over this temperature range.

**3.10 (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, $\mu$, at 5°C, assuming it remains constant over this temperature range.

**3.11 (a)** For a van der Waals gas, $\pi_T = a/V_\mathrm{m}^2$. Calculate $\Delta U_\mathrm{m}$ for the isothermal reversible expansion of nitrogen gas from an initial volume of 1.00 L to 24.8 L at 298 K. What are the values of $q$ and $w$?

**3.11 (b)** For a van der Waals gas, $\pi_T = a/V_\mathrm{m}^2$. Calculate $\Delta U_\mathrm{m}$ for the isothermal reversible expansion of argon from an initial volume of 1.00 L to 22.1 L at 298 K. What are the values of $q$ and $w$?

**3.12 (a)** The volume of a certain liquid varies with temperature as

$$V = V'\{0.75 + 3.9 \times 10^{-4}(T/\mathrm{K}) + 1.48 \times 10^{-6}(T/\mathrm{K})^2\}$$

where $V'$ is its volume at 300 K. Calculate its expansion coefficient, $\alpha$, at 320 K.

**3.12 (b)** The volume of a certain liquid varies with temperature as

$$V = V'\{0.77 + 3.7 \times 10^{-4}(T/\mathrm{K}) + 1.52 \times 10^{-6}(T/\mathrm{K})^2\}$$

where $V'$ is its volume at 298 K. Calculate its expansion coefficient, $\alpha$, at 310 K.

**3.13 (a)** The isothermal compressibility of copper at 293 K is $7.35 \times 10^{-7}\ \mathrm{atm}^{-1}$. Calculate the pressure that must be applied in order to increase its density by 0.08 per cent.

**3.13 (b)** The isothermal compressibility of lead at 293 K is $2.21 \times 10^{-6}\ \mathrm{atm}^{-1}$. Calculate the pressure that must be applied in order to increase its density by 0.08 per cent.

**3.14 (a)** Given that $\mu = 0.25\ \mathrm{K\,atm}^{-1}$ 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 $\mathrm{N_2}$ flows through a throttle in an isothermal Joule–Thomson experiment and the pressure drop is 75 atm.

**3.14 (b)** Given that $\mu = 1.11\ \mathrm{K\,atm}^{-1}$ 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 $\mathrm{CO_2}$ flows through a throttle in an isothermal Joule–Thomson experiment and the pressure drop is 55 atm.

**3.15 (a)** To design a particular kind of refrigerator we need to know the temperature reduction brought about by adiabatic expansion of the refrigerant gas. For one type of freon, $\mu = 1.2\ \mathrm{K\,atm}^{-1}$. What pressure difference is needed to produce a temperature drop of 5.0 K?

**3.15 (b)** For another type of freon (see previous exercise), $\mu = 13.3\ \mathrm{mK\,kPa}^{-1}$. What pressure difference is needed to produce a temperature drop of 4.5 K?

---

# Problems

Assume all gases are perfect unless stated otherwise. Unless otherwise stated, thermochemical data are for 298.15 K.

## Numerical problems

**3.1** The isothermal compressibility of lead is $2.21 \times 10^{-6}\ \mathrm{atm}^{-1}$. Express this value in $\mathrm{Pa}^{-1}$. A cube of lead of side 10 cm at 25°C was to be inserted in the keel of an underwater exploration TV camera, and its designers needed to know the stresses in the equipment. Calculate the change of volume of the cube at a depth of 1.000 km (disregarding the effects of temperature). Take the mean density of sea water as $1.03\ \mathrm{g\,cm}^{-3}$. Given that the expansion coefficient of lead is $8.61 \times 10^{-5}\ \mathrm{K}^{-1}$ and that the temperature where the camera operates is −5°C, calculate the volume of the block taking the temperature into account too.

**3.2** Calculate the change in (a) the molar internal energy and (b) the molar enthalpy of water when its temperature is raised by 10 K. Account for the difference between the two quantities.

**3.3** 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 $\gamma$ (the ratio of heat capacities, $C_p/C_V$) 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 1522.2 Torr to 613.85 Torr. Evaluate $C_p$.

**3.4** A sample consisting of 1.00 mol of a van der Waals gas is compressed from 20.0 L to 10.0 L 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 $C_{p,\mathrm{m}} = 38.4\ \mathrm{J\,K^{-1}\,mol^{-1}}$, $a = 3.60\ \mathrm{L^2\,atm\,mol^{-2}}$, and $b = 0.44\ \mathrm{L\,mol^{-1}}$, calculate $\Delta H$ for the process.

**3.5** Estimate $\gamma$ (the ratio of heat capacities) for xenon at 100 °C and 1.00 atm on the assumption that it is a van der Waals gas (see Problem 3.22).

## Theoretical problems

**3.6** Determine whether or not $\mathrm{d}z = xy\,\mathrm{d}x + xy\,\mathrm{d}y$ is exact by integrating it around the closed curve formed by the paths $y = x$ and $y = x^2$ between the points (0, 0) and (1, 1).

**3.7** Decide whether $\mathrm{d}q = (RT/p)\,\mathrm{d}p - R\,\mathrm{d}T$ is exact. Then determine whether multiplication of $\mathrm{d}q$ by $1/T$ is exact. Comment on the significance of your result.

**3.8** Obtain the total differential of the function $w = xy + yz + xz$. Demonstrate that $\mathrm{d}w$ is exact by integration between the points (0, 0, 0) and (1, 1, 1) along the two different paths (a) $z = y = x$ and (b) $z = y = x^2$.

**3.9** Derive the relation $C_V = -(\partial U/\partial V)_T(\partial V/\partial T)_U$ from the expression for the total differential of $U(T, V)$.

**3.10** 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, $\mu$.

**3.11** 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

$$C_p - C_V = \frac{T(\partial V/\partial T)_p^2}{(\partial V/\partial p)_T}$$

Evaluate $C_p - C_V$ for a perfect gas.

**3.12** From an analysis of Joule's free expansion experiment, demonstrate that it is possible to calculate the change in internal energy of a perfect gas for any process by knowing only $C_V$ and $\Delta T$.

**3.13** By the consideration of a suitable cycle involving a perfect gas, demonstrate that $\mathrm{d}q$ is an inexact differential and, therefore, that $q$ is not a state function.

**3.14** 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 $\mu$ and appropriate relations between partial derivatives. (*Hint*: Use the approximation $pV_\mathrm{m} \approx RT$ when it is justifiable to do so.)

**3.15** Obtain the expression for the total differential $\mathrm{d}p$ for a van der Waals gas in terms of $\mathrm{d}T$ and $\mathrm{d}V$. Also obtain $(\partial V/\partial T)_p$. Demonstrate that $\mathrm{d}p$ is not an exact differential by integrating it from $(T_1, V_1)$ to $(T_2, V_2)$ along the two different paths, namely (a) $(T_1, V_1) \rightarrow (T_2, V_1) \rightarrow (T_2, V_2)$ and (b) $(T_1, V_1) \rightarrow (T_1, V_2) \rightarrow (T_2, V_2)$.

**3.16** Take nitrogen to be a van der Waals gas with $a = 1.408\ \mathrm{atm\,L^2\,mol^{-2}}$ and $b = 0.03913\ \mathrm{L\,mol^{-1}}$, and calculate $\Delta H_\mathrm{m}$ 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 $C_{p,\mathrm{m}} = \frac{7}{2}R$.

**3.17** The pressure of a given amount of a van der Waals gas depends on $T$ and $V$. Find an expression for $\mathrm{d}p$ in terms of $\mathrm{d}T$ and $\mathrm{d}V$.

**3.18** 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.

**3.19** Calculate the isothermal compressibility and the expansion coefficient of a van der Waals gas. Show, using Euler's chain relation, that $\kappa_T R = \alpha(V_\mathrm{m} - b)$.

**3.20** Given that $\mu C_p = T(\partial V/\partial T)_p - V$, derive an expression for $\mu$ in terms of the van der Waals parameters $a$ and $b$, and express it in terms of reduced variables. Evaluate $\mu$ at 25 °C and 1.0 atm, when the molar volume of the gas is 24.6 L 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.

**3.21** 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.

**3.22** 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.

**3.23** The speed of sound, $c_\mathrm{s}$, in a gas of molar mass $M$ is related to the ratio of heat capacities $\gamma$ by $c_\mathrm{s} = (\gamma RT/M)^{1/2}$. Show that $c_\mathrm{s} = (\gamma p/\rho)^{1/2}$, where $\rho$ is the mass density of the gas. Calculate the speed of sound in argon at 25 °C.

## Additional problems supplied by Carmen Giunta and Charles Trapp

**3.24** In 1995, the Intergovernmental Panel on Climate Change considered a global average temperature rise of 1.0–3.5°C likely by the year 2100, with 2.0°C its best estimate (IPCC Second Assessment Synthesis of Scientific–Technical Information Relevant to Interpreting Article 2 of the UN Framework Convention on Climate Change (1995)). 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 $1.37 \times 10^9\ \mathrm{km^3}$ and their surface area is $361 \times 10^6\ \mathrm{km^2}$, and state the approximations that go into the estimates.

**3.25** 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 $\mu$ can be computed. (a) Compute $\mu$ at 1.00 bar and 50°C given that $(\partial H/\partial p)_T = -3.29 \times 10^3\ \mathrm{J\,MPa^{-1}\,mol^{-1}}$ 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.

**3.26** 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 $\mu$ can be computed.

(a) Compute $\mu$ 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/($\mathrm{kJ\,kg^{-1}}$) | 426.48 | 426.12 | 425.76 |

(The specific constant-pressure heat capacity is 0.7649 $\mathrm{kJ\,K^{-1}\,kg^{-1}}$.)

(b) Compute $\mu$ 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/($\mathrm{kJ\,kg^{-1}}$) | 461.93 | 459.12 | 456.15 |

(The specific constant-pressure heat capacity is 1.0392 $\mathrm{kJ\,K^{-1}\,kg^{-1}}$.)

**3.27** A cylindrical container of fixed total volume is divided into three sections, $S_1$, $S_2$, and $S_3$. The sections $S_1$ and $S_2$ are separated by an adiabatic piston, whereas $S_2$ and $S_3$ are separated by a diathermic (heat-conducting) piston. The pistons can slide along the walls of the cylinder without friction. Each section of the cylinder contains 1.00 mol of a perfect diatomic gas. Initially the gas pressure in all three sections is 1.00 bar and the temperature is 298 K. The gas in $S_1$ is heated slowly until the temperature of the gas in $S_3$ reaches 348 K. Find the final temperature, pressure, and volume, as well as the change in internal energy for each section. Determine the total energy supplied to the gas in $S_1$.

**3.28** Solve Problem 3.27 for the case where both pistons are (a) adiabatic, (b) diathermic.

**3.29** A gas obeying the equation of state $p(V - b) = nRT$ is subjected to a Joule–Thomson expansion. Will the temperature increase, decrease, or remain the same?

**3.30** 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) the constant-volume heat capacity of the gas.

# 4

# The Second Law: the concepts

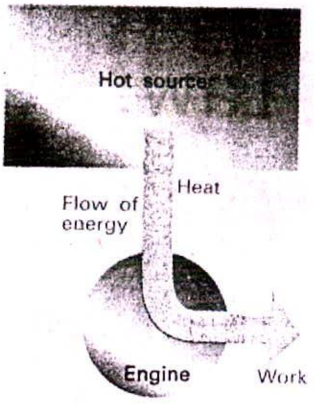
*The purpose of this chapter is to explain the origin of the spontaneity of physical and chemical change. We examine two simple processes and show that a property, the entropy, can be defined, measured, and used to discuss spontaneous changes quantitatively. The chapter also introduces a major subsidiary thermodynamic property, the Gibbs energy. The introduction of the Gibbs energy enables the spontaneity of a process to be expressed solely in terms of the properties of a system (instead of having to consider entropy changes in the system and its surroundings). The Gibbs energy also enables us to predict the maximum non-expansion work that a process can do.*

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. We *can* confine a gas to a smaller volume, we *can* cool an object with a refrigerator, and we *can* force some reactions to go in reverse (as in the electrolysis of water). However, none of these processes happens spontaneously; each one must be brought about by doing work.

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, and some heat is always discarded into the cold sink 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.



4.1 **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.

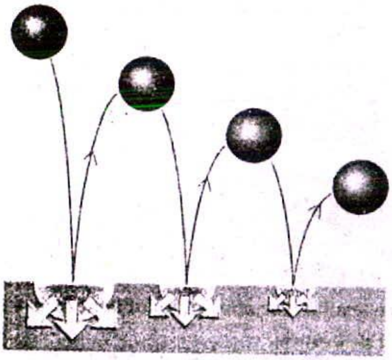
Is it perhaps the energy of the system of interest that tends towards a minimum? Two arguments show that this cannot be so. First, a perfect gas expands spontaneously into a vacuum, yet its internal energy remains constant as it does so. Secondly, if the energy of a system does happen to decrease during 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 into a more disordered form*.

### 4.1 The dispersal of energy

The role of the distribution of energy can be illustrated by thinking about a ball (the system of interest) 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 (that is, the conversion of kinetic energy of the ball's overall motion into the energy of thermal motion). The direction of spontaneous change is towards a state in which the ball is at rest with all its energy degraded into the thermal motion of the atoms of the virtually infinite floor (Fig. 4.2).

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. 4.3). Furthermore, whereas the thermal motion is disorderly, for the ball to move upwards its atoms must all move in the same direction. The localization of random motion as orderly motion is so unlikely that we can dismiss it as virtually impossible.[1]

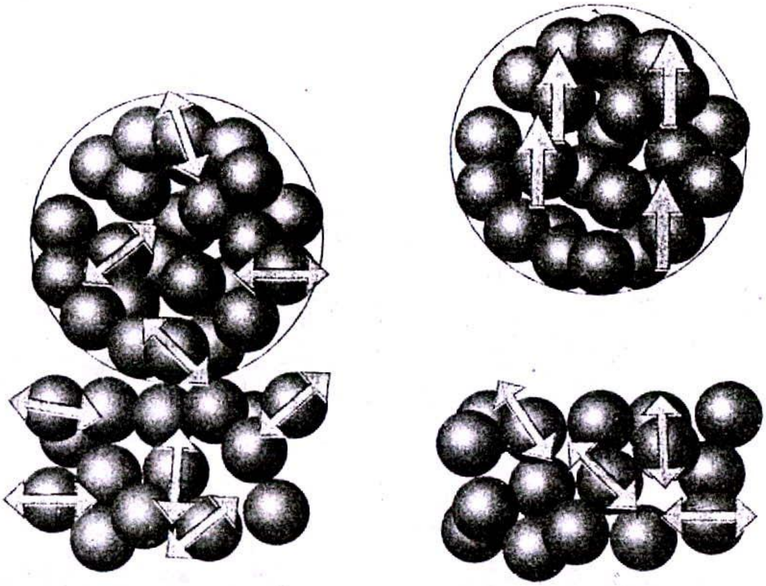


4.2 **The direction of spontaneous change for a ball bouncing on a floor. On each bounce some of its energy is degraded into the thermal motion of the atoms of the floor, and that energy disperses. The reverse has never been observed to take place on a macroscopic scale.**

We appear to have found the signpost of spontaneous change: we look for the direction of change that leads to the greater chaotic 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 dissipated as thermal motion of the atoms of the floor. The reverse process is not spontaneous because it is highly improbable that the chaotic distribution of energy will become organized into localized, uniform motion. A gas does not spontaneously contract, because to do so the chaotic motion of its molecules would have to take them all into the same region of the container; the opposite change, spontaneous expansion, is a natural consequence of increasing disorder. 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 accumulation of excess thermal motion in the

---

[1] It occurs on a much smaller scale in the form of the fluctuations of position known as Brownian motion.



(a) (b)

4.2 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 (chaotic 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.

object. The opposite change, the spreading of the object's energy into the surroundings as thermal motion, is a natural consequence of chaos.

It may seem very puzzling that collapse into disorder can account for the formation of such ordered substances as crystals or proteins. Nevertheless, in due course we shall see that organized structures can emerge as energy and matter disperse. We shall see, in fact, that collapse into disorder accounts for change in all its forms.

## 4.2 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 which is a measure of the molecular disorder of a system) 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:**

$$\Delta S_{\text{tot}} > 0 \qquad (1)$$

where $S_{\text{tot}}$ 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 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 in a disorderly manner depends on the quantity of energy transferred as heat. As we have remarked, heat stimulates disorderly motion in the surroundings. Work, which stimulates uniform motion of atoms in the surroundings, does not change the degree of disorder, and so does not change the entropy.

The thermodynamic definition of entropy is based on the expression

$$dS = \frac{dq_{\text{rev}}}{T} \qquad [2]$$

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

$$\Delta S = \int_{\text{i}}^{\text{f}} \frac{dq_{\text{rev}}}{T} \qquad (3)$$

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 heat supplied at each stage of the path divided by the temperature at which the heat is supplied.

Molecular interpretation 4.1 The molecules in a system at high temperature are highly disorganized, either in terms of their locations or in terms of the occupation of their available translational, rotational, and vibrational energy states. A small additional transfer of energy will result in a relatively small additional disorder, much as sneezing in a busy street may be barely noticed. In contrast, the molecules in a system at low temperature have access to far fewer energy states (at $T = 0$, only the lowest state is accessible), and the same quantity of heat will have a pronounced effect on the degree of disorder, much as sneezing in a quiet library can be very disruptive. Hence, the change in entropy when a given quantity of heat is transferred will be greater when it 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 2.

According to eqn 2, when the heat transferred is expressed in joules and the temperature is in kelvins, the units of entropy are joules per kelvin ($\text{J K}^{-1}$). Molar entropy, the entropy divided by the amount of substance, is expressed in joules per kelvin per mole ($\text{J K}^{-1}\,\text{mol}^{-1}$), the same units as those of the gas constant, $R$, and molar heat capacities.

### **Example 4.1** 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 $V_{\text{i}}$ to a volume $V_{\text{f}}$.

Method The definition of entropy instructs us to find the heat absorbed 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. The heat absorbed 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 (eqn 2.13).

**Answer** Because the temperature is constant, eqn 3 becomes

$$\Delta S = \frac{1}{T}\int_{\text{i}}^{\text{f}} \mathrm{d}q_{\text{rev}} = \frac{q_{\text{rev}}}{T}$$

From eqn 2.13, we know that

$$q_{\text{rev}} = -w_{\text{rev}} = nRT \ln\left(\frac{V_{\text{f}}}{V_{\text{i}}}\right)$$

Therefore, it follows that

$$\Delta S = nR \ln\left(\frac{V_{\text{f}}}{V_{\text{i}}}\right)$$

**Comment** As an illustration of this formula, when the volume of 1.00 mol of any perfect gas is doubled at any constant temperature,

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

**Self-test 4.1** Calculate the change in entropy when the pressure of a perfect gas is changed isothermally from $p_{\text{i}}$ to $p_{\text{f}}$.

$[\Delta S = nR \ln(p_{\text{i}}/p_{\text{f}})]$

The definition in eqn 2 can be used to formulate an expression for the change in entropy of the surroundings, $\Delta S_{\text{sur}}$. Consider an infinitesimal transfer of heat $\mathrm{d}q_{\text{sur}}$ to the surroundings. The surroundings consist of a reservoir of constant volume,[2] so the heat supplied to them can be identified with the change in their internal energy, $\mathrm{d}U_{\text{sur}}$. The internal energy is a state function, and $\mathrm{d}U_{\text{sur}}$ is an exact differential. As we have seen, these properties imply that $\mathrm{d}U_{\text{sur}}$ 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 $\mathrm{d}q_{\text{sur}}$, to which $\mathrm{d}U_{\text{sur}}$ is equal. Therefore, we can adapt the definition of entropy change in eqn 2 to write

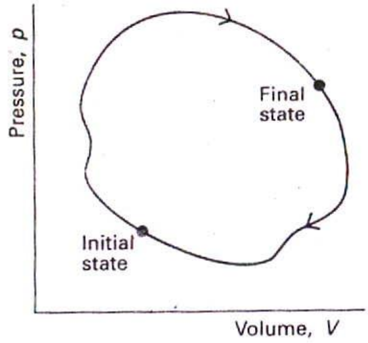
$$\mathrm{d}S_{\text{sur}} = \frac{\mathrm{d}q_{\text{sur,rev}}}{T_{\text{sur}}} = \frac{\mathrm{d}q_{\text{sur}}}{T_{\text{sur}}} \tag{4}$$

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

$$\Delta S_{\text{sur}} = \frac{q_{\text{sur}}}{T_{\text{sur}}} \tag{5}$$

That is, regardless of how the change is brought about in the system, the change of entropy of the surroundings can be calculated by dividing the heat transferred by the temperature at which the transfer takes place.

[2] Alternatively, the surroundings can be regarded as being at constant pressure, in which case we could equate $\mathrm{d}q_{\text{sur}}$ to $\mathrm{d}H_{\text{sur}}$.



4.4 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.

Equation 5 makes it very simple to calculate the changes in entropy of the surroundings that accompany any process. For instance, for any adiabatic change, $q_{\text{sur}} = 0$, so

$$\Delta S_{\text{sur}} = 0 \tag{6}$$

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

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 2.6. The heat released is supplied to the surroundings, now regarded as being at constant pressure, so $q_{\text{sur}} = +286$ kJ. Therefore,

$$\Delta S_{\text{sur}} = \frac{2.86 \times 10^5 \text{ J}}{298 \text{ K}} = +959 \text{ J K}^{-1}$$

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

Self-test 4.2 Calculate the entropy change in the surroundings when 1.00 mol $N_2O_4(g)$ is formed from 2.00 mol $NO_2(g)$ under standard conditions at 298 K.

[$-192$ J K$^{-1}$]

### (b) The entropy as a state function

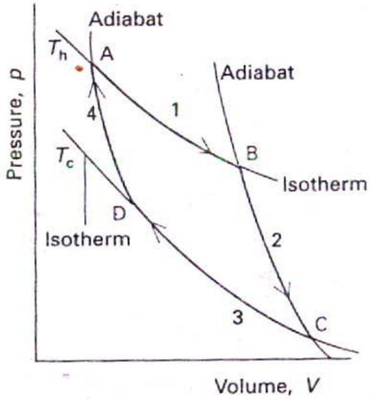
The entropy is a state function. To prove this assertion, we need to show that the integral of $dS$ is independent of path. To do so, it is sufficient to prove that the integral of eqn 2 around an arbitrary cycle is zero, for that guarantees that the entropy is the same at the initial and final states of the system regardless of the path taken between them (Fig. 4.4). That is, we need to show that

$$\oint \frac{dq_{\text{rev}}}{T} = 0 \tag{7}$$

where the symbol $\oint$ denotes integration around a closed path.

To prove eqn 7, we first consider the special **Carnot cycle** shown in Fig. 4.5. A Carnot cycle, which is named after the French engineer Sadi Carnot, consists of four reversible stages:

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



4.5 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.

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 the *Justification* below that

$$\frac{q_\mathrm{h}}{q_\mathrm{c}} = -\frac{T_\mathrm{h}}{T_\mathrm{c}} \tag{8}$$

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

### Justification 4.1

As explained in Example 4.1, for a perfect gas:

$$q_\mathrm{h} = nRT_\mathrm{h} \ln\left(\frac{V_\mathrm{B}}{V_\mathrm{A}}\right) \qquad q_\mathrm{c} = nRT_\mathrm{c} \ln\left(\frac{V_\mathrm{D}}{V_\mathrm{C}}\right)$$

From the relations between temperature and volume for reversible adiabatic processes (eqn 2.34):

$$V_\mathrm{A}T_\mathrm{h}^c = V_\mathrm{D}T_\mathrm{c}^c \qquad V_\mathrm{C}T_\mathrm{c}^c = V_\mathrm{B}T_\mathrm{h}^c$$

Multiplication of the first of these expressions by the second gives

$$V_\mathrm{A}V_\mathrm{C}T_\mathrm{h}^cT_\mathrm{c}^c = V_\mathrm{D}V_\mathrm{B}T_\mathrm{h}^cT_\mathrm{c}^c$$

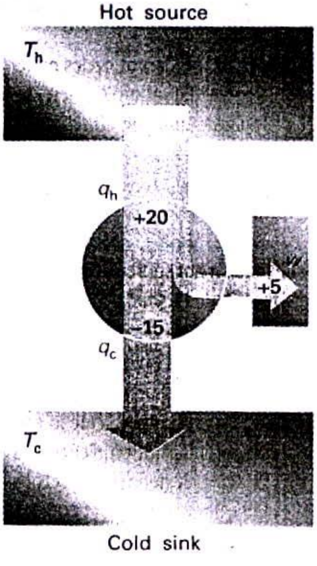
which simplifies to

$$\frac{V_\mathrm{A}}{V_\mathrm{B}} = \frac{V_\mathrm{D}}{V_\mathrm{C}}$$

Consequently,

$$q_\mathrm{c} = nRT_\mathrm{c} \ln\left(\frac{V_\mathrm{A}}{V_\mathrm{B}}\right)$$

and eqn 8 follows.



4.6 Suppose an energy $q_\mathrm{h}$ (for example, 20 kJ) is supplied to the engine and $q_\mathrm{c}$ 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 heat supplied from the hot source.

Now we need to show that the same conclusion applies to any material, not just a perfect gas. To do so, consider the **efficiency**, $\varepsilon$, of a heat engine:

$$\varepsilon = \frac{\text{work performed}}{\text{heat absorbed}} = \frac{|w|}{q_\mathrm{h}} \tag*{[9]}$$

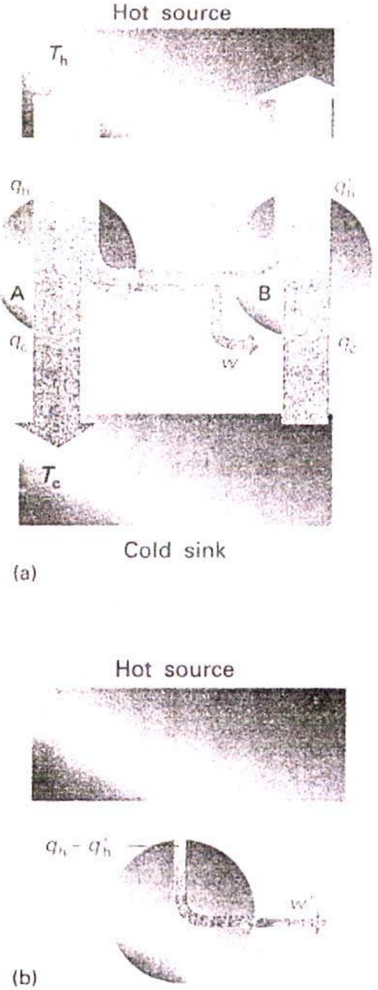
The definition implies that, the greater the work output for a given supply of heat from the hot reservoir, the greater the efficiency of the engine. The definition can be expressed in terms of the heat transactions alone, because (as shown in Fig. 4.6) the work performed by the engine is the difference between the heat supplied by the hot reservoir and that returned to the cold reservoir:

$$\varepsilon = \frac{q_\mathrm{h} + q_\mathrm{c}}{q_\mathrm{h}} = 1 + \frac{q_\mathrm{c}}{q_\mathrm{h}} \tag{10}$$

(Remember that $q_\mathrm{c} < 0$.) It then follows that for a Carnot engine

$$\varepsilon_\mathrm{rev} = 1 - \frac{T_\mathrm{c}}{T_\mathrm{h}} \tag{11}$$

Now, 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



4.7 (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.

reversible engines are coupled together and run between the same two reservoirs (Fig. 4.7). The working substances and details of construction of the two engines are entirely arbitrary. Initially, suppose that engine A is more efficient than engine B, and that we choose a setting of the controls that causes engine B to acquire the heat $q_c$ from the cold reservoir and to release a certain quantity of 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 produced, 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 disordered 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 (eqn 11) must also be independent of the working material, and therefore that eqn 8 is always true for any substance involved in a Carnot cycle.

To complete the argument, we note that any reversible cycle can be approximated as a collection of Carnot cycles (Fig. 4.8). 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 interior of the overall cycle, the entropy change along any 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 7 then follows immediately. This result implies that $\mathrm{d}S$ is an exact differential and therefore that $S$ is a state function.

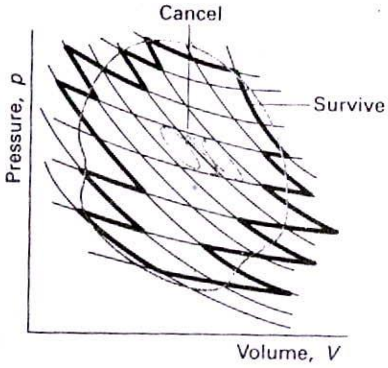
## (c) The thermodynamic temperature

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 11 that

$$T = (1 - \varepsilon)T_h \qquad (12)$$

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.

An additional point is that, as we saw in Section 2.2c, heat transferred can, in principle, be measured mechanically (in terms of the location of a weight). Therefore, it is possible, in principle at least, to use the distance moved by a weight to measure temperature. Kelvin's definition of the thermodynamic temperature scale puts the measurement of temperature on to a purely mechanical basis.



4.8 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.

## *(d) The Clausius inequality*

So far, we have verified that the entropy as defined in eqn 2 is a state function. We now need to verify that the entropy is a signpost of spontaneous change in the sense that $dS_{tot} \geq 0$ for *any* spontaneous change.

Consider a system in thermal and mechanical contact with its surroundings at the same temperature, $T$. The system and the surroundings are not necessarily in mechanical equilibrium (for instance, a gas might have a greater pressure than that of its surroundings). Any change of state is accompanied by a change in entropy of the system, $dS$, and of the surroundings, $dS_{sur}$. Because the process might be irreversible, the total entropy will increase when a process occurs in the system, so we can write

$$dS + dS_{sur} \geq 0, \qquad \text{or } dS \geq -dS_{sur}$$

(The equality applies if the process is reversible.) Because eqn 5 implies that $dS_{sur} = -dq/T$, where $dq$ is the heat supplied to the system during the process (that is, $dq_{sur} = -dq$, because the heat that enters the system comes from the surroundings), it follows that for any change

$$dS \geq \frac{dq}{T} \tag{13}$$

This expression is the **Clausius inequality**.

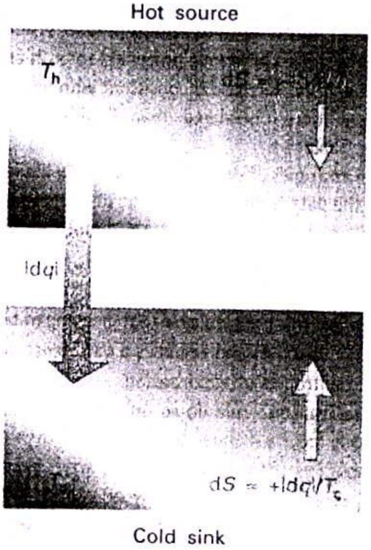
Suppose the system is isolated from its surroundings. Then $dq = 0$, and the Clausius inequality implies that

$$dS \geq 0 \tag{14}$$

This is exactly the characteristic we need for the entropy to be the signpost of spontaneous change, for it tells us that in an *isolated* system *the entropy of the system alone* cannot decrease when a spontaneous change takes place.

We can illustrate the content of the Clausius inequality in two simple cases. First, suppose a system undergoes an irreversible adiabatic change. Then $dq = 0$ and, by eqn 13, $dS \geq 0$. That is, for this type of spontaneous change, the entropy of the system has increased. Because no heat flows into the surroundings, their entropy remains constant and $dS_{sur} = 0$. Therefore, the total entropy of the system and its surroundings obeys $dS_{total} \geq 0$.

Now consider irreversible isothermal expansion of a perfect gas. As we saw in Example 4.1, for such a change $dq = -dw$ (because $dU = 0$). If the gas expands freely into a vacuum, it does no work and $dw = 0$, which implies that $dq = 0$ too. Therefore, according to the Clausius inequality, $dS \geq 0$. Next, consider the surroundings. No heat is transferred into the surroundings, so $dS_{sur} = 0$. Therefore, in this case too $dS_{tot} \geq 0$.



4.9 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.

Another type of irreversible process is spontaneous cooling. Consider a transfer of energy as heat $dq$ from one system—the hot source—at a temperature $T_h$ to another system—the cold sink—at a temperature $T_c$ (Fig. 4.9). When $|dq|$ leaves the hot source, the entropy of the source changes by $-|dq|/T_h$ (a decrease). When $|dq|$ enters the cold sink its entropy changes by $+|dq|/T_c$ (an increase). The overall change in entropy is therefore

$$dS = \frac{|dq|}{T_c} - \frac{|dq|}{T_h} = |dq|\left(\frac{1}{T_c} - \frac{1}{T_h}\right) \tag{15}$$

which is positive (because $T_h \geq T_c$). Hence, cooling (the transfer of heat from hot to cold) is spontaneous, as we know from experience. When the temperatures of the two systems are equal, $dS_{tot} = 0$: the two systems are then at thermal equilibrium.

## 4.3 Entropy changes accompanying specific processes

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

### *(a) The entropy of phase transition at the transition temperature*

Because a change in the degree of molecular order occurs when a substance freezes or boils, 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 substance increases when it melts to a liquid, and it also increases when the liquid phase turns into a gas.

Consider a system and its surroundings at the normal transition temperature $T_{\mathrm{trs}}$, 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 heat between the system and its surroundings is reversible because the two phases in the system are in equilibrium. Because at constant pressure $q = \Delta_{\mathrm{trs}}H$, the change in molar entropy[3] of the system is

$$\Delta_{\mathrm{trs}}S = \frac{\Delta_{\mathrm{trs}}H}{T_{\mathrm{trs}}} \tag{16}$$

If the phase transition is exothermic ($\Delta_{\mathrm{trs}}H < 0$, as in freezing or condensing), then the entropy change is negative. This decrease in entropy is consistent with the system becoming more ordered when a solid forms from a liquid. If the transition is endothermic ($\Delta_{\mathrm{trs}}H > 0$, as in melting), then the entropy change is positive, which is consistent with the system becoming more disordered. Melting and vaporizing are endothermic processes, so both are accompanied by an increase in the system's entropy. This increase is consistent with liquids being more disordered than solids, and gases more disordered than liquids. Some experimental entropies of transition are listed in Table 4.1.

In Table 4.2 we list 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 $\mathrm{J\,K^{-1}\,mol^{-1}}$): this empirical observation is called **Trouton's rule**.

---

Molecular interpretation 4.2 The explanation of Trouton's rule is that a comparable amount of disorder is generated when any liquid evaporates and becomes a gas. Hence, all liquids can be expected to have similar standard entropies of vaporization.

Liquids that show significant deviations from Trouton's rule do so on account of the molecules in the liquid being arranged in a partially orderly manner. In such cases, a greater change of disorder occurs when the liquid evaporates than if the molecules were highly disordered in the liquid. An example is water, where the large entropy of vaporization reflects the presence of structure arising from hydrogen-bonding in the liquid. Hydrogen bonds tend to organize the molecules in the liquid so that they are less random than, for example, the molecules in liquid hydrogen sulfide (which is not hydrogen bonded).

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 $\mathrm{J\,K^{-1}\,mol^{-1}}$ at 298 K); the entropy of $N_2$ under the same conditions is 192 $\mathrm{J\,K^{-1}\,mol^{-1}}$. As we shall see in Chapter 19, light molecules are

---

[3] Recall from Section 2.7 that $\Delta_{\mathrm{trs}}H$ is an enthalpy change per mole of substance, so $\Delta_{\mathrm{trs}}S$ is also a molar quantity.

Table 4.1* Standard entropies (and temperatures) of phase transitions, $\Delta_{trs}S^{\ominus}/(\mathrm{J\,K^{-1}\,mol^{-1}})$

| | Fusion (at $T_f$) | Vaporization (at $T_b$) |
|---|---|---|
| Argon, Ar | 14.17 (at 83.8 K) | 74.53 (at 87.3 K) |
| Benzene, $C_6H_6$ | 38.00 (at 279 K) | 87.19 (at 353 K) |
| Water, $H_2O$ | 22.00 (at 273.15 K) | 109.0 (at 373.15 K) |
| Helium, He | 4.8 (at 1.8 K and 30 bar) | 19.9 (at 4.22 K) |

* More values are given in the *Data section* at the end of this volume.

Table 4.2* The standard entropies of vaporization of liquids

| | $\Delta_{vap}H^{\ominus}/(\mathrm{kJ\,mol^{-1}})$ | $\theta_b/{}^{\circ}\mathrm{C}$ | $\Delta_{vap}S^{\ominus}/(\mathrm{J\,K^{-1}\,mol^{-1}})$ |
|---|---|---|---|
| Benzene | +30.8 | 80.1 | +87.2 |
| Carbon tetrachloride | +30.00 | 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.*

difficult to excite into rotation; as a result, only a few rotational states are accessible at room temperature, and the disorder associated with the population of rotational states is low.

### Example 4.2 Using Trouton's rule

Predict the standard molar enthalpy of vaporization of bromine given that it boils at 59.2 °C.

Method We need to judge whether there is the likelihood of anomalous structural organization in the liquid phase or some anomaly in the gas phase. If there is not, it is permissible to use Trouton's rule in the form

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

Answer 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 would seem safe to use Trouton's rule. Substitution of the data then gives

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

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

Self-test 4.3 Predict the enthalpy of vaporization of ethane from its boiling point, −88.6 °C.

[$+16\ \mathrm{kJ\,mol^{-1}}$]

### *(b) The expansion of a perfect gas*

We established in Example 4.1 that the change in entropy of a perfect gas that expands isothermally from $V_i$ to $V_f$ is

$$\Delta S = nR\ln\left(\frac{V_f}{V_i}\right) \qquad (17)^{\circ}$$

Because $S$ is a state function, this expression applies whether the change of state occurs reversibly or irreversibly.

If the change is reversible, the entropy change in the surroundings (which are in thermal and mechanical equilibrium with the system) must be such as to give $\Delta S_{\text{tot}} = 0$. Therefore, in this case, the change of entropy of the surroundings is the negative of the expression in eqn 17. If the expansion occurs freely ($w = 0$) and irreversibly, and if the temperature remains constant, then $q = 0$. Consequently, $\Delta S_{\text{sur}} = 0$, and the total entropy change is given by eqn 17.

## *(c) The variation of entropy with temperature*

Equation 3 can be used to calculate the entropy of a system at a temperature $T_f$ from a knowledge of its entropy at a temperature $T_i$ and the heat supplied to change its temperature from one value to the other:

$$S(T_f) = S(T_i) + \int_i^f \frac{dq_{\text{rev}}}{T} \tag{18}$$

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 2.27),

$$dq_{\text{rev}} = C_p\, dT$$

so long as the system is doing no non-expansion work. Consequently, at constant pressure:

$$S(T_f) = S(T_i) + \int_i^f \frac{C_p\, dT}{T} \tag{19}$$

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, we obtain

$$S(T_f) = S(T_i) + C_p \int_i^f \frac{dT}{T} = S(T_i) + C_p \ln\left(\frac{T_f}{T_i}\right) \tag{20}$$

with a similar expression for heating at constant volume.

### Example 4.3 Calculating the entropy change

Calculate the entropy change when argon at 25°C and 1.00 atm in a container of volume 500 cm$^3$ is allowed to expand to 1000 cm$^3$ 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 17 and that of the second step, provided $C_V$ is independent of temperature, by eqn 20 (with $C_V$ in place of $C_p$). In each case we need to know $n$, the amount of gas, and can calculate it from the perfect gas equation and the data for the initial state. The heat capacity at constant volume can be obtained from the value of $C_{p,\text{m}}$ in Table 2.6 and the relation $C_{p,\text{m}} - C_{V,\text{m}} = R$.

Answer The amount of Ar present (from $n = pV/RT$) is 0.0204 mol. The entropy change in the first step (expansion from 500 cm$^3$ to 1000 cm$^3$ at 298 K) is

$$\Delta S = nR \ln 2.00 = +0.118\ \text{J K}^{-1}$$

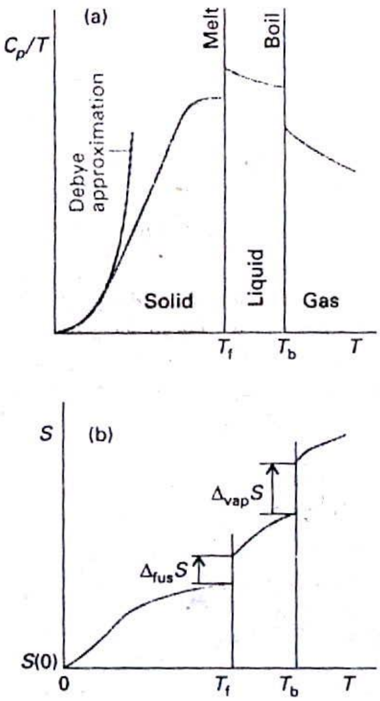
The entropy change in the second step, from 298 K to 373 K at constant volume, is

$$\Delta S = (0.0204\ \text{mol}) \times (12.48\ \text{J K}^{-1}\,\text{mol}^{-1}) \times \ln\left(\frac{373\ \text{K}}{298\ \text{K}}\right) = +0.057\ \text{J K}^{-1}$$

The overall entropy change, the sum of these two changes, is $\Delta S = +0.175\ \text{J K}^{-1}$

Self-test 4.4 Calculate the entropy change when the same initial sample is compressed to $50.0\ \text{cm}^3$ and cooled to $-25\,^\circ\text{C}$.

$[-0.44\ \text{J K}^{-1}]$



4.10 The determination 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.

## *(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 19. The entropy of transition ($\Delta_{trs}H/T_{trs}$) must be added for each phase transition between $T = 0$ and the temperature of interest. For example, if a substance melts at $T_f$ and boils at $T_b$, then its entropy above its boiling temperature is given by

$$S(T) = S(0) + \int_0^{T_f} \frac{C_p(\text{s})\,\text{d}T}{T} + \frac{\Delta_{fus}H}{T_f} + \int_{T_f}^{T_b} \frac{C_p(\text{l})\,\text{d}T}{T} + \frac{\Delta_{vap}H}{T_b} + \int_{T_b}^{T} \frac{C_p(\text{g})\,\text{d}T}{T} \qquad (21)$$

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 procedure is illustrated in Fig. 4.10: the area under the curve of $C_p/T$ against $T$ is the integral required. Because $\text{d}T/T = \text{d}\ln T$, an alternative procedure is to evaluate the area under a plot of $C_p$ against $\ln T$.

One problem with the measurement 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 11.1c), 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 $T = 0$.

### Illustration

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

| | $S_m^\ominus/(\text{J K}^{-1}\,\text{mol}^{-1})$ |
|---|---|
| Debye extrapolation | 1.92 |
| Integration, from 10 K to 35.61 K | 25.25 |
| Phase transition at 35.61 K | 6.43 |
| Integration, from 35.61 K to 63.14 K | 23.38 |
| Fusion at 63.14 K | 11.42 |
| Integration, from 63.14 K to 77.32 K | 11.41 |
| Vaporization at 77.32 K | 72.13 |
| Integration, from 77.32 K to 298.15 K | 39.20 |
| Correction for gas imperfection[4] | 0.92 |
| Total | 192.06 |

---

[4] See Section 20.5.

Therefore,

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

……

## Example 4.4 Calculating the entropy at low temperatures

The molar constant-pressure heat capacity of a certain solid at 10 K is 0.43 $\text{J K}^{-1}\ \text{mol}^{-1}$. What is its molar entropy at that temperature?

**Method** Because the temperature is so low, we can assume that the heat capacity varies with temperature as $aT^3$, in which case we can use eqn 19 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

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

**Self-test 4.5** 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.

$[S(T) = S(0) + C_p(T)]$

## 4.4 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 absence of both spatial disorder and thermal motion suggests 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.

### (a) The Nernst heat theorem

The thermodynamic 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 known as the Nernst heat theorem:

> **The entropy change accompanying any physical or chemical transformation approaches zero as the temperature approaches zero: $\Delta S \rightarrow 0$ as $T \rightarrow 0$.**

As an example of the experimental evidence for this law, 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

$$S_{\mathrm{m}}(\alpha) = S_{\mathrm{m}}(\alpha, 0) + 37\ \mathrm{J\,K^{-1}\,mol^{-1}}$$
$$S_{\mathrm{m}}(\beta) = S_{\mathrm{m}}(\beta, 0) + 38\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

These two values imply that, at the transition temperature,

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

On comparing this value with the one above, we conclude that

$$S_{\mathrm{m}}(\alpha, 0) - S_{\mathrm{m}}(\beta, 0) \approx 0$$

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). Hence, *all* perfect crystals may be taken to have zero entropy at $T = 0$. This conclusion is summarized by the **Third Law of thermodynamics**:

> **If the entropy of every element in its most stable state at $T = 0$ is taken as zero, then every substance has a positive entropy which at $T = 0$ may become zero, and which does become zero for all perfect crystalline substances, including compounds.**

**Table 4.3*** Standard Third-Law entropies at 298 K

| | $S^{\ominus}_{\mathrm{m}}/(\mathrm{J\,K^{-1}\,mol^{-1}})$ |
|---|---|
| *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(g) | 126.2 |
| Ammonia, $NH_3$(g) | 192.3 |

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

Note that a non-crystalline perfect state, such as the superfluid state of He (Section 6.3c), is included by the opening phrase.

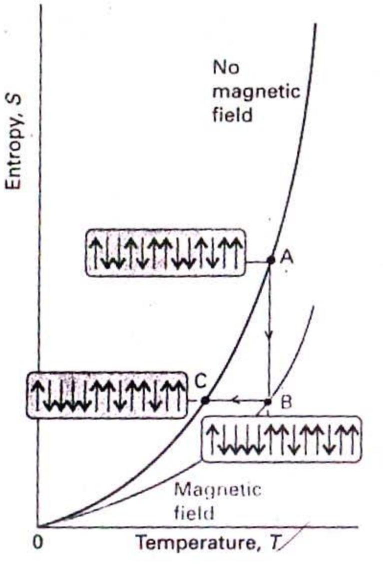
It should also be noted that the Third Law does not state that entropies *are* zero at $T = 0$: it merely implies that all perfect materials have the same entropy at that temperature. As far as thermodynamics is concerned, choosing this common value as zero is then a matter of convenience. The molecular interpretation of entropy, however, implies that $S = 0$ at $T = 0$.

## (b) Third-Law entropies

The choice $S(0) = 0$ for perfect crystals will be made from now on. Entropies reported on the basis of this choice are called **Third-Law entropies** (and often just 'standard 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 4.3.

The **standard reaction entropy**, $\Delta_{\mathrm{r}}S^{\ominus}$, 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:

$$\Delta_{\mathrm{r}}S^{\ominus} = \sum_{\text{Products}} \nu S^{\ominus}_{\mathrm{m}} - \sum_{\text{Reactants}} \nu S^{\ominus}_{\mathrm{m}} \qquad (22a)$$



4.11 The technique of adiabatic demagnetization is used to attain very low temperatures. The upper curve shows the variation of the entropy of a paramagnetic system in the absence of an applied field. The lower curve shows the variation in entropy when a field is applied and has made the electron magnets more orderly. The isothermal magnetization step is from A to B; the adiabatic demagnetization step (at constant entropy) is from B to C.

In this expression, each term is weighted by the appropriate stoichiometric coefficient. More formally, in the notation introduced in eqn 2.41,

$$\Delta_r S^\ominus = \sum_J \nu_J S_m^\ominus(J) \qquad (22b)$$

### Illustration

To calculate the standard reaction entropy of $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ at 25°C, we use the data in Table 2.6 of the *Data section* to write

$$\Delta_r S^\ominus = S_m^\ominus(H_2O, l) - \{S_m^\ominus(H_2, g) + \tfrac{1}{2}S_m^\ominus(O_2, g)\}$$

$$= 69.9 - \{130.7 + \tfrac{1}{2}(205.0)\}\ \mathrm{J\,K^{-1}\,mol^{-1}} = -163.3\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

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

Self-test 4.6 Calculate the standard reaction entropy for the combustion of methane to carbon dioxide and liquid water at 25°C.

[$-243\ \mathrm{J\,K^{-1}\,mol^{-1}}$]

## 4.5 Reaching very low temperatures

The world record low temperature stands at about 20 nK. Gases may be cooled by Joule–Thomson expansion below their inversion temperature, and temperatures lower than 4 K (the boiling point of helium) can be reached by the evaporation of liquid helium by pumping rapidly through large-diameter pipes. Temperatures as low as about 1 K can be reached in this way, but at lower temperatures helium is too involatile for this procedure to be effective; moreover, the superfluid phase begins to interfere with the cooling process by creeping round the apparatus.

The method used to reach very low temperatures is **adiabatic demagnetization**. In the absence of a magnetic field, the unpaired electrons of a paramagnetic material are orientated at random, but in the presence of a magnetic field there are more $\beta$ spins ($m_s = -\frac{1}{2}$; these terms are explained in Section 12.8) than $\alpha$ spins ($m_s = +\frac{1}{2}$). In thermodynamic terms, the application of a magnetic field lowers the entropy of a sample (Fig. 4.11) and, at a given temperature, the entropy of a sample is lower when the field is on than when it is off.

A sample of paramagnetic material, such as a *d*- or *f*-metal complex, is cooled to about 1 K by using helium. Gadolinium(III) sulfate octahydrate, $Gd_2(SO_4)_3 \cdot 8H_2O$, has been used because each gadolinium ion carries several unpaired electrons but is separated from its neighbours by a coordination sphere of hydrating $H_2O$ molecules. The sample is then exposed to a strong magnetic field while it is surrounded by helium, which provides thermal contact with the cold reservoir. This magnetization step is isothermal, and heat leaves the sample as the electron spins adopt the lower energy state (AB in Fig. 4.11). Thermal contact between the sample and the surroundings is now broken by pumping away the helium and the magnetic field is reduced to zero. This step is adiabatic and effectively reversible, so the state of the sample changes from B to C. At the end of this step the sample is the same as it was at A except that it now has a lower entropy. That lower entropy in the absence of a magnetic field corresponds to a lower temperature. That is, adiabatic demagnetization has cooled the sample.

Even lower temperatures can be reached if nuclear spins (which also behave like small magnets) are used instead of electron spins in the technique of **adiabatic nuclear demagnetization**. This technique was used to reach the current world record (in copper).

# Concentrating on the system

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

## 4.6 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 13, reads

$$\mathrm{d}S - \frac{\mathrm{d}q}{T} \geq 0 \tag{23}$$

This inequality can be developed in two ways according to the conditions (of constant volume or constant pressure) under which the process occurs.

First, consider heat transfer at constant volume. Then, in the absence of non-expansion work, we can write $\mathrm{d}q_V = \mathrm{d}U$; consequently

$$\mathrm{d}S - \frac{\mathrm{d}U}{T} \geq 0 \tag{24}$$

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

$$T\,\mathrm{d}S \geq \mathrm{d}U \qquad \text{(constant } V\text{, no non-expansion work)} \tag{25}$$

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

$$\mathrm{d}S_{U,V} \geq 0 \qquad \mathrm{d}U_{S,V} \leq 0 \tag{26}$$

where the subscripts indicate the constant properties.

Equation 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 heat is transferred at constant pressure, and there is no work other than expansion work, we can write $\mathrm{d}q_p = \mathrm{d}H$ and obtain

$$T\,\mathrm{d}S \geq \mathrm{d}H \qquad \text{(constant } p\text{, no non-expansion work)} \tag{27}$$

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

$$\mathrm{d}S_{H,p} \geq 0 \qquad \mathrm{d}H_{S,p} \leq 0 \tag{28}$$

The interpretations of these inequalities are similar to those of eqn 26. The entropy of the system at constant pressure must increase if its enthalpy remains constant (for there can then be no change in entropy of the surroundings). Alternatively, the enthalpy must decrease if the entropy of the system is constant, for then it is essential to have an increase in entropy of the surroundings.

Because eqns 25 and 27 have the forms $\mathrm{d}U - T\,\mathrm{d}S \leq 0$ and $\mathrm{d}H - T\,\mathrm{d}S \leq 0$, respectively, they can be expressed more simply by introducing two more thermodynamic quantities. One is the **Helmholtz energy**, $A$, which is defined as

$$A = U - TS \qquad [29]$$

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

$$G = H - TS \qquad [30]$$

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

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

$$\text{(a)} \quad \mathrm{d}A = \mathrm{d}U - T\,\mathrm{d}S \qquad \text{(b)} \quad \mathrm{d}G = \mathrm{d}H - T\,\mathrm{d}S \tag{31}$$

When we introduce eqns 25 and 27, respectively, we obtain the criteria of spontaneous change as

$$\mathrm{d}A_{T,V} \leq 0 \qquad \mathrm{d}G_{T,p} \leq 0 \tag{32}$$

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

### *(a) Some remarks on the Helmholtz energy*

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

$$\mathrm{d}A_{T,V} = 0 \tag{33}$$

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.

### *(b) Maximum work*

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

$$\mathrm{d}w_{\max} = \mathrm{d}A \tag{34}$$

As a result, $A$ is sometimes called the 'maximum work function', or the 'work function' (*Arbeit* is the German word for work; hence the symbol $A$).

### Justification 4.2

First we prove that a system does maximum work when it is working reversibly. (This conclusion was demonstrated in Section 2.3e for the expansion of a perfect gas; now we prove its universal validity.) 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

$$\mathrm{d}w_{\max} = \mathrm{d}U - T\,\mathrm{d}S$$

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 $\mathrm{d}w_{\max} = \mathrm{d}A$.

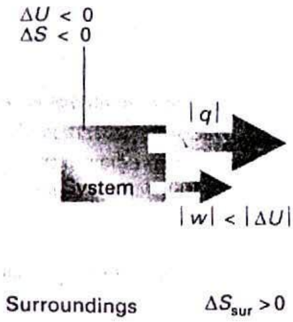
When a macroscopic isothermal change takes place in the system, eqn 34 becomes

$$w_{\max} = \Delta A \tag{35}$$

where

$$\Delta A = \Delta U - T\Delta S \tag{36}$$

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 $\Delta U$ itself, and consequently the maximum work is less than $|\Delta U|$. 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. 4.12). 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 $\Delta A$ is that part of the change in internal energy that we are free to use to do work.

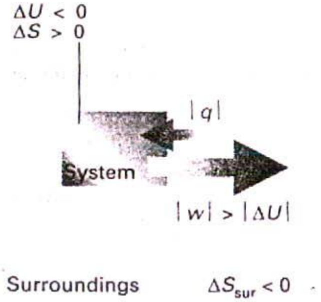


4.12 In a system not isolated from its surroundings, the work done may be different from the change in internal energy. Moreover, the process is spontaneous if, overall, the entropy of the global, isolated system increases. In the process depicted here, the entropy of the system decreases, so that of 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 $|\Delta U|$ can be obtained.

**Molecular interpretation 4.3** Further insight into the relation between the work that a system can do and the Helmholtz energy is to recall that work is energy transferred to the surroundings as the uniform motion of atoms. The expression $A = U - TS$ can be interpreted as showing that $A$ is the total internal energy of the system, $U$, less a contribution that is stored chaotically (the quantity $TS$). Because chaotically stored energy cannot be used to achieve uniform motion in the surroundings, only the part of $U$ that is not stored chaotically, 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 eqn 36 is more negative than $\Delta U$. In this case, the maximum work that can be obtained from the system is greater than $\Delta U$. 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 heat (no more than the value of $T\Delta S$) may leave the surroundings and contribute to the work the change is generating (Fig. 4.13). Nature is now providing a tax refund.



4.13 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 $\Delta U$.

---

### Example 4.5 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

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)$$

calorimetric measurements give $\Delta_r U^\ominus = -2808 \text{ kJ mol}^{-1}$ and $\Delta_r S = +182.4 \text{ J K}^{-1} \text{ mol}^{-1}$ at 25°C. How much of this energy change can be extracted as (a) heat at constant pressure, (b) work?

**Method** We know that the heat released at constant pressure is equal to the value of $\Delta H$, 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 2.26 in the form $\Delta_r H = \Delta_r U + \Delta n_g RT$. For the maximum work available from the process we use eqn 35.

**Answer** (a) Because $\Delta n_g = 0$, we know that $\Delta_r H^\ominus = \Delta_r U^\ominus = -2808 \text{ kJ mol}^{-1}$. Therefore, at constant pressure, the energy available as heat is $2808 \text{ kJ mol}^{-1}$. (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.

**Comment** 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 4.7** Repeat the calculation for the combustion of 1.000 mol $CH_4$(g) under the same conditions, using data from Table 2.5.

$[|q_p| = 890 \text{ kJ}, |w_{max}| = 813 \text{ kJ}]$

---

## (c) Some remarks on the Gibbs energy

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

The existence of spontaneous endothermic reactions provides an illustration of the role of $G$. In such reactions, $H$ increases, the system rises spontaneously to states of higher enthalpy, and $\mathrm{d}H > 0$. 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 $T\,\mathrm{d}S$ is strongly positive and 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 ($\mathrm{d}S_{\mathrm{sur}} = -\mathrm{d}H/T$ at constant pressure).

### *(d) Maximum non-expansion work*

The analogue of the maximum work interpretation of $\Delta A$, and the origin of the name free energy, can be found for $\Delta G$. In the *Justification* below, we show that, at constant temperature and pressure, the maximum *non-expansion* work, $w_{\mathrm{e}}$ (with 'e' denoting 'extra'), is given by the change in Gibbs energy:

$$\mathrm{d}w_{\mathrm{e,max}} = \mathrm{d}G \tag{37}$$

The corresponding expression for a measurable change is

$$w_{\mathrm{e,max}} = \Delta G \tag{38}$$

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 4.3

Because $H = U + pV$, in a general change,

$$\mathrm{d}H = \mathrm{d}q + \mathrm{d}w + \mathrm{d}(pV)$$

When the change is reversible, $\mathrm{d}w = \mathrm{d}w_{\mathrm{rev}}$ and $\mathrm{d}q = \mathrm{d}q_{\mathrm{rev}} = T\,\mathrm{d}S$, so

$$\mathrm{d}G = T\,\mathrm{d}S + \mathrm{d}w_{\mathrm{rev}} + \mathrm{d}(pV) - T\,\mathrm{d}S = \mathrm{d}w_{\mathrm{rev}} + \mathrm{d}(pV)$$

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 non-expansion work we denote $\mathrm{d}w_{\mathrm{e}}$. Therefore, with $\mathrm{d}(pV) = p\,\mathrm{d}V + V\,\mathrm{d}p$,

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

If the change occurs at constant pressure (as well as constant temperature), the last term disappears, and $\mathrm{d}G = \mathrm{d}w_{\mathrm{e,rev}}$. Therefore, at constant temperature and pressure, $\mathrm{d}w_{\mathrm{e,rev}} = \mathrm{d}G$. However, because the process is reversible, the work done must now have its maximum value, so eqn 37 follows.

### **Example 4.6** 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, $w_{\mathrm{e,max}} = -2865$ 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.

**Comment** A person of mass 70 kg would need 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 4.8** How much non-expansion work can be obtained from the combustion of 1.00 mol $CH_4$(g) under standard conditions at 298 K? Use $\Delta_r S^\ominus = -243\ \mathrm{J\,K^{-1}\,mol^{-1}}$.

[818 kJ]

## 4.7 Standard molar Gibbs energies

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

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus \qquad [39]$$

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 Gibbs energy of formation is the standard reaction Gibbs energy for the formation of a compound from its elements in their reference states.**

The reference state of an element was defined in Section 2.7. Standard Gibbs energies of formation of the elements in their reference states are zero, because their formation is a 'null' reaction. A selection of values for compounds is given in Table 4.4. From the values there, it is a simple matter to obtain the standard Gibbs energy of reaction by taking the appropriate combination:

$$\Delta_r G^\ominus = \sum_{\text{Products}} \nu\Delta_f G^\ominus - \sum_{\text{Reactants}} \nu\Delta_f G^\ominus \qquad (40a)$$

with each term weighted by the appropriate stoichiometric coefficient. More formally, in the notation introduced in Section 2.7,

$$\Delta_r G^\ominus = \sum_J \nu_J \Delta_f G^\ominus(\mathrm{J}) \qquad (40b)$$

**Table 4.4*** Standard Gibbs energies of formation at 298 K

| | $\Delta_f G^\ominus/(\mathrm{kJ\,mol^{-1}})$ |
|---|---|
| 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*.

### Illustration

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

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

**Self-test 4.9** Calculate the standard reaction Gibbs energy for the combustion of $CH_4(g)$ at 298 K.

[$-818$ kJ mol$^{-1}$]

Calorimetry (for $\Delta H$ directly, and for $S$ via heat capacities) is only one of the ways of determining the values of Gibbs energies. They may also be obtained from equilibrium constants (Chapter 9) and electrochemical measurements (Chapter 10), and they may be calculated using data from spectroscopic observations (Chapter 20). The information in Tables 2.5 and 2.6 of the *Data section*; however, together with the machinery we shall now construct, is all we need in order to draw far-reaching conclusions about reactions and other processes of interest in chemistry.

## Checklist of key ideas

- ☐ Kelvin statement of Second Law of thermodynamics

### The direction of spontaneous change

#### 4.1 The dispersal of energy

- ☐ spontaneity and the rise of disorder
- ☐ collapse into disorder as the driving force of change

#### 4.2 Entropy

- ☐ Second Law ($\Delta S_{tot} > 0$)
- ☐ thermodynamic definition of entropy
- ☐ entropy change in the surroundings (4,5)
- ☐ entropy change for an adiabatic process
- ☐ Carnot cycle
- ☐ efficiency of a heat engine
- ☐ Carnot efficiency
- ☐ proof that entropy is a state function
- ☐ thermodynamic temperature scale
- ☐ Kelvin scale
- ☐ Clausius inequality
- ☐ entropy as a signpost of spontaneous change
- ☐ spontaneous cooling

#### 4.3 Entropy changes accompanying specific processes

- ☐ entropy of phase transition at the transition temperature
- ☐ Trouton's rule
- ☐ entropy of expansion of a perfect gas
- ☐ variation of entropy with temperature (19,20)
- ☐ measurement of entropy
- ☐ Debye extrapolation

#### 4.4 The Third Law of thermodynamics

- ☐ Nernst heat theorem
- ☐ Third Law of thermodynamics
- ☐ Third-Law entropy
- ☐ standard reaction entropy ($\Delta_r S^\ominus$, 22)

#### 4.5 Reaching very low temperatures

- ☐ adiabatic demagnetization
- ☐ adiabatic nuclear demagnetization

### Concentrating on the system

#### 4.6 The Helmholtz and Gibbs energies

- ☐ the criteria $dS_{U,V} \geq 0$ and $dU_{S,V} \leq 0$
- ☐ Helmholtz energy
- ☐ Gibbs energy
- ☐ the criteria $dA_{T,V} \leq 0$ and $dG_{T,p} \leq 0$
- ☐ the criterion of equilibrium at constant temperature and volume
- ☐ maximum work and the Helmholtz energy (34,35)
- ☐ the criterion of equilibrium at constant temperature and pressure
- ☐ maximum non-expansion work and the Gibbs energy (37,38)

#### 4.7 Standard molar Gibbs energies

- ☐ standard Gibbs energy of reaction ($\Delta_r G^\ominus$, 39)
- ☐ standard Gibbs energy of formation ($\Delta_f G^\ominus$)
- ☐ expressing $\Delta_r G^\ominus$ in terms of $\Delta_f G^\ominus$ (40)

# Further reading

## Articles of general interest

K. Seidman and T.R. Michalik, The efficiency of reversible heat engines: the possible misinterpretation of a corollary to Carnot's theorem. *J. Chem. Educ.* **68**, 208 (1991).

H.B. Hollinger and M.J. Zenzen, Thermodynamic irreversibility: 1. What is it? *J. Chem. Educ.* **68**, 31 (1991).

E.F. Meyer, The Carnot cycle revisited. *J. Chem. Educ.* **65**, 873 (1988).

N.C. Craig, Entropy analyses of four familiar processes. *J. Chem. Educ.* **65**, 760 (1988).

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

J. Waser and V. Schomaker, A note on thermodynamic inequalities. *J. Chem. Educ.* **65**, 393 (1988).

P. Djurdjevic and I. Gutman, A simple method for showing that entropy is a function of state. *J. Chem. Educ.* **65**, 399 (1988).

W.H. Cropper, Walther Nernst and the last law. *J. Chem. Educ.* **64**, 3 (1988).

L. Glasser, Order, chaos, and all that! *J. Chem. Educ.* **66**, 997 (1989).

M. Barón, With Clausius from energy to entropy. *J. Chem. Educ.* **66**, 1001 (1989).

D.F.R. Gilson, Order and disorder and entropies of fusion. *J. Chem. Educ.* **69**, 23 (1992).

R.S. Ochs, Thermodynamics and spontaneity. *J. Chem. Educ.* **73**, 952 (1996).

N.C. Craig, Entropy diagrams. *J. Chem. Educ.* **73**, 710 (1996).

H. Frohlich, On the entropy change of surroundings of finite and infinite size. *J. Chem. Educ.* **73**, 716 (1996).

F.J. Hale, Heat engines and refrigerators. In *Encyclopedia of applied physics* (ed. G.L. Trigg), **7**, 383. VCH, New York (1993).

## Texts and sources of data and information

P.W. Atkins, *The second law*. Scientific American Books, New York (1994).

J.B. Fenn, Engines, energy, and entropy. W.H. Freeman & Co, New York (1982).

J.M. Smith and H.C. Van Ness, *Introduction to chemical engineering thermodynamics*. McGraw-Hill, New York (1987).

K.E. Bett, J.S. Rowlinson, and G. Saville, *Thermodynamics for chemical engineers*. MIT Press, Cambridge (1975).

# Exercises

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

**4.1 (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.

**4.1 (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.

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

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

**4.3 (a)** A sample consisting of 1.00 mol of a monatomic perfect gas with $C_{V,\mathrm{m}} = \frac{3}{2}R$ is heated from 100°C to 300°C at constant pressure. Calculate $\Delta S$ (for the system).

**4.3 (b)** A sample consisting of 1.00 mol of a diatomic perfect gas with $C_{V,\mathrm{m}} = \frac{5}{2}R$ is heated from 0°C to 100°C at constant pressure. Calculate $\Delta S$ (for the system).

**4.4 (a)** Calculate $\Delta S$ (for the system) when the state of 3.00 mol of a monatomic perfect gas, 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 $\Delta S$?

**4.4 (b)** Calculate $\Delta S$ (for the system) when the state of 2.00 mol of a diatomic perfect gas, 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 $\Delta S$?

**4.5 (a)** A sample consisting of 3.00 mol of a diatomic perfect gas at 200 K is compressed reversibly and adiabatically until its temperature reaches 250 K. Given that $C_{V,\mathrm{m}} = 27.5\ \mathrm{J\,K^{-1}\,mol^{-1}}$, calculate $q$, $w$, $\Delta U$, $\Delta H$, and $\Delta S$.

**4.5 (b)** A sample consisting of 2.00 mol of a diatomic perfect gas at 250 K is compressed reversibly and adiabatically until its temperature reaches 300 K. Given that $C_{V,\mathrm{m}} = 27.5\ \mathrm{J\,K^{-1}\,mol^{-1}}$, calculate $q$, $w$, $\Delta U$, $\Delta H$, and $\Delta S$.

**4.6 (a)** Calculate the increase in entropy when 1.00 mol of a monatomic perfect gas with $C_{p,\mathrm{m}} = \frac{5}{2}R$, is heated from 300 K to 600 K and simultaneously expanded from 30.0 L to 50.0 L.

**4.6 (b)** Calculate the increase in entropy when 3.50 mol of a monatomic perfect gas with $C_{p,\mathrm{m}} = \frac{5}{2}R$, is heated from 250 K to 700 K and simultaneously expanded from 20.0 L to 60.0 L.

**4.7 (a)** A system undergoes a process in which the entropy change is $+2.41\ \mathrm{J\,K^{-1}}$. During the process, 1.00 kJ of heat is added to the system at 500 K. Is the process thermodynamically reversible? Explain your reasoning.

**4.7 (b)** A system undergoes a process in which the entropy change is $+5.51\ \mathrm{J\,K^{-1}}$. During the process, 1.50 kJ of heat is added to the system at 350 K. Is the process thermodynamically reversible? Explain your reasoning.

**4.8 (a)** A sample of aluminium of mass 1.75 kg is cooled at constant pressure from 300 K to 265 K. Calculate (a) the energy that must be removed as heat and (b) the change in entropy of the sample.

**4.8 (b)** A sample of copper of mass 2.75 kg is cooled at constant pressure from 330 K to 275 K. Calculate (a) the energy that must be removed as heat and (b) the change in entropy of the sample.

**4.9 (a)** A sample of methane gas of mass 25 g at 250 K and 18.5 atm expands isothermally until its pressure is 2.5 atm. Calculate the change in entropy of the gas.

**4.9 (b)** A sample of nitrogen gas of mass 35 g at 230 K and 21.1 atm expands isothermally until its pressure is 4.3 atm. Calculate the change in entropy of the gas.

**4.10 (a)** A sample of perfect gas that initially occupies 15.0 L at 250 K and 1.00 atm is compressed isothermally. To what volume must the gas be compressed to reduce its entropy by $5.0\ \mathrm{J\,K^{-1}}$?

**4.10 (b)** A sample of perfect gas that initially occupies 11.0 L at 270 K and 1.20 atm is compressed isothermally. To what volume must the gas be compressed to reduce its entropy by $3.0\ \mathrm{J\,K^{-1}}$?

**4.11 (a)** Calculate the change in entropy when 50 g of water at 80°C is poured into 100 g of water at 10°C in an insulated vessel given that $C_{p,\mathrm{m}} = 75.5\ \mathrm{J\,K^{-1}\,mol^{-1}}$.

**4.11 (b)** Calculate the change in entropy when 25 g of ethanol at 50°C is poured into 70 g of ethanol at 10°C in an insulated vessel, given that $C_{p,\mathrm{m}} = 111.5\ \mathrm{J\,K^{-1}\,mol^{-1}}$.

**4.12 (a)** Calculate $\Delta H$ and $\Delta S_{\mathrm{tot}}$ 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 $0.385\ \mathrm{J\,K^{-1}\,g^{-1}}$ and may be assumed constant over the temperature range involved.

**4.12 (b)** Calculate $\Delta H$ and $\Delta S_{\mathrm{tot}}$ 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 $0.449\ \mathrm{J\,K^{-1}\,g^{-1}}$ and may be assumed constant over the temperature range involved.

**4.13 (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 $10.0\ \mathrm{cm^2}$. 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 $C_{V,\mathrm{m}} = 28.8\ \mathrm{J\,K^{-1}\,mol^{-1}}$ and calculate (a) $q$, (b) $w$, (c) $\Delta U$, (d) $\Delta T$, (e) $\Delta S$.

**4.13 (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 $100.0\ \mathrm{cm^2}$. 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 $C_{V,\mathrm{m}} = 28.8\ \mathrm{J\,K^{-1}\,mol^{-1}}$, and calculate (a) $q$, (b) $w$, (c) $\Delta U$, (d) $\Delta T$, (e) $\Delta S$.

**4.14 (a)** The enthalpy of vaporization of chloroform ($CHCl_3$) is $29.4\ \mathrm{kJ\,mol^{-1}}$ 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.

**4.14 (b)** The enthalpy of vaporization of methanol is $35.27\ \mathrm{kJ\,mol^{-1}}$ 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.

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

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

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

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

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

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

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

**4.16 (a)** Combine the reaction entropies calculated in Exercise 4.15a with the reaction enthalpies, and calculate the standard reaction Gibbs energies at 298 K.

**4.16 (b)** Combine the reaction entropies calculated in Exercise 4.15b with the reaction enthalpies, and calculate the standard reaction Gibbs energies at 298 K.

**4.17 (a)** Use standard Gibbs energies of formation to calculate the standard reaction Gibbs energies at 298 K of the reactions in Exercise 4.15a.

**4.17 (b)** Use standard Gibbs energies of formation to calculate the standard reaction Gibbs energies at 298 K of the reactions in Exercise 4.15b.

**4.18 (a)** Calculate the standard Gibbs energy of the reaction $4HCl(g) + O_2(g) \rightarrow 2Cl_2(g) + 2H_2O(l)$ at 298 K, from the standard entropies and enthalpies of formation given in Table 2.6.

**4.18 (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 Tables 2.5 and 2.6.

**4.19 (a)** The standard enthalpy of combustion of solid phenol ($C_6H_5OH$) is $-3054\ \mathrm{kJ\,mol^{-1}}$ at 298 K and its standard molar entropy is $144.0\ \mathrm{J\,K^{-1}\,mol^{-1}}$. Calculate the standard Gibbs energy of formation of phenol at 298 K.

**4.19 (b)** The standard enthalpy of combustion of solid urea ($CO(NH_2)_2$) is $-632\ \mathrm{kJ\,mol^{-1}}$ at 298 K and its standard molar entropy is $104.60\ \mathrm{J\,K^{-1}\,mol^{-1}}$. Calculate the standard Gibbs energy of formation of urea at 298 K.

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

**4.20 (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 L to 4.60 L in (a) an isothermal reversible expansion, (b) an isothermal irreversible expansion against $p_{ex} = 0$, and (c) an adiabatic reversible expansion.

**4.21 (a)** Calculate the change in entropy when a monatomic perfect gas is compressed to half its volume and simultaneously heated to twice its initial temperature.

**4.21 (b)** Calculate the change in entropy when a diatomic perfect gas is compressed to one-third its volume and simultaneously heated to three times its initial temperature.

**4.22 (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.

**4.22 (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.

**4.23 (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.

**4.23 (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 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?

## Problems

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

### Numerical problems

**4.1** 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 $37.3\ \mathrm{J\,K^{-1}\,mol^{-1}}$ and $-41.9\ \mathrm{J\,K^{-1}\,mol^{-1}}$, 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.

**4.2** The heat capacity of chloroform (trichloromethane, $CHCl_3$) in the range 240 K to 330 K is given by $C_{p,m}/(\mathrm{J\,K^{-1}\,mol^{-1}}) = 91.47 + 7.5 \times 10^{-2}(T/\mathrm{K})$. 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.

**4.3** A block of copper of mass 2.00 kg ($C_{p,s} = 0.385\ \mathrm{J\,K^{-1}\,g^{-1}}$) 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.)

**4.4** Consider a perfect gas contained in a cylinder and separated by a frictionless adiabatic piston into two sections A and B. All changes in B are isothermal, that is, a thermostat surrounds B to keep its temperature constant. There is 2.00 mol of the gas in each section. Initially, $T_A = T_B = 300\ \mathrm{K}$, $V_A = V_B = 2.00\ \mathrm{L}$. Heat is added to Section A and the piston moves to the right reversibly until the final volume of Section B is 1.00 L. Calculate (a) $\Delta S_A$ and $\Delta S_B$, (b) $\Delta A_A$ and $\Delta A_B$, (c) $\Delta G_A$ and $\Delta G_B$, (d) $\Delta S$ 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 $C_{V,m} = 20\ \mathrm{J\,K^{-1}\,mol^{-1}}$.)

**4.5** 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 $q$, $w$, $\Delta U$, $\Delta H$, $\Delta S$, and $\Delta S_{tot}$ for each stage of the cycle and for the cycle as a whole. Express your answer as a table of values.

**4.6** 1.00 mol of a perfect gas 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 $q$, $w$, $\Delta U$, $\Delta H$, $\Delta S$, $\Delta S_{surr}$, and $\Delta S_{tot}$ for each path.

**4.7** A sample of 1.00 mol of a monatomic perfect gas at 27°C and 1.00 atm is expanded adiabatically in two ways: (a) reversibly to 0.50 atm, and (b) against a constant external pressure of 0.50 atm. Determine the values of $q$, $w$, $\Delta U$, $\Delta H$, $\Delta S$, $\Delta S_{surr}$, and $\Delta S_{tot}$ for each path where the data permit. Take $C_{V,m} = \frac{3}{2}R$.

**4.8** A sample of 1.00 mol of a monatomic perfect gas with $C_{V,m} = \frac{3}{2}R$, initially at 298 K and 10 L, is expanded, with the surroundings maintained at 298 K, to a final volume of 20 L, in three ways: (a) isothermally and reversibly, (b) isothermally against a constant external pressure of 0.50 atm, (c) adiabatically against a constant external pressure of 0.50 atm. Calculate $\Delta S$, $\Delta S_{surr}$, $\Delta H$, $\Delta T$, $\Delta A$, and $\Delta G$ for each path. If a numerical answer cannot be obtained from the data, write +, or −, or ? as appropriate.

**4.9** 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 2.30 with the coefficients given in Table 2.2. Calculate the standard molar entropy at (a) 100°C and (b) 500°C.

**4.10** 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.

**4.11** Calculate the standard Helmholtz energy of formation, $\Delta_f A$, of $CH_3OH(l)$ at 298 K from the standard Gibbs energy of formation and the assumption that $H_2$ and $O_2$ are perfect gases.

**4.12** Calculate the change in entropy when 200 g of (a) water at 0°C, (b) ice at 0°C is added to 200 g of water at 90°C in an insulated container.

**4.13** Calculate (a) the maximum work and (b) the maximum non-expansion work that can be obtained from the freezing of supercooled water at −5°C and 1.0 atm. The densities of water and ice are 0.999 $g\,cm^{-3}$ and 0.917 $g\,cm^{-3}$, respectively, at −5°C.

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

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

**4.15** 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?

**4.16** 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 $CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$. Assume that the heat capacities are constant over the temperature range involved.

**4.17** The standard reaction Gibbs energy of

$$K_4[Fe(CN)_6]\cdot 3H_2O(s) \longrightarrow 4K^+(aq) + [Fe(CN)_6]^{4-}(aq) + 3H_2O(l)$$

is +26.120 $kJ\,mol^{-1}$ (I.R. Malcolm, L.A.K. Staveley, and R.D. Worswick, *J. Chem. Soc. Faraday Trans. I*, 1532 (1973). The enthalpy of solution of the trihydrate is +55.000 $kJ\,mol^{-1}$. Calculate (a) the standard molar entropy of the hexacyanoferrate(II) ion in water and (b) the standard reaction entropy given that the standard molar entropy of the solid trihydrate is 599.7 $J\,K^{-1}\,mol^{-1}$ and that of the $K^+$ ion in water is 102.5 $J\,K^{-1}\,mol^{-1}$.

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

| $T/K$ | $C_{p,m}/(J\,K^{-1}\,mol^{-1})$ | $T/K$ | $C_{p,m}/(J\,K^{-1}\,mol^{-1})$ |
|---|---|---|---|
| 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.

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

| | | | | | | |
|---|---|---|---|---|---|---|
| $T/K$ | 14.14 | 16.33 | 20.03 | 31.15 | 44.08 | 64.81 |
| $C_{p,m}/(J\,K^{-1}\,mol^{-1})$ | 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 |
| $C_{p,m}/(J\,K^{-1}\,mol^{-1})$ | 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 entropy of the compound at these temperatures.

## Theoretical problems

**4.20** Show that the integral of $dq_{rev}/T$ round a Carnot cycle is zero. Then show that the integral is negative if the isothermal reversible expansion stage is replaced by an isothermal irreversible expansion.

**4.21** 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.)

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

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

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

**4.25** 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, $V = 4.00\ \mathrm{L}$, $p = 1.00\ \mathrm{atm}$, and $T = 300\ \mathrm{K}$, that $V_\mathrm{A} = 10V_\mathrm{B}$, $p_\mathrm{C}/p_\mathrm{B} = 5$, and that $C_{p,\mathrm{m}} = \frac{7}{2}R$.

**4.26** 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.

**4.27** The definitions of the enthalpy, Gibbs energy, and Helmholtz energy have all been of the form $g = f + yz$. Show that the addition of the product $yz$ is a general way of converting a function of $x$ and $y$ to a function of $x$ and $z$ in the sense that, if $\mathrm{d}f = a\,\mathrm{d}x - z\,\mathrm{d}y$, then $\mathrm{d}g = a\,\mathrm{d}x + y\,\mathrm{d}z$.

## Additional problems supplied by Carmen Giunta and Charles Trapp

**4.28** Alkyl radicals are important intermediates in the combustion and atmospheric chemistry of hydrocarbons. N. Cohen reports group additivity tables for the thermochemistry of alkyl free radicals (N. Cohen, *J. Phys. Chem.* **96**, 9052 (1992)). A portion of the table follows. Use the table to estimate the standard molar entropies of $C_2H_5$, *sec*-$C_4H_9$, and *tert*-$C_4H_9$. Note that $S_\mathrm{m}^\ominus = S_\mathrm{int}^\ominus - R\ln s$, where $S_\mathrm{int}^\ominus$ is the so-called intrinsic molar entropy, computed by group additivity and $s$ is a symmetry number. ($s = 6$ for $C_2H_5$, $3^2$ for *sec*-$C_4H_9$, and $3^4$ for *tert*-$C_4H_9$.)

| Group | $S_\mathrm{int}^\ominus/(\mathrm{J\,K^{-1}\,mol^{-1}})$ |
|---|---|
| $\mathrm{C{-}(C)(H)_3}$ | 126.8 |
| $\mathrm{\cdot C{-}(C)(H)_2}$ | 135.9 |
| $\mathrm{\cdot C{-}(C)_2(H)}$ | 59.3 |
| $\mathrm{\cdot C{-}(C)_3}$ | −29.2 |
| $\mathrm{C{-}(\cdot C)(H)_3}$ | 126.8 |
| $\mathrm{C{-}(\cdot C)(C)(H)_2}$ | 42.0 |

**4.29** Use the following enthalpies of formation reported by Seakins *et al.* (P.W. Seakins, M.J. Pilling, J.T. Niiranen, D. Gutman, and L.N. Krasnoperov, *J. Phys. Chem.* **96**, 9847 (1992)) and entropies based on group additivity tables of Cohen (N. Cohen, *J. Phys. Chem.* **96**, 9052 (1992)) to compute $\Delta_\mathrm{r}G^\ominus$ for three possible fates of the *tert*-butyl radical at 700 K, 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 | $\Delta_\mathrm{f}H^\ominus/(\mathrm{kJ\,mol^{-1}})$ | $S_\mathrm{m}^\ominus/(\mathrm{J\,K^{-1}\,mol^{-1}})$ |
|---|---|---|
| $C_2H_5$ | +121.0 | 247.8 |
| *sec*-$C_4H_9$ | +67.5 | 336.6 |
| *tert*-$C_4H_9$ | +51.3 | 314.6 |

**4.30** Given that $S_\mathrm{m}^\ominus = 29.79\ \mathrm{J\,K^{-1}\,mol^{-1}}$ for bismuth at 100 K and the following tabulated heat capacity data (D.G. Archer, *J. Chem. Eng. Data* **40**, 1015 (1995)), compute the standard molar entropy of bismuth at 200 K.

| $T/\mathrm{K}$ | 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 this 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.

**4.31** Consider a Carnot engine operating in outer space between the temperatures $T_\mathrm{h}$ and $T_\mathrm{c}$. The only way that the engine can discard heat at $T_\mathrm{c}$ is by radiation. The power radiated by the engine at $T_\mathrm{c}$ follows the Stefan–Boltzmann law (see Section 11.1), which for our purposes here is written $\mathrm{d}q_\mathrm{c}/\mathrm{d}t = kAT_\mathrm{c}^4$, where $k$ is a constant related to the Stefan–Boltzmann constant. Find the ratio $T_\mathrm{c}/T_\mathrm{h}$ that corresponds to a minimum area $A$ of the radiator for a fixed power output and constant $T_\mathrm{h}$.

**4.32** Polytropic processes are those that satisfy the relation $pV^n = C$. Make schematic plots of polytropic processes on a $pV$ and $TS$ diagram for $n = 0, \pm 1, \gamma$ (the heat capacity ratio), and $\pm\infty$.

# 5

# The Second Law: the machinery

*One of the principal applications 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. These expressions will prove useful later when we need to discuss the effect of temperature and pressure on equilibrium constants. This chapter also introduces the chemical potential, a property that will be at the centre of discussions in the remaining chapters of this part of the text. We shall also see how to formulate expressions that are valid for real gases.*

The Gibbs energy, $G$, is of central importance to chemistry, and in this chapter it begins to move to the centre of the stage. We shall also meet the 'chemical potential', the quantity on which almost all the most important applications of thermodynamics to chemistry are based.

## Combining the First and Second Laws

We have seen that the First Law of thermodynamics may be written

$$dU = dq + dw \qquad (1)$$

For a reversible change in a closed system of constant composition, and in the absence of any non-expansion work,

$$dw_{\text{rev}} = -p\,dV \qquad dq_{\text{rev}} = T\,dS$$

Therefore,

$$dU = T\,dS - p\,dV \qquad (2)$$

However, because $dU$ is an exact differential, its value is independent of path. Therefore, the same value of $dU$ is obtained whether the change is brought about irreversibly or reversibly. Consequently, eqn 2 applies to any change—reversible or irreversible—of a closed system that does no 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 $T\,dS$ be identified with $dq$ and $-p\,dV$ with $dw$. When the change is irreversible, $T\,dS > dq$ (the Clausius inequality) and $-p\,dV > dw$. The sum of $dw$ and $dq$ remains equal to the sum of $T\,dS$ and $-p\,dV$, provided the composition is constant.

## 5.1 Properties of the internal energy

Equation 2 shows that the internal energy of a closed system changes in a simple way when $S$ and $V$ are changed ($dU \propto dS$ and $dU \propto dV$). These simple proportionalities suggest that $U$ should be regarded as a function of $S$ and $V$. We could regard $U$ as a function of other variables, such as $S$ and $p$ or $T$ and $V$, because they are all interrelated; but the simplicity of the fundamental equation suggests that $U(S, V)$ is the best choice.

The mathematical consequence of $U$ being a function of $S$ and $V$ is that a change $dU$ can be expressed in terms of the changes $dS$ and $dV$ by[1]

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \tag{3}$$

This expression states that the change in $U$ is proportional to the change in $S$ and to the change in $V$, the two coefficients being the slopes of the plots of $U$ against $S$ and $V$, respectively. When this expression is compared to the thermodynamic relation, eqn 2, we see that, for systems of constant composition,

$$\left(\frac{\partial U}{\partial S}\right)_V = T \qquad \left(\frac{\partial U}{\partial V}\right)_S = -p \tag{4}$$

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

### *(a) The Maxwell relations*

Because the fundamental equation, eqn 2, is an expression for an exact differential, the coefficients of $dS$ and $dV$ must pass the test for exact differentials (see *Further information 1*). That is,

$$df = g\,dx + h\,dy \text{ is exact if } \left(\frac{\partial g}{\partial y}\right)_x = \left(\frac{\partial h}{\partial x}\right)_y \tag{5}$$

Therefore, because we know that $dU = T\,dS - p\,dV$ is exact, it must be the case that

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \tag{6}$$

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

The equation just derived 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, the fact that $H$, $G$, and $A$ are all state functions can be used to derive three more Maxwell relations. The argument to obtain

---

[1] For a review of partial differential properties, see *Further information 1*.

Table 5.1 The Maxwell relations

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

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

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

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

them runs in the same way in each case: because $H$, $G$, and $A$ are state functions, the expressions for $\mathrm{d}H$, $\mathrm{d}G$, and $\mathrm{d}A$ satisfy the relation like eqn 6. All four relations are listed in Table 5.1. In the next section we derive one of them, but as no new principles are involved we shall not derive them all.

## (b) The variation of internal energy with volume

The coefficient we have called the internal pressure,

$$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T \qquad [7]$$

played a central role in the manipulation of the First Law, and in *Justification* 3.2 we used the relation

$$\pi_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \qquad (8)$$

This relation is called a **thermodynamic equation of state** because it expresses a quantity in terms of the two variables $T$ and $p$ and applies to any substance. We are now ready to derive it from the equations we have just established.

We can obtain the coefficient $\pi_T$ by dividing both sides of eqn 3 by $\mathrm{d}V$, imposing the constraint of constant temperature, and then introducing the two relations in eqn 4:

$$\begin{aligned}\left(\frac{\partial U}{\partial V}\right)_T &= \left(\frac{\partial U}{\partial S}\right)_V\left(\frac{\partial S}{\partial V}\right)_T + \left(\frac{\partial U}{\partial V}\right)_S\\ &= T\left(\frac{\partial S}{\partial V}\right)_T - p\end{aligned}$$

This equation is already beginning to look like the expression we want. One of the Maxwell relations does the job of turning $(\partial S/\partial V)_T$ into something else:

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

The substitution of this relation completes the proof of eqn 8.

### Example 5.1 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 8. 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 8.

**Answer** Because $(\partial p/\partial T)_V = nR/V$ for a perfect gas (by differentiation of the equation of state), eqn 8 becomes

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

The equation of state of a van der Waals gas is

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

Therefore, because $a$ and $b$ are independent of temperature, we can write

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

That is,

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

Comment This result for $\pi_T$ 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.

Self-test 5.1 Calculate $\pi_T$ for a gas that obeys the virial equation of state.
[$\pi_T = RT^2(\partial B/\partial T)_V/V_m^2 + \cdots$]

## 5.2 Properties of the Gibbs energy

The same arguments that were applied to the fundamental equation for $U$ may be applied to the Gibbs energy $G = H - TS$. When the system undegoes a change of state, $G$ may change because $H$, $T$, and $S$ change. For infinitesimal changes in each property,

$$dG = dH - T\,dS - S\,dT$$

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

$$dH = dU + p\,dV + V\,dp$$

For a closed system doing no non-expansion work, $dU$ can be replaced by the fundamental equation $dU = T\,dS - p\,dV$. The result of these steps is

$$dG = (T\,dS - p\,dV) + p\,dV + V\,dp - T\,dS - S\,dT$$

That is, for a closed system in the absence of non-expansion work and at constant composition

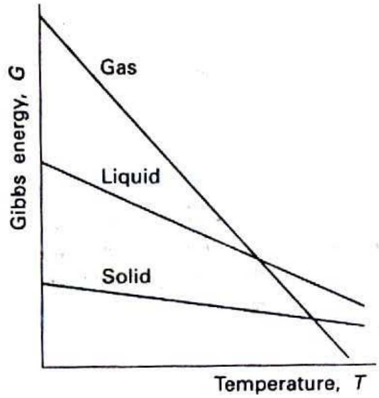
$$dG = V\,dp - S\,dT \tag{9}$$

This expression, which shows that a change in $G$ is proportional to changes in $p$ and $T$, 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 4, when applied to the exact differential $dG$, now gives

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \qquad \left(\frac{\partial G}{\partial p}\right)_T = V \tag{10}$$

These relations show how the Gibbs energy varies with temperature and pressure. Because $S$ is positive, it follows that $G$ decreases when the temperature is raised at constant pressure and composition. Moreover, the relation shows that $G$ 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



5.1 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.

and solid phases (Fig. 5.1). Because $V$ is positive, $G$ always increases when the pressure of the system is increased at constant temperature (and composition). Because the molar volumes of gases are large, $G$ is more sensitive to pressure for the gaseous phase of a substance than for its liquid and solid phases (Fig. 5.2).

## Example 5.2 Calculating the effect of pressure on the Gibbs energy

Calculate the change in the molar Gibbs energy of (a) liquid water treated as an incompressible fluid and (b) water vapour treated as a perfect gas, when the pressure is increased isothermally from 1.0 bar to 2.0 bar at 298 K.

**Method** In each case, the change in molar Gibbs energy can be obtained by integration of eqn 9 with the temperature held constant (that is, setting $\mathrm{d}T = 0$):

$$G_\mathrm{m}(p_\mathrm{f}) - G_\mathrm{m}(p_\mathrm{i}) = \int_{p_\mathrm{i}}^{p_\mathrm{f}} V_\mathrm{m}\,\mathrm{d}p$$

For an incompressible fluid, the molar volume is independent of the pressure, so $V_\mathrm{m}$ can be treated as a constant. For a perfect gas, the molar volume varies with pressure as $V_\mathrm{m} = RT/p$, so this expression must be used in the integrand, and the integration performed treating $RT$ as a constant.

**Answer** For the incompressible liquid, $V_\mathrm{m}$ is constant at 18.0 cm$^3$ mol$^{-1}$, so

$$\begin{aligned}G_\mathrm{m}(p_\mathrm{f}) - G_\mathrm{m}(p_\mathrm{i}) &= V_\mathrm{m}\int_{p_\mathrm{i}}^{p_\mathrm{f}} \mathrm{d}p = V_\mathrm{m} \times (p_\mathrm{f} - p_\mathrm{i})\\ &= (18.0 \times 10^{-6}\ \mathrm{m^3\,mol^{-1}}) \times (1.0 \times 10^5\ \mathrm{Pa})\\ &= +1.8\ \mathrm{J\,mol^{-1}}\end{aligned}$$

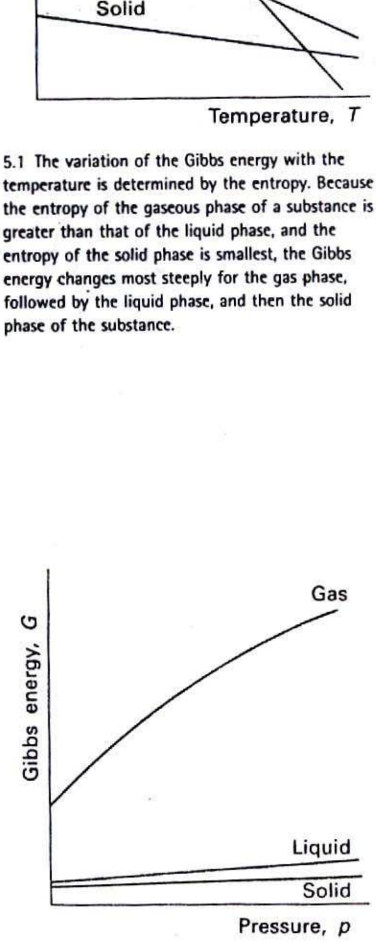
(because $1\ \mathrm{Pa\,m^3} = 1\ \mathrm{N\,m} = 1\ \mathrm{J}$). For a perfect gas:

$$\begin{aligned}G_\mathrm{m}(p_\mathrm{f}) - G_\mathrm{m}(p_\mathrm{i}) &= \int_{p_\mathrm{i}}^{p_\mathrm{f}} \frac{RT}{p}\,\mathrm{d}p = RT\ \ln\left(\frac{p_\mathrm{f}}{p_\mathrm{i}}\right)\\ &= (2.48\ \mathrm{kJ\,mol^{-1}}) \times \ln 2.0 = +1.7\ \mathrm{kJ\,mol^{-1}}\end{aligned}$$

**Comment** Note that $G$ increases in both cases, and that the increase for a gas is about 1000 times greater than for the liquid.

**Self-test 5.2** Calculate the change in $G_\mathrm{m}$ for ice at −10°C when it has density 0.917 g cm$^{-3}$, when the pressure is increased from 1.0 bar to 2.0 bar.

[+2.0 J mol$^{-1}$]



5.2 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 volume 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, they vary by similar amounts as the pressure is changed.

### (a) The temperature dependence of the Gibbs energy

In due course we shall see that the equilibrium composition of a system depends on the Gibbs energy, and that to discuss the response of the composition to temperature it is necessary to know how $G$ varies with temperature. The first expression in eqn 10 is the starting point; although it expresses the variation of $G$ in terms of the entropy, it can be expressed in terms of the enthalpy by using the definition of $G$ to write $S = (H - G)/T$. Then

$$\left(\frac{\partial G}{\partial T}\right)_p = \frac{G - H}{T} \qquad (11)$$

We shall see later that the equilibrium constant of a reaction is related to $G/T$ rather than to $G$ itself,[2] and it turns out the variation of this quantity with temperature is simpler than the temperature variation of $G$ alone. In fact, it is easy to deduce from the last equation (see the *Justification* below) that

$$\left(\frac{\partial}{\partial T}\left(\frac{G}{T}\right)\right)_p = -\frac{H}{T^2} \tag{12}$$

This expression is called the **Gibbs–Helmholtz equation.** ($G$–$H$ is a helpful way of remembering what this equation relates.) It shows that, if the enthalpy of the system is known, then the temperature dependence of $G/T$ is also known.

### Justification 5.1

First, we write eqn 11 as

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

The expression on the left is simplified by noting that

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

When we substitute eqn 11 into this expression, we obtain eqn 12.

### Example 5.3 Manipulating the Gibbs–Helmholtz equation

Show that

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

Method This example is an exercise in manipulating partial differentials. The desired expression resembles the Gibbs–Helmholtz equation, so eqn 12 is a good starting point. To obtain the desired result, we need to convert the variable of differentiation from $T$ to $1/T$, which can be done by standard techniques of manipulating derivatives.

Answer The left-hand side of eqn 12 can be written

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

Substitution of this result into eqn 12 and multiplication of both sides by $-T^2$ gives the expression required.

---

[2] In Section 9.1d we derive the result that the equilibrium constant for a reaction is related to its standard reaction free energy by $\Delta_r G^\ominus/T = -R\ln K$.

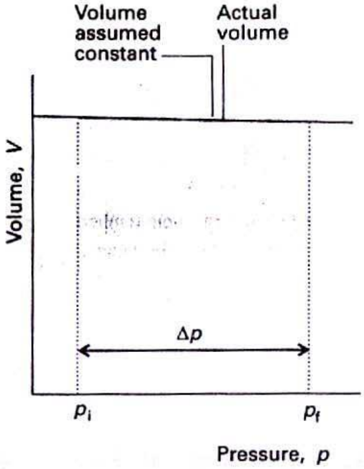
Comment The result shows that, if $H$ is independent of temperature over a range, then a plot of $G/T$ against $1/T$ should be a straight line of slope $H$. We see the usefulness of this result in Chapter 9.

Self-test 5.3 Find the equation for the temperature dependence of $A$ that corresponds to that just derived for $G$.

$[(\partial(A/T)/\partial(1/T))_V = U]$

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, with $\Delta G = G_f - G_i$ for the change of Gibbs energy between the final and initial states, because the equation applies to both $G_f$ and $G_i$, we can write

$$\left(\frac{\partial(\Delta G/T)}{\partial T}\right)_p = -\frac{\Delta H}{T^2} \tag{13}$$



5.3 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.

## (b) The pressure dependence of the Gibbs energy

To find the Gibbs energy at one pressure in terms of its value at another pressure, the temperature being constant, we set $dT = 0$ in eqn 9 and integrate the remaining expression:

$$G(p_f) = G(p_i) + \int_{p_i}^{p_f} V\,dp \tag{14}$$

For a liquid or solid, the volume changes only slightly as the pressure changes (Fig. 5.3), so $V$ may be treated as a constant and taken outside the integral. Then, for molar quantities,

$$\begin{aligned} G_m(p_f) &= G_m(p_i) + V_m(p_f - p_i) \\ &= G_m(p_i) + V_m\Delta p \end{aligned} \tag{15}$$

where $\Delta p = p_f - p_i$. Under normal laboratory conditions $V_m\Delta p$ is very small, as we saw in Example 5.2, 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, we must use the complete expression, eqn 14.

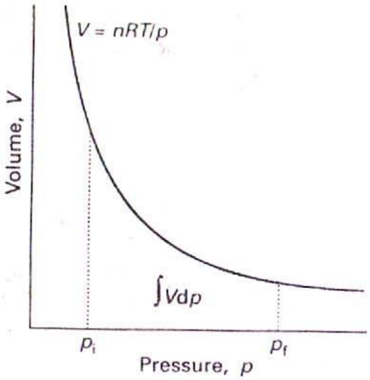
### Illustration

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

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

Self-test 5.4 Calculate the difference in molar Gibbs energy between the top and bottom of a column of mercury in a barometer. The mass density of mercury is 13.6 $\mathrm{g\,cm^{-3}}$.

$[+1.5\ \mathrm{J\,mol^{-1}}]$



5.4 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 may depend 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 14 (Fig. 5.4). For a perfect gas we substitute $V = nRT/p$ into the integral, and find

$$G(p_f) = G(p_i) + nRT\int_{p_i}^{p_f}\frac{\mathrm{d}p}{p} = G(p_i) + nRT\ \ln\left(\frac{p_f}{p_i}\right) \qquad (16)^{\circ}$$

This expression shows that, when the pressure is increased ten-fold at room temperature, the molar Gibbs energy increases by about 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 Gibbs energy of a perfect gas at a pressure $p$ is related to its standard value by

$$G(p) = G^{\ominus} + nRT\ \ln\left(\frac{p}{p^{\ominus}}\right) \qquad (17)^{\circ}$$

## 5.3 The chemical potential of a pure substance

Now we switch attention from the Gibbs energy itself to a quantity, the chemical potential, that is closely related and which will play a central role in all subsequent discussions of equilibrium. First, we introduce the chemical potential of a pure substance, and in particular the chemical potential of a perfect gas. At this stage its introduction will seem to be no more than a change of notation. However, the definition prepares the ground for the introduction (in Section 7.1b) of the chemical potential of a substance in a mixture (including a reaction mixture), which is a powerful and general concept.

The chemical potential, $\mu$, of a pure substance is defined as

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{T,p} \qquad [18]$$

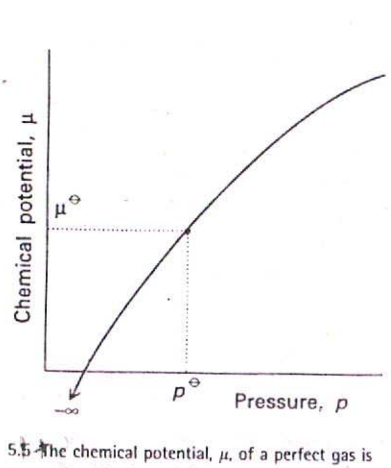
That is, the chemical potential shows how the Gibbs energy of a system changes as a substance is added to it. For a pure substance, the Gibbs energy is simply $G = n \times G_m$, so

$$\mu = \left(\frac{\partial nG_m}{\partial n}\right)_{T,p} = G_m \qquad (19)$$

and the chemical potential is the same as the molar Gibbs energy. For example, the chemical potential of a perfect gas at a pressure $p$ can be written from eqn 17:

$$\mu = \mu^{\ominus} + RT\ \ln\left(\frac{p}{p^{\ominus}}\right) \qquad (20)^{\circ}$$

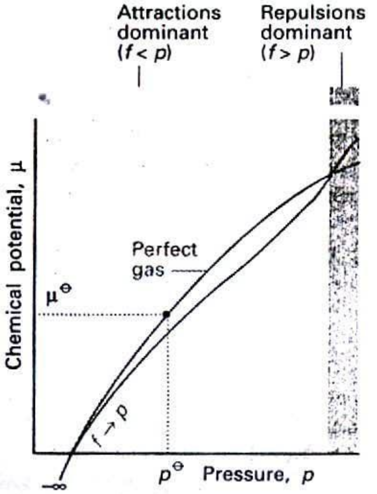
where $\mu^{\ominus}$ is the standard chemical potential, the molar Gibbs energy of the pure gas at 1 bar. The logarithmic variation of the chemical potential with the pressure given by eqn 20 is illustrated in Fig. 5.5.



5.5 The chemical potential, $\mu$, of a perfect gas is proportional to ln $p$, and the standard state is reached at $p^{\ominus}$. Note that, as $p \rightarrow 0$, $\mu$ becomes negatively infinite.

# 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 the idealized system. Then deviations from the idealized behaviour can be expressed most simply. We shall illustrate such a procedure in this section by considering how the expressions that have been derived for perfect gases, particularly eqn 20 for the chemical potential of a perfect gas, are adapted to describe real gases.



5.6 The chemical potential of a real gas. As $p \to 0$, $\mu$ coincides with the value for a perfect gas (shown by the pale line). When attractive forces are dominant (at intermediate pressures), the chemical potential 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 chemical potential of a real gas is greater than that of a perfect gas. Then the 'escaping tendency' is increased.

## 5.4 The definition of fugacity

The pressure dependence of the chemical potential of a real gas might resemble that shown in Fig. 5.6. To adapt eqn 20 to this case, we replace the true pressure, $p$, by an effective pressure, called the **fugacity**, $f$, and write

$$\mu = \mu^{\ominus} + RT \ln\left(\frac{f}{p^{\ominus}}\right) \qquad [21]$$

The name 'fugacity' comes from the Latin for 'fleetness' in the sense of 'escaping tendency'; fugacity has the same dimensions as pressure. In later chapters we derive thermodynamically exact expressions in terms of chemical potentials, and therefore in terms of fugacities. For example, from elementary chemistry we know that the equilibrium constant for a reaction such as $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$ should be written

$$K_p = \frac{p_{HBr}^2}{p_{H_2}p_{Br_2}}$$

where $p_J$ is the partial pressure of substance J; however, this expression is only an approximation. The thermodynamically exact expression is

$$K = \frac{f_{HBr}^2}{f_{H_2}f_{Br_2}}$$

where $f_J$ is the fugacity of J. Although the latter expression is exact, it is useful only if we know how to interpret the fugacities in terms of the partial pressures. This is the task we deal with in the remainder of this chapter.

## 5.5 Standard states of real gases

A perfect gas is in its standard state when its pressure is $p^{\ominus}$ (that is, 1 bar): the pressure arises solely from the kinetic energy of the molecules and there are no intermolecular forces to take into account. We aim to recapture this 'kinetic energy only' definition for the standard state of a real gas by picturing it as a hypothetical state in which all the intermolecular forces have been extinguished:

> **The standard state of a real gas is a hypothetical state in which the gas is at a pressure $p^{\ominus}$ and behaving perfectly.**

The advantage of this definition is that it ensures that the standard state of a real gas has the simple properties of a perfect gas. If we had defined the standard state as the one for which $f = p^{\ominus}$, then the standard states of different gases would have had relatively complex properties. The choice of a hypothetical standard state literally standardizes the interactions between the particles by setting them to zero.[3] Then differences of standard chemical potential of different gases arise solely from the internal structure and properties of the molecules, not from the way they interact with each other.

## 5.6 The relation between fugacity and pressure

We shall write the fugacity as

$$f = \phi p \qquad [22]$$

---

[3] The alternative choice, of selecting as the standard state the gas at zero pressure, at which it certainly behaves perfectly, runs into difficulty because $\mu \to -\infty$ as $p \to 0$.

where $\phi$ is the dimensionless **fugacity coefficient**. In general, $\phi$ depends on the identity of the gas, the pressure, and the temperature. With the introduction of $\phi$, eqn 21 becomes

$$\mu = \mu^{\ominus} + RT \ln (p/p^{\ominus}) + RT \ln \phi \tag{23}$$

As $\mu^{\ominus}$ refers to a hypothetical 'kinetic energy only' gas, and the term $\ln p$ is the same as for a perfect gas, the term $RT \ln \phi$ must express the entire effect of all the intermolecular forces. Because all gases become perfect as the pressure approaches zero (so $f \rightarrow p$ as $p \rightarrow 0$), we know that $\phi \rightarrow 1$ as $p \rightarrow 0$.

We shall now show that, at a general pressure $p$, the fugacity coefficient of a gas is given by the expression

$$\ln \phi = \int_0^p \left(\frac{Z-1}{p}\right) \mathrm{d}p \tag{24}$$

where $Z$ is the compression factor of the gas ($Z = pV_\mathrm{m}/RT$; this quantity was introduced in Section 1.4a). Equation 24 is an explicit expression for the fugacity coefficient at any pressure $p$ and therefore, through eqn 22, for the fugacity of the gas at that pressure.

## Justification 5.2

Equation 14 is true for all gases, whether real or perfect. Expressing it in terms of molar quantities and then using eqn 21 gives

$$\int_{p'}^{p} V_\mathrm{m}\,\mathrm{d}p = \mu - \mu' = RT \ln\left(\frac{f}{f'}\right)$$

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

$$\int_{p'}^{p} V_\mathrm{perfect,m}\,\mathrm{d}p = \mu_\mathrm{perfect} - \mu'_\mathrm{perfect} = RT \ln\left(\frac{p}{p'}\right)$$

The difference of the two equations is

$$\int_{p'}^{p} (V_\mathrm{m} - V_\mathrm{perfect,m})\,\mathrm{d}p = RT\left\{\ln\left(\frac{f}{f'}\right) - \ln\left(\frac{p}{p'}\right)\right\}$$

which can be rearranged to

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

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

$$\ln\left(\frac{f}{p}\right) = \frac{1}{RT}\int_{0}^{p} (V_\mathrm{m} - V_\mathrm{perfect,m})\,\mathrm{d}p$$

With $\phi = f/p$,

$$\ln \phi = \frac{1}{RT}\int_{0}^{p} (V_\mathrm{m} - V_\mathrm{perfect,m})\,\mathrm{d}p$$

For a perfect gas $V_\mathrm{perfect,m} = RT/p$. For a real gas, $V_\mathrm{m} = RTZ/p$, where $Z$ is the compression factor. With these two substitutions, we obtain eqn 24.

---

To evaluate $\phi$ from eqn 24, we need experimental data on the compression factor from very low pressures up to the pressure of interest. Some information of this kind is available in numerical tables, in which case the integral may be evaluated numerically. Sometimes an algebraic expression is available for $Z$ (for instance, from one of the equations of state,

Table 1.7) and it may be possible to evaluate the integral analytically. Thus, if we know the virial coefficients for the gas we can obtain the fugacity by using

$$\ln \phi = B'p + \tfrac{1}{2}C'p^2 + \cdots \qquad (25)$$

This expression was obtained by explicit evaluation of eqn 24.

## Example 5.4 Calculating a fugacity

Suppose that the attractive interactions between gas particles can be neglected, and find an expression for the fugacity of a van der Waals gas in terms of the pressure. Estimate its value for ammonia at 10.00 atm and 298.15 K.

**Method** The starting point for the calculation is eqn 24. To evaluate the integral, we need an analytical expression for Z, which can be obtained from the equation of state. We saw in Section 1.5 that the van der Waals coefficient $a$ represents the attractions between molecules, so it may be set equal to zero in this calculation.

**Answer** When we neglect $a$ in the van der Waals equation, that equation becomes

$$p = \frac{RT}{V_m - b}$$

and hence

$$Z = 1 + \frac{bp}{RT}$$

The integral in eqn 24 that we require is therefore

$$\int_0^p \left(\frac{Z-1}{p}\right) \mathrm{d}p = \int_0^p \left(\frac{b}{RT}\right) \mathrm{d}p = \frac{bp}{RT}$$

Consequently, from eqns 24 and 22, the fugacity at the pressure $p$ is

$$f = pe^{bp/RT}$$

From Table 1.6, $b = 3.707 \times 10^{-2}\ \mathrm{L\,mol^{-1}}$, so $pb/RT = 1.515 \times 10^{-2}$, giving

$$f = (10.00\ \mathrm{atm}) \times e^{0.01515} = 10.2\ \mathrm{atm}$$

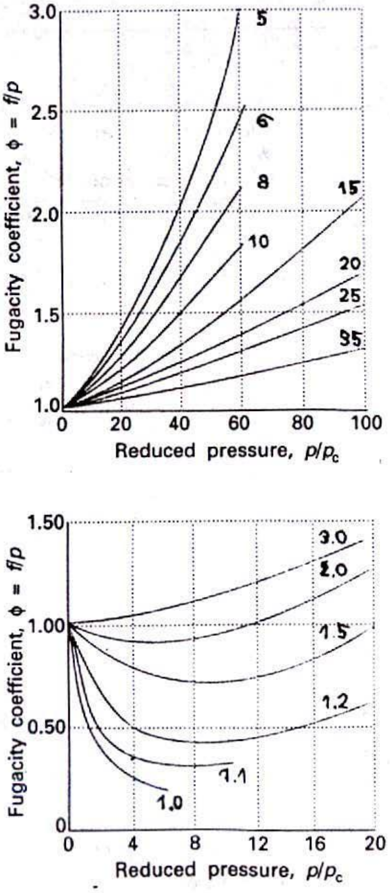
**Comment** The effect of the repulsive term (as represented by the coefficient $b$ in the van der Waals equation) is to increase the fugacity above the pressure, and so the effective pressure of the gas—its 'escaping tendency'—is greater than if it were perfect.

**Self-test 5.5** Find an expression for the fugacity coefficient when the attractive interaction is dominant in a van der Waals gas, and the pressure is low enough to make the approximation $4ap/(RT)^2 \ll 1$. Evaluate the fugacity for ammonia, as above.

[$\ln \phi = -ap/(RT)^2$, 9.32 atm]

It is clear from Fig. 1.27 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 24 is negative and $\phi < 1$. This implies that $f < p$ (the molecules tend to stick together) and that the chemical potential 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 chemical potential of the gas is greater than that of the perfect gas at the same pressure.

Figure 5.7, which has been calculated using the full van der Waals equation of state, shows how the fugacity depends on the pressure in terms of their reduced variables



5.7 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 $T_r = T/T_c$.

**Table 5.2*** The fugacity of nitrogen at 273 K

| $p$/atm | $f$/atm |
|---|---|
| 1 | 0.99955 |
| 10 | 9.9560 |
| 100 | 97.03 |
| 1000 | 1839 |

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

(Section 1.6). Because the critical constants are available in Table 1.5, the graphs can be used for quick estimates of the fugacities of a wide range of gases. Table 5.2 gives some explicit values for nitrogen.

### Illustration

To estimate the fugacity of nitrogen at 500 atm and 0°C, we first convert the reduced pressure ($p_r = p/p_c$) and temperature ($T_r = T/T_c$) of the gas by using the critical pressure and temperature of nitrogen (33.5 atm and 126.2 K); hence $p_r = 14.9$ and $T_r = 2.16$. These values correspond to $\phi = 1.15$ in Fig. 5.7. Therefore, the fugacity of nitrogen is approximately $f = 1.15 \times (500 \text{ atm}) = 575$ atm under the stated conditions. Because $\phi > 1$, the repulsive contributions are dominant in nitrogen at 500 atm and 0°C.

Self-test 5.6 Estimate the fugacity of carbon dioxide at 90°C and 580 atm.

[230 atm]

## Checklist of key ideas

**Combining the First and Second Laws**

☐ fundamental equation

**5.1 Properties of the internal energy**

☐ the relations $(\partial U/\partial S)_V = T$ and $(\partial U/\partial V)_S = -p$

☐ Maxwell relations (Table 5.1)

☐ thermodynamic equation of state

**5.2 Properties of the Gibbs energy**

☐ the relations $(\partial G/\partial T)_p = -S$ and $(\partial G/\partial p)_T = V$

☐ the Gibbs–Helmholtz equation

☐ the variation of Gibbs energy with pressure for a condensed phase (15) and a perfect gas (17)

**5.3 The chemical potential of a pure substance**

☐ chemical potential

☐ chemical potential of a perfect gas (20)

**Real gases: the fugacity**

**5.4 The definition of fugacity**

☐ fugacity

☐ the chemical potential of a real gas

☐ equilibrium constants in terms of fugacities

**5.5 Standard states of real gases**

☐ standard state of a real gas

**5.6 The relation between fugacity and pressure**

☐ fugacity coefficient

☐ the fugacity coefficient in terms of the compression factor (24) and the virial coefficients

## Further reading

### Articles of general interest

J.S. Winn, The fugacity of van der Waals gas. *J. Chem. Educ.* 65, 772 (1988).

R.M. Noyes, Thermodynamics of a process in a rigid container. *J. Chem. Educ.* 69, 470 (1992).

L.L. Combs, An alternative view of fugacity. *J. Chem. Educ.* 69, 218 (1992).

L. D'Alessio, On the fugacity of a van der Waals gas: an approximate expression that separates attractive and repulsive forces. *J. Chem. Educ.* 70, 96 (1993).

R.J. Tykodi, The Gibbs function, spontaneity, and walls. *J. Chem. Educ.* 73, 398 (1996).

R.M. Noyes, Application of the Gibbs function to chemical systems and subsystems. *J. Chem. Educ.* 73, 404 (1996).

S.E. Wood and R. Battino, The Gibbs function controversy. *J. Chem. Educ.* 73, 408, (1996).

R.J. Tykodi, Spontaneity, accessibility, irreversibility, 'useful work': the availability function, the Helmholtz function, and the Gibbs function. *J. Chem. Educ.* 72, 103 (1995).

### Texts and sources of data and information

J.M. Smith and H.C. Van Ness, *Introduction to chemical engineering thermodynamics*. McGraw–Hill, New York (1987).

B.D. Wood, *Applications of thermodynamics*. Addison–Wesley, New York (1982).

G.N. Lewis and M. Randall, *Thermodynamics*, revised by K.S. Pitzer and L. Brewer. McGraw–Hill, New York (1961).

# Exercises

Assume all gases are perfect and that the temperature is 298.15 K unless stated otherwise.

**5.1 (a)** Express $(\partial S/\partial V)_T = (\partial p/\partial T)_V$ in terms of $\alpha$ and $\kappa_T$ (see eqns 3.7 and 3.13 for definitions).

**5.1 (b)** Express $(\partial S/\partial p)_T = -(\partial V/\partial T)_p$ in terms of $\alpha$ (see eqns 3.7 and 3.13 for definitions).

**5.2 (a)** Suppose that 3.0 mmol $N_2(g)$ occupies 36 $cm^3$ at 300 K and expands to 60 $cm^3$. Calculate $\Delta G$ for the process.

**5.2 (b)** Suppose that 2.5 mmol Ar(g) occupies 72 $dm^3$ at 298 K and expands to 100 $dm^3$. Calculate $\Delta G$ for the process.

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

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

**5.4 (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.

**5.4 (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.

**5.5 (a)** When 2.00 mol of a gas at 330 K and 3.50 atm is subjected to isothermal compression, its entropy decreases by 25.0 $J\,K^{-1}$. Calculate (a) the final pressure of the gas and (b) $\Delta G$ for the compression.

**5.5 (b)** When 3.00 mol of a gas at 230 K and 150 kPa is subjected to isothermal compression, its entropy decreases by 15.0 $J\,K^{-1}$. Calculate (a) the final pressure of the gas and (b) $\Delta G$ for the compression.

**5.6 (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.

**5.6 (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.

**5.7 (a)** The fugacity coefficient of a certain gas at 200 K and 50 bar is 0.72. Calculate the difference of its chemical potential from that of a perfect gas in the same state.

**5.7 (b)** The fugacity coefficient of a certain gas at 290 K and 2.1 MPa is 0.68. Calculate the difference of its chemical potential from that of a perfect gas in the same state.

**5.8 (a)** At 373 K, the second virial coefficient $B$ of xenon is $-81.7$ $cm^3\,mol^{-1}$. Calculate the value of $B'$ and hence estimate the fugacity coefficient of xenon at 50 atm and 373 K.

**5.8 (b)** At 100 K, the second virial coefficient $B$ of nitrogen is $-160.0$ $cm^3\,mol^{-1}$. Calculate the value of $B'$ and hence estimate the fugacity coefficient of nitrogen at 62 MPa and 100 K.

**5.9 (a)** Estimate the change in the Gibbs energy of 1.0 L of benzene when the pressure acting on it is increased from 1.0 atm to 100 atm.

**5.9 (b)** Estimate the change in the Gibbs energy of 1.0 L of water when the pressure acting on it is increased from 100 kPa to 300 kPa.

**5.10 (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.

**5.10 (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.

**5.11 (a)** The molar Helmholtz energy of a certain gas is given by:

$$A_m = -\frac{a}{V_m} - RT\ln(V_m - b) + f(T)$$

where $a$ and $b$ are constants and $f(T)$ is a function of temperature only. Obtain the equation of state of the gas.

**5.11 (b)** The molar Gibbs energy of a certain gas is given by:

$$G_m = RT\ln p + A' + B'p + \tfrac{1}{2}C'p^2 + \tfrac{1}{3}D'p^3$$

where $A$, $B$, $C$, and $D$ are constants. Obtain the equation of state of the gas.

**5.12 (a)** Evaluate $(\partial S/\partial V)_T$ for a van der Waals gas. For an isothermal expansion, will $\Delta S$ be greater for a perfect gas or a van der Waals gas? Explain your conclusion.

# Problems

## Numerical problems

**5.1** Calculate $\Delta_r G^\ominus(375\text{ K})$ for the reaction $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$ from the value of $\Delta_r G^\ominus(298\text{ K})$, $\Delta_r H^\ominus(298\text{ K})$, and the Gibbs–Helmholtz equation.

**5.2** Estimate the standard reaction Gibbs energy of $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ at (a) 500 K, (b) 1000 K from their values at 298 K.

**5.3** At 298 K the standard enthalpy of combustion of sucrose is $-5645$ $kJ\,mol^{-1}$ 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.

**5.4** 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

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

**5.6** 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 $(\partial T/\partial p)_S = (\partial V/\partial S)_p$.

**5.7** Use the Maxwell relations to express the derivatives $(\partial S/\partial V)_T$ and $(\partial V/\partial S)_p$ in terms of the expansion coefficient $\alpha$ and the isothermal compressibility $\kappa_T$.

**5.8** Use the Maxwell relations and Euler's chain relation to express $(\partial p/\partial S)_V$ in terms of the heat capacities, the expansion coefficient, and the isothermal compressibility.

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

**5.10** 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?

**5.11** Prove the following relation:

$$\left(\frac{\partial H}{\partial V}\right)_T = -V^2\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial (T/V)}{\partial V}\right)_p$$

**5.12** 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

$$\pi_T \approx \frac{RT^2\Delta B}{V_m^2\Delta T}$$

Estimate $\pi_T$ 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.

**5.13** (a) Prove that the heat capacities $C_V$ and $C_p$ of a perfect gas are independent of both volume and pressure. May they depend on the temperature? (b) Deduce an expression for the dependence of $C_V$ on volume of a gas that is described by the equation of state $pV_m/RT = 1 + B/V_m$.

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

**5.15** Evaluate $\pi_T$ for a Dieterici gas (Table 1.7). Justify physically the form of the expression obtained.

**5.16** Instead of assuming that the volume of a condensed phase is constant when pressure is applied, assume only that the compressibility is constant. Show that, when the pressure is changed isothermally by $\Delta p$, $G$ changes to

$$G' = G + V_m\Delta p(1 - \tfrac{1}{2}\kappa_T\Delta p)$$

Assess the error in assuming that a solid is incompressible by applying this expression to the compression of copper when $\Delta p = 500$ atm. (For copper at 25 °C, $\kappa_T = 0.8 \times 10^{-6}\ \mathrm{atm^{-1}}$ and $\rho = 8.93\ \mathrm{g\,cm^{-3}}$.)

**5.17** Derive an expression for the standard reaction Gibbs energy $\Delta_r G^\ominus$ (the analogue of the standard reaction enthalpy) at a temperature $T'$ in terms of its value $\Delta_r G^\ominus$ at $T$ by using the Gibbs–Helmholtz equation and (a) assuming that $\Delta_r H^\ominus$ does not vary with temperature, (b) assuming instead that $\Delta_r C_p^\ominus$ does not vary with temperature and using Kirchhoff's law.

**5.18** The adiabatic compressibility, $\kappa_S$, is defined like $\kappa_T$ (eqn 3.13) but at constant entropy. Show that for a perfect gas $p\gamma\kappa_S = 1$ (where $\gamma$ is the ratio of heat capacities).

**5.19** Show that, if $S$ is regarded as a function of $T$ and $p$, then

$$T\,\mathrm{d}S = C_V\,\mathrm{d}T + T\left(\frac{\partial p}{\partial T}\right)_V \mathrm{d}V$$

Calculate the energy that must be transferred as heat to a van der Waals gas that expands reversibly and isothermally from $V_i$ to $V_f$.

**5.20** Suppose that $S$ is regarded as a function of $p$ and $T$. Show that

$$T\,\mathrm{d}S = C_p\,\mathrm{d}T - \alpha TV\,\mathrm{d}p$$

Hence, show that the energy transferred as heat when the pressure on an incompressible liquid or solid is increased by $\Delta p$ is equal to $-\alpha TV\Delta p$. Evaluate $q$ when the pressure acting on 100 cm³ of mercury at 0 °C is increased by 1.0 kbar. ($\alpha = 1.82 \times 10^{-4}\ \mathrm{K^{-1}}$.)

**5.21** The volume of a newly synthesized polymer was found to depend exponentially on the pressure as $V = V_0 e^{-p/p^*}$, where $p$ is the excess pressure and $p^*$ is a constant. Deduce an expression for the Gibbs energy of the polymer as a function of excess pressure. What is the natural direction of change of the compressed material when the pressure is relaxed?

**5.22** Find an expression for the fugacity coefficient of a gas that obeys the equation of state

$$\frac{pV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2}$$

Use the resulting expression to estimate the fugacity of argon at 1.00 atm and 100 K using $B = -21.13\ \mathrm{cm^3\,mol^{-1}}$ and $C = 1054\ \mathrm{cm^6\,mol^{-2}}$.

**5.23** Derive an expression for the fugacity coefficient of a gas that obeys the equation of state

$$\frac{pV_m}{RT} = 1 + \frac{qT}{V_m}$$

where $q$ is a constant, and plot $\phi$ against $4pq/R$.

## Additional problems supplied by Carmen Giunta and Charles Trapp

**5.24** In 1995, the Intergovernmental Panel on Climate Change considered a global average temperature rise of 1.0–3.5°C likely by the year 2100, with 2.0°C its best estimate (IPCC Second Assessment Synthesis of Scientific–Technical Information Relevant to Interpreting Article 2 of the UN Framework Convention on Climate Change (1995)). 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.)

**5.25** Nitric acid hydrates have received much attention as possible catalysts for heterogeneous reactions which 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, $HNO_3 \cdot nH_2O(s) \rightarrow HNO_3(g) + nH_2O(g)$, 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 |
|---|---|---|---|
| $\Delta_r G^\ominus/(\mathrm{kJ\,mol^{-1}})$ | 46.2 | 69.4 | 93.2 |
| $\Delta_r H^\ominus/(\mathrm{kJ\,mol^{-1}})$ | 127 | 188 | 237 |

**5.26** In an investigation of thermophysical properties of toluene (R.D. Goodwin, *J. Phys. Chem. Ref. Data* 18, 1565 (1989)), Goodwin tabulated (among other quantities) the compression factor, $Z$, at several temperatures and pressures. From the following information, compute the fugacity coefficient of toluene at 600 K and (a) 30.0 bar and (b) 1000 bar.

| | | | | | | |
|---|---|---|---|---|---|---|
| $p$/bar | 0.500 | 1.013 | 2.00 | 3.00 | 5.00 | |
| $Z$ | 0.994 12 | 0.988 96 | 0.979 42 | 0.969 95 | 0.951 33 | |
| $p$/bar | 10.00 | 20.0 | 30.0 | 42.4 | 50.0 | |
| $Z$ | 0.905 69 | 0.812 27 | 0.701 77 | 0.471 98 | 0.223 76 | |
| $p$/bar | 70.0 | 100.0 | 200 | 300 | 500 | 1000 |
| $Z$ | 0.265 20 | 0.349 20 | 0.623 62 | 0.882 88 | 1.371 09 | 2.488 36 |

**5.27** 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 from 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 $l$.

**5.28** You are told that the differential of pressure consistent with an equation of state is given by *one* of the following two expressions. Determine the equation of state.

$$\mathrm{d}p = \frac{2(V-b)\,\mathrm{d}V}{RT} + \frac{(V-b)^2\,\mathrm{d}T}{RT^2}$$

$$\mathrm{d}p = -\frac{RT\,\mathrm{d}V}{(V-b)^2} + \frac{R\,\mathrm{d}T}{V-b}$$

**5.29** At 1 atm, liquid water has its maximum density at 4°C. What can be concluded about the variation of the entropy of liquid water with pressure at constant temperature at 3°C, 4°C, and 5°C?