The properties of gases

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

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

The perfect gas

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

1.1 The states of gases

Key points **Each substance is described by an equation of state. (a) Pressure, force divided by area, provides a criterion of mechanical equilibrium for systems free to change their volume. (b) Pressure is measured with a barometer. (c) Through the Zeroth Law of thermodynamics, temperature provides a criterion of thermal equilibrium.**

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

The general form of an equation of state is

$$p = f(T,V,n) \qquad (1.1)$$

General form of an equation of state

This equation tells us that, if we know the values of n, T, and V for a particular substance, then the pressure has a fixed value. Each substance is described by its own equation of state, but we know the explicit form of the equation in only a few special cases. One very important example is the equation of state of a 'perfect gas', which has the form $p = nRT/V$, where R is a constant (Section F.3). Much of the rest of this chapter will examine the origin of this equation of state and its applications.

(a) Pressure

Pressure, p, is defined as force, F, divided by the area, A, to which the force is applied:

$$p = \frac{F}{A} \qquad \text{Definition of pressure} \qquad [1.2]$$

That is, 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, 1 Pa = 1 N m^{-2}) was introduced in Section F.7. As we saw there, several other units are still widely used (Table 1.1). A pressure of 1 bar is the **standard pressure** for reporting data; we denote it $p^{\ominus}$.

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

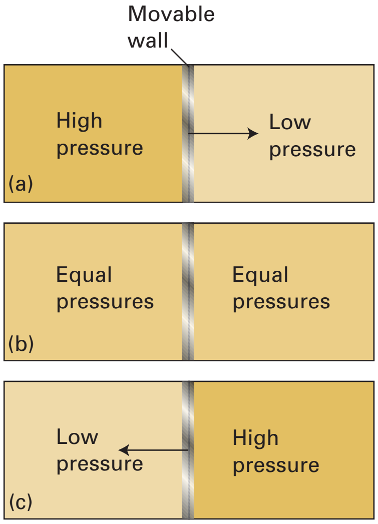


Fig. 1.1 When a region of high pressure is separated from a region of low pressure by a movable wall, the wall will be pushed into one region or the other, as in (a) and (c). However, if the two pressures are identical, the wall will not move (b). The latter condition is one of mechanical equilibrium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

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

Table 1.1 Pressure units

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

(b) The measurement of pressure

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

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

Derive an equation for the pressure at the base of a column of liquid of mass density ρ (rho) and height h at the surface of the Earth. The pressure exerted by a column of liquid is commonly called the 'hydrostatic pressure'.

Method Use the definition of pressure in eqn 1.2 with $F = mg$. To calculate F we need to know the mass m of the column of liquid, which is its mass density, ρ, multiplied by its volume, V: $m = \rho V$. The first step, therefore, is to calculate the volume of a cylindrical column of liquid.

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

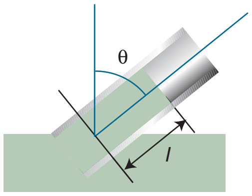
$$F = mg = \rho Ahg$$

The pressure at the base of the column is therefore

$$p = \frac{F}{A} = \frac{\rho Agh}{A} = \rho gh \qquad \boxed{\text{Hydrostatic pressure}} \qquad (1.3)$$

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

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



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

(c) Temperature

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

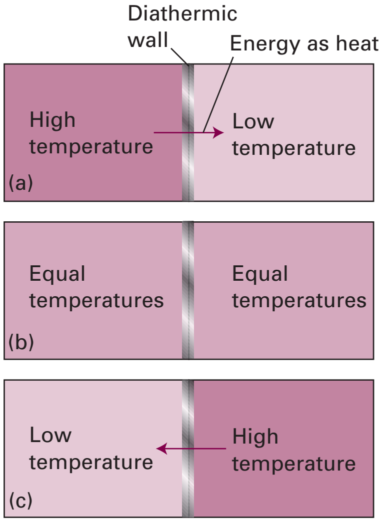

Fig. 1.2 Energy flows as heat from a region at a higher temperature to one at a lower temperature if the two are in contact through a diathermic wall, as in (a) and (c). However, if the two regions have identical temperatures, there is no net transfer of energy as heat even though the two regions are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

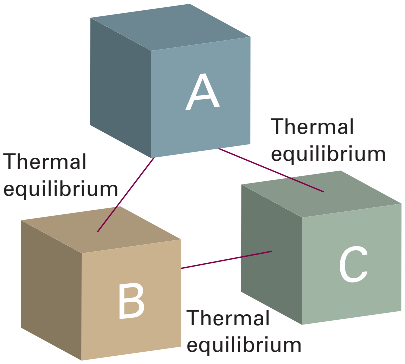

Fig. 1.3 The experience summarized by the Zeroth Law of thermodynamics is that, if an object A is in thermal equilibrium with B and B is in thermal equilibrium with C, then C is in thermal equilibrium with A.

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

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

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

Zeroth Law of thermodynamics

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

In the early days of thermometry (and still in laboratory practice today), temperatures were related to the length of a column of liquid, and the difference in lengths shown when the thermometer was first in contact with melting ice and then with boiling water was divided into 100 steps called 'degrees', the lower point being labelled 0. This procedure led to the **Celsius scale** of temperature. In this text, temperatures on the Celsius scale are denoted θ (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 independent of the identity of the gas. The perfect-gas scale turns out to be identical to the **thermodynamic temperature scale** to be introduced in Section 3.2d, so we shall use the latter term from now on to avoid a proliferation of names. On the thermodynamic temperature scale, temperatures are denoted T and are normally reported in *kelvins* (K; not °K). Thermodynamic and Celsius temperatures are related by the exact expression

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

Definition of Celsius scale

This relation is the current definition of the Celsius scale in terms of the more fundamental Kelvin scale. It implies that a difference in temperature of 1°C is equivalent to a difference of 1 K.

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

• A brief illustration

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

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

Note how the units (in this case, °C) are cancelled like numbers. This is the procedure called 'quantity calculus' in which a physical quantity (such as the temperature) is the product of a numerical value (25.00) and a unit (1°C); see Section F.7. Multiplication of both sides by the unit K then gives $T = 298.15$ K. •

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

1.2 The gas laws

Key points **(a) The perfect gas law, a limiting law valid in the limit of zero pressure, summarizes Boyle's and Charles's laws and Avogadro's principle. (b) The kinetic theory of gases, in which molecules are in ceaseless random motion, provides a model that accounts for the gas laws and a relation between average speed and temperature. (c) A mixture of perfect gases behaves like a single perfect gas; its components each contribute their partial pressure to the total pressure.**

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

(a) The perfect gas law

We assume that the following individual gas laws are familiar:

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

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

$p = \text{constant} \times T$, at constant n, V $\qquad (1.6\mathrm{b})^\circ$

Avogadro's principle: $V = \text{constant} \times n$ at constant p, T $\qquad (1.7)^\circ$

A brief comment

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

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

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

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

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

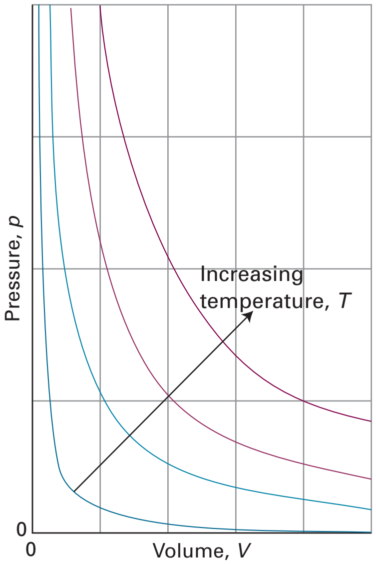

Fig. 1.4 The pressure–volume dependence of a fixed amount of perfect gas at different temperatures. Each curve is a hyperbola ($pV = \text{constant}$) and is called an isotherm.

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

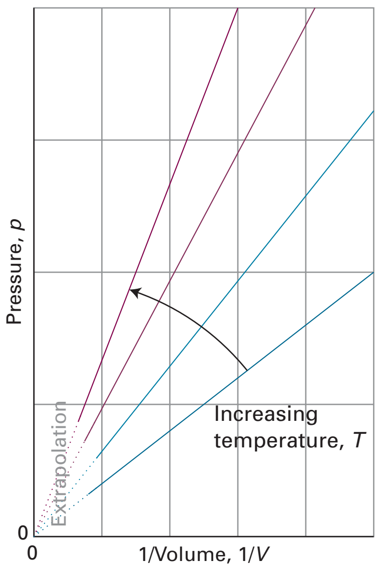

Fig. 1.5 Straight lines are obtained when the pressure is plotted against $1/V$ at constant temperature.

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

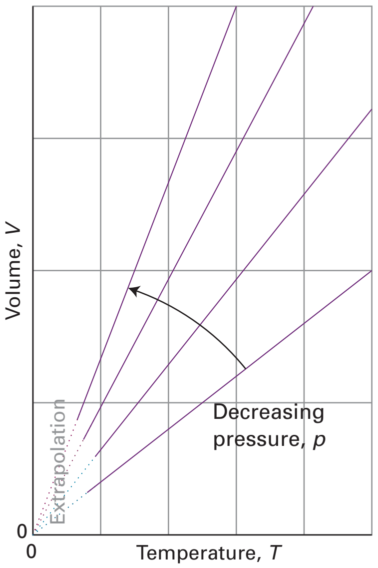

Fig. 1.6 The variation of the volume of a fixed amount of gas with the temperature at constant pressure. Note that in each case the isobars extrapolate to zero volume at $T = 0$ or $\theta = -273$°C.

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

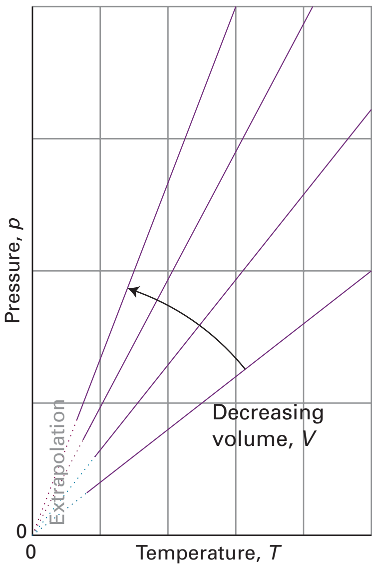

Fig. 1.7 The pressure also varies linearly with the temperature at constant volume, and extrapolates to zero at $T = 0$ (−273°C).

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

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

$$pV = nRT \qquad \boxed{\text{Perfect gas law}} \qquad (1.8)^\circ$$

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

The surface in Fig. 1.8 is a plot of the pressure of a fixed amount of perfect gas against its volume and thermodynamic temperature as given by eqn 1.8. The surface depicts the only possible states of a perfect gas: the gas cannot exist in states that do not correspond to points on the surface. The graphs in Figs. 1.4, 1.6, and 1.7 correspond to the sections through the surface (Fig. 1.9).

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

Table 1.2 The gas constant

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

Example 1.2 *Using the perfect gas law*

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

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

$$\frac{p_1V_1}{n_1T_1}=\frac{p_2V_2}{n_2T_2} \qquad \boxed{\text{Combined gas law}} \qquad (1.9)^\circ$$

This expression is easily rearranged to give the unknown quantity (in this case p_2) in terms of the known. The known and unknown data are summarized in (2).

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

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

which can be rearranged into

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

Substitution of the data then gives

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

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

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

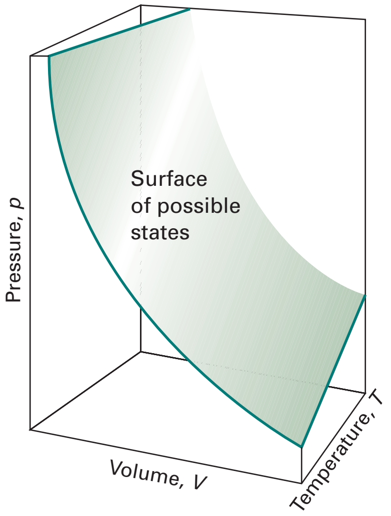

Fig. 1.8 A region of the p,V,T surface of a fixed amount of perfect gas. The points forming the surface represent the only states of the gas that can exist.

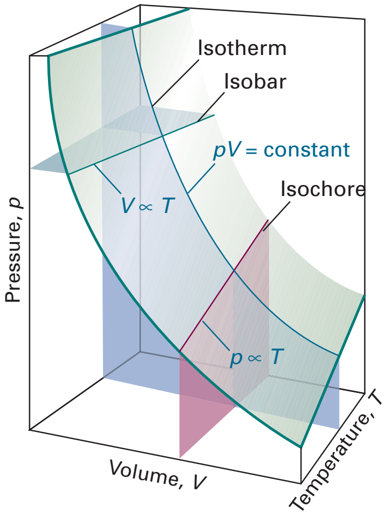

Fig. 1.9 Sections through the surface shown in Fig. 1.8 at constant temperature give the isotherms shown in Fig. 1.4 and the isobars shown in Fig. 1.6.

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

2

The perfect gas law is of the greatest importance in physical chemistry because it is used to derive a wide range of relations that are used throughout thermodynamics. However, it is also of considerable practical utility for calculating the properties of a gas under a variety of conditions. For instance, the molar volume, $V_m = V/n$, of a perfect gas under the conditions called **standard ambient temperature and pressure** (SATP), which means 298.15 K and 1 bar (that is, exactly 10^5 Pa), is easily calculated from $V_m = RT/p$ to be 24.789 dm^3 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 dm^3 mol^{-1}.

(b) The kinetic model of gases

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

These qualitative concepts are expressed quantitatively in terms of the kinetic model of gases, which is described more fully in Chapter 20. Briefly, the kinetic model is based on three assumptions:

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

An *elastic collision* is a collision in which the total translational kinetic energy of the molecules is conserved. From the very economical assumptions of the kinetic model, it can be deduced (as we show in detail in Chapter 20) that the pressure and volume of the gas are related by

$$pV = \tfrac{1}{3}nMc^2 \qquad (1.10)^\circ$$

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

$$c = \langle v^2 \rangle^{1/2} \qquad (1.11)$$

We see that, if the root mean square speed of the molecules depends only on the temperature, then at constant temperature pV = constant, which is the content of Boyle's law. Moreover, for eqn 1.10 to be the equation of state of a perfect gas, its right-hand side must be equal to nRT. It follows that the root mean square speed of the molecules in a gas at a temperature T must be

$$c = \left(\frac{3RT}{M}\right)^{1/2} \qquad \boxed{\text{Relation between molecular speed and temperature}} \qquad (1.12)^\circ$$

We can conclude that *the root mean square speed of the molecules of a gas is proportional to the square root of the temperature and inversely proportional to the square root of the molar mass*. That is, the higher the temperature, the higher the root mean square speed of the molecules, and, at a given temperature, heavy molecules travel more slowly than light molecules. The root mean square speed of N_2 molecules, for instance, is found from eqn 1.12 to be 515 m s^{-1} at 298 K.

(c) Mixtures of gases

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

$$p_J = x_J p \qquad \boxed{\text{Definition of partial pressure}} \qquad [1.13]$$

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

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

Definition of mole fraction

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

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

This relation is true for both real and perfect gases.

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

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

Dalton's law

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

Example 1.3 *Calculating partial pressures*

The mass percentage composition of dry air at sea level is approximately N_2: 75.5; O_2: 23.2; Ar: 1.3. What is the partial pressure of each component when the total pressure is 1.20 atm?

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

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

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

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

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

These three amounts work out as 2.69 mol, 0.725 mol, and 0.033 mol, respectively, for a total of 3.45 mol. The mole fractions are obtained by dividing each of the above amounts by 3.45 mol and the partial pressures are then obtained by multiplying the mole fraction by the total pressure (1.20 atm):

	N_2	O_2	Ar
Mole fraction:	0.780	0.210	0.0096
Partial pressure/atm:	0.936	0.252	0.012

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

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

IMPACT ON ENVIRONMENTAL SCIENCE

I1.1 The gas laws and the weather

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

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

Table 1.3 The composition of dry air at sea level

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

$$p = p_0 e^{-h/H} \qquad (1.16)$$

where p_0 is the pressure at sea level and H is a constant approximately equal to 8 km. More specifically, $H = RT/Mg$, where M is the average molar mass of air and T is the temperature. This formula represents the outcome of the competition between the potential energy of the molecules in the gravitational field of the Earth and the stirring effects of thermal motion; it is derived on the basis of the Boltzmann distribution (Section F.5a). The barometric formula fits the observed pressure distribution quite well even for regions well above the troposphere (Fig. 1.10). It implies that the pressure of the air falls to half its sea-level value at $h = H \ln 2$, or 6 km.

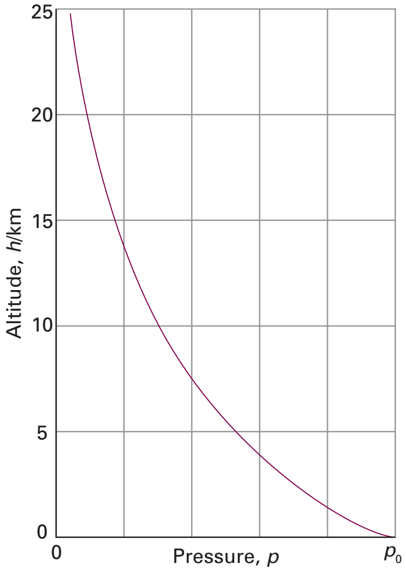

Fig. 1.10 The variation of atmospheric pressure with altitude, as predicted by the barometric formula and as suggested by the 'US Standard Atmosphere', which takes into account the variation of temperature with altitude.

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

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

The motion of air in the upper altitudes may lead to an accumulation in some regions and a loss of molecules from other regions. The former result in the formation of regions of high pressure ('highs' or anticyclones) and the latter result in regions of low pressure ('lows', depressions, or cyclones). On a weather map, such as that shown in Fig. 1.11, the lines of constant pressure marked on it are called *isobars*. Elongated regions of high and low pressure are known, respectively, as *ridges* and *troughs*.

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

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

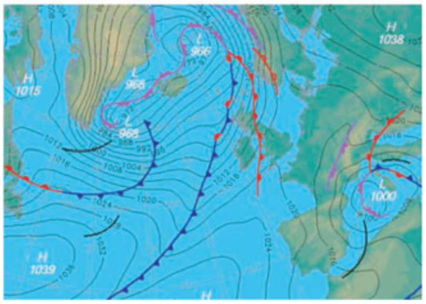

Fig. 1.11 A typical weather map; in this case, for the North Atlantic and neighbouring regions on 16 December 2008.

Real gases

Real gases do not obey the perfect gas law exactly except in the limit of $p \to 0$. 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 The van der Waals equation

Key points **(a) The van der Waals equation is a model equation of state for a real gas expressed in terms of two parameters, one corresponding to molecular attractions and the other to molecular repulsions. (b) The van der Waals equation captures the general features of the behaviour of real gases, including their critical behaviour. (c) The properties of real gases are coordinated by expressing their equations of state in terms of reduced variables.**

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

(a) Formulation of the equation

The van der Waals equation is

$$p=\frac{nRT}{V-nb}-a\frac{n^2}{V^2} \tag{1.21a}$$

van der Waals equation of state

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

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

The constants a and b are called the **van der Waals coefficients**. As can be understood from the following *Justification*, a represents the strength of attractive interactions and b that of the repulsive interactions between the molecules. They are characteristic of each gas but independent of the temperature (Table 1.6). Although a and b are not precisely defined molecular properties, they correlate with physical properties such as critical temperature, vapor pressure, and enthalpy of vaporization that reflect the strength of intermolecular interactions. Correlations have also been sought where intermolecular forces might play a role. For example, the potencies of certain general anaesthetics show a correlation in the sense that a higher activity is observed with lower values of a (Fig. 1.17).

Table 1.6* van der Waals coefficients

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

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

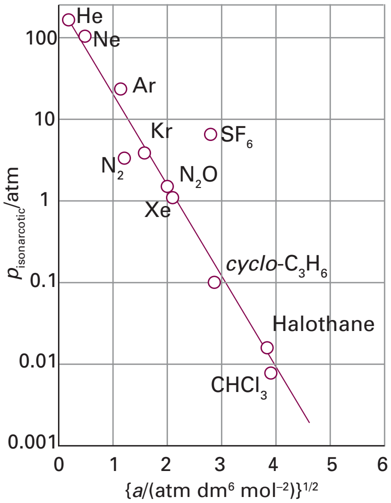

Fig. 1.17 The correlation of the effectiveness of a gas as an anaesthetic and the van der Waals parameter a. (Based on R.J. Wulf and R.M. Featherstone, *Anesthesiology*, **18**, 97 (1957).) The isonarcotic pressure is the pressure required to bring about the same degree of anaesthesia.

Justification 1.1 *The van der Waals equation of state*

The repulsive interactions between molecules are taken into account by supposing that they cause the molecules to behave as small but impenetrable spheres. The 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. To calculate the excluded volume we note that the closest distance of two hard-sphere molecules of radius r, and volume $V_{\text{molecule}} = \frac{4}{3}\pi r^3$, is $2r$, so the volume excluded is $\frac{4}{3}\pi(2r)^3$, or $8V_{\text{molecule}}$. The volume excluded per molecule is one-half this volume, or $4V_{\text{molecule}}$, so $b \approx 4V_{\text{molecule}}N_A$.

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

In this *Justification* we have built the van der Waals equation using vague arguments about the volumes of molecules and the effects of forces. The equation can be derived in other ways, but the present method has the advantage that it shows how to derive the form of an equation from 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 that represent attractions and repulsions, respectively, rather than as precisely defined molecular properties.

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

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

Method We need to find an expression for the molar volume by solving the van der Waals equation, eqn 1.21b. To do so, we multiply both sides of the equation by $(V_m - b)V_m^2$, to obtain

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

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

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

Although closed expressions for the roots of a cubic equation can be given, they are very complicated. Unless analytical solutions are essential, it is usually more expedient to solve such equations with commercial software; graphing calculators can also be used to help identify the acceptable root.

Answer According to Table 1.6, $a = 3.610\ \mathrm{dm^6\ atm\ mol^{-2}}$ and $b = 4.29 \times 10^{-2}\ \mathrm{dm^3\ mol^{-1}}$. Under the stated conditions, $RT/p = 0.410\ \mathrm{dm^3\ mol^{-1}}$. The coefficients in the equation for V_m are therefore

$$b + RT/p = 0.453\ \mathrm{dm^3\ mol^{-1}}$$
$$a/p = 3.61 \times 10^{-2}\ (\mathrm{dm^3\ mol^{-1}})^2$$
$$ab/p = 1.55 \times 10^{-3}\ (\mathrm{dm^3\ mol^{-1}})^3$$

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

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

The acceptable root is $x = 0.366$ (Fig. 1.18), which implies that $V_m = 0.366\ \mathrm{dm^3\ mol^{-1}}$. For a perfect gas under these conditions, the molar volume is $0.410\ \mathrm{dm^3\ mol^{-1}}$.

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

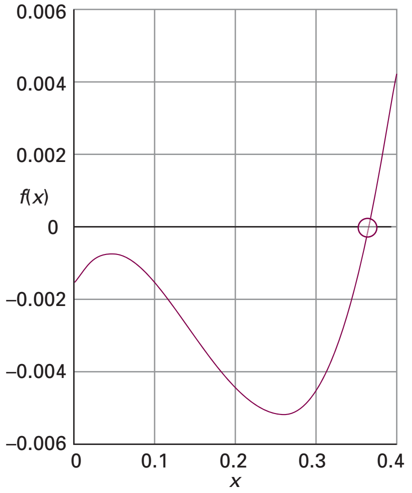

Fig. 1.18 The graphical solution of the cubic equation for V in Example 1.4.

Discussion questions

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

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

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

1.4 What is the significance of the critical constants?

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

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

Exercises

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

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

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

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

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

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

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

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

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

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

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

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

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

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

p/atm	0.750 000	0.500 000	0.250 000
$V_m/(dm^3\ mol^{-1})$	29.8649	44.8090	89.6384

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

1.8(b) At 100°C and 16.0 kPa, the mass density of phosphorus vapour is 0.6388 kg m^{-3}. What is the molecular formula of phosphorus under these conditions?

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

1.20(b) Use the van der Waals parameters for hydrogen sulfide (Table 1.6 in the *Data section*) 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.

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

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

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

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

Problems*

Numerical problems

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

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

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

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

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

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

20.1 The kinetic model of gases

Key points **The kinetic model of a gas considers only the contribution to the energy from the kinetic energies of the molecules. (a) Important results from the model include expressions for the pressure and the root mean square speed. The Maxwell distribution of speeds gives the fraction of molecules that have speeds in a specified range. (b) The collision frequency is the number of collisions made by a molecule in an interval divided by the length of the interval. (c) The mean free path is the average distance a molecule travels between collisions.**

The kinetic model is based on three assumptions:

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

An **elastic collision** is a collision in which the total translational kinetic energy of the molecules is conserved.

(a) Pressure and molecular speeds

From the very economical assumptions of the kinetic model, we show in the following *Justification* that the pressure and volume of the gas are related by

$$pV = \tfrac{1}{3}nMc^2 \qquad (20.1)°$$

The pressure of a perfect gas according to the kinetic model

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:

$$c = \langle v^2 \rangle^{1/2} \qquad [20.2]$$

Definition of the root mean square speed

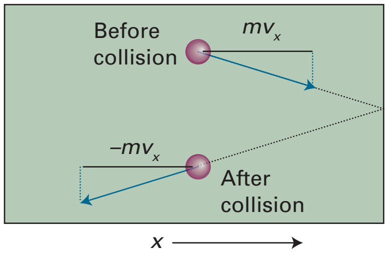

Fig. 20.1 The pressure of a gas arises from the impact of its molecules on the walls. In an elastic collision of a molecule with a wall perpendicular to the x-axis, the x-component of velocity is reversed but the y- and z-components are unchanged.

Justification 20.1 *The pressure of a gas according to the kinetic model*

Consider the arrangement in Fig. 20.1. 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 x-component of 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 Δt, 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.

Because a molecule with velocity component v_x can travel a distance $v_x\Delta t$ along the x-axis in an interval Δt, all the molecules within a distance $v_x\Delta t$ of the wall will strike it if they are travelling towards it (Fig. 20.2). 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 Avogadro's constant, so the number of molecules in the volume $Av_x\Delta t$ is $(nN_A/V) \times Av_x\Delta t$.

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 Δt

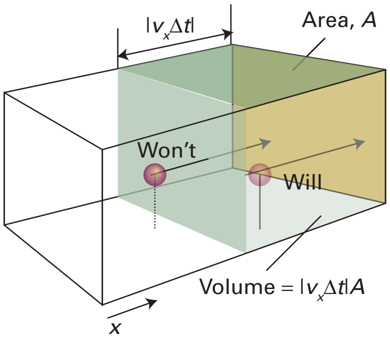

Fig. 20.2 A molecule will reach the wall on the right within an interval Δt if it is within a distance $v_x\Delta t$ of the wall and travelling to the right.

is $\frac{1}{2}nN_A Av_x\Delta t/V$. The total momentum change in that interval is the product of this number and the change $2mv_x$:

$$\text{Momentum change} = \frac{nN_A Av_x\Delta t}{2V} \times 2mv_x = \frac{nmAN_A v_x^2\Delta t}{V} = \frac{nMAv_x^2\Delta t}{V}$$

where $M = mN_A$.

Next, to find the force, we calculate the rate of change of momentum, which is this change of momentum divided by the interval Δt 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

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

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.

To write an expression of the pressure in terms of the root mean square speed, c, we begin by writing the speed of a single molecule, v, as $v = v_x^2 + v_y^2 + v_z^2$. Because the root-mean-square speed, c, is defined as $c = \langle v^2\rangle^{1/2}$ (eqn 20.2), it follows that

$$c^2 = \langle v^2\rangle = \langle v_x^2\rangle + \langle v_y^2\rangle + \langle v_z^2\rangle$$

However, because the molecules are moving randomly, all three averages are the same. It follows that $c^2 = 3\langle v_x^2\rangle$. Equation 20.1 follows immediately by substituting $\langle v_x^2\rangle = \frac{1}{3}c^2$ into $p = nM\langle v_x^2\rangle/V$.

Equation 20.1 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 (Section 1.2). Moreover, for eqn 20.1 to be the equation of state of a perfect gas, its right-hand side must be equal to nRT. It follows that the root mean square speed of the molecules in a gas at a temperature T must be

$$c = \left(\frac{3RT}{M}\right)^{1/2} \qquad (20.3)^\circ$$

Root mean square speed in a perfect gas

We can conclude that the root mean square speed of the molecules of a gas is proportional to the square root of the temperature and inversely proportional to the square root of the molar mass. That is, the higher the temperature, the higher the root mean square speed of the molecules, and, at a given temperature, heavy molecules travel more slowly than light molecules.

• A brief illustration

The root mean square speed of N_2 molecules ($M = 28.02\ \text{g mol}^{-1}$) at 298 K is found from eqn 20.3 to be

$$c = \left(\frac{3 \times 8.3145\ \text{J K}^{-1}\ \text{mol}^{-1} \times 298\ \text{K}}{28.02 \times 10^{-3}\ \text{kg mol}^{-1}}\right)^{1/2} = 515\ \text{m s}^{-1}$$

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 speed of sound in air to be approximately 500 m s^{-1}. The experimental value is 340 m s^{-1}. •

Equation 20.3 is an expression for the 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 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 $f(v)$ is called the **distribution of speeds**. Note that, in common with other distribution functions, $f(v)$ acquires physical significance only after it is multiplied by the range of speeds of interest.

The precise form of f for molecules of a gas at a temperature T was derived by J.C. Maxwell, and is

$$f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 \mathrm{e}^{-Mv^2/2RT} \qquad (20.4)$$

Maxwell distribution of speeds

This expression is called the **Maxwell distribution of speeds** and is derived in the following *Justification*. Let's consider its features, which are also shown pictorially in Fig. 20.3:

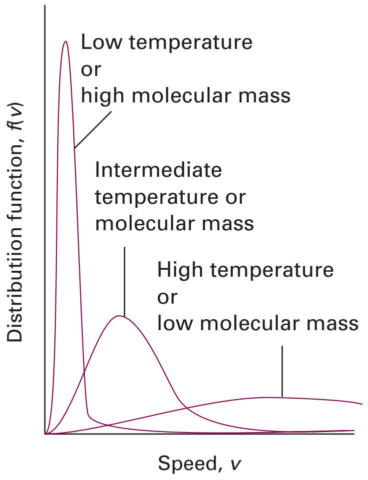

Fig. 20.3 The distribution of molecular speeds with temperature and molar mass. Note that the most probable speed (corresponding to the peak of the distribution) increases with temperature and with decreasing molar mass, and simultaneously the distribution becomes broader.

interActivity (a) Plot different distributions by keeping the molar mass constant at 100 g mol^{-1} and varying the temperature of the sample between 200 K and 2000 K. (b) Use mathematical software or the *Living graph* applet from the text's web site to evaluate numerically the fraction of molecules with speeds in the range 100 m s^{-1} to 200 m s^{-1} at 300 K and 1000 K. (c) Based on your observations, provide a molecular interpretation of temperature.

1. Equation 20.4 includes a decaying exponential function, the term $\mathrm{e}^{-Mv^2/2RT}$. Its presence implies that the fraction of molecules with very high speeds will be very small because e^{-x^2} becomes very small when x^2 is large.
2. The factor $M/2RT$ multiplying v^2 in the exponent is large when the molar mass, M, is large, so the exponential factor goes most rapidly towards zero when M is large. That is, heavy molecules are unlikely to be found with very high speeds.
3. The opposite is true when the temperature, T, is high: then the factor $M/2RT$ in the exponent is small, so the exponential factor falls towards zero relatively slowly as v increases. In other words, a greater fraction of the molecules can be expected to have high speeds at high temperatures than at low temperatures.
4. A factor v^2 (the term before the e) multiplies the exponential. This factor goes to zero as v goes to zero, so the fraction of molecules with very low speeds will also be very small.
5. The remaining factors (the term in parentheses in eqn 20.4 and the 4π) simply ensure that, when we add together the fractions over the entire range of speeds from zero to infinity, then we get 1.

To use eqn 20.4 to calculate the fraction of molecules in a given narrow range of speeds, Δv, 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 too wide to be treated as infinitesimal, we evaluate the integral:

$$\text{Fraction in the range } v_1 \text{ to } v_2 = \int_{v_1}^{v_2} f(v)\mathrm{d}v \qquad (20.5)$$

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 by using mathematical software (Fig. 20.4).

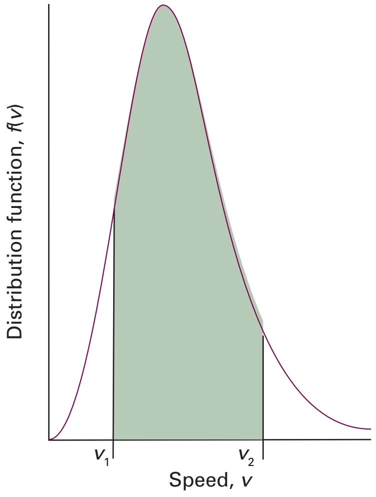

Fig. 20.4 To calculate the probability that a molecule will have a speed in the range v_1 to v_2, we integrate the distribution between those two limits; the integral is equal to the area of the curve between the limits, as shown shaded here.

Justification 20.2 *The Maxwell distribution of speeds*

The Boltzmann distribution is a key result of physical chemistry; it was introduced in *Fundamentals F.5* and treated fully in Section 15.1. It implies that the fraction of molecules with velocity components v_x, v_y, v_z is proportional to an exponential function of their kinetic energy, E_k, which is

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

Therefore, we can use the relation $a^{x+y+z+\cdots} = a^x a^y a^z \ldots$ to write

$$f = Ke^{-E_k/kT} = Ke^{-(\frac{1}{2}mv_x^2+\frac{1}{2}mv_y^2+\frac{1}{2}mv_z^2)/kT} = Ke^{-mv_x^2/2kT}e^{-mv_y^2/2kT}e^{-mv_z^2/2kT}$$

where K is a constant of proportionality (at constant temperature) and $f\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z$ is the fraction of molecules in the velocity range v_x to $v_x + \mathrm{d}v_x$, v_y to $v_y + \mathrm{d}v_y$, and v_z to $v_z + \mathrm{d}v_z$. We see that the fraction factorizes into three factors, one for each axis, and we can write $f = f(v_x)f(v_y)f(v_z)$ with

$$f(v_x) = K^{1/3}e^{-mv_x^2/2kT}$$

and likewise for the two other directions.

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

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

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

$$1 = K^{1/3}\int_{-\infty}^{\infty} e^{-mv_x^2/2kT}\mathrm{d}v_x = K^{1/3}\left(\frac{2\pi kT}{m}\right)^{1/2}$$

where we have used the standard integral

$$\int_{-\infty}^{\infty} e^{-ax^2}\mathrm{d}x = \left(\frac{\pi}{a}\right)^{1/2}$$

Therefore, $K = (m/2\pi kT)^{3/2} = (M/2\pi RT)^{3/2}$, where M is the molar mass of the molecules. At this stage we know that

$$f(v_x) = \left(\frac{M}{2\pi RT}\right)^{1/2} e^{-Mv_x^2/2RT} \qquad (20.6)$$

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 the product of these individual probabilities:

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

where $v^2 = v_x^2 + v_y^2 + v_z^2$. 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 and thickness $\mathrm{d}v$ (Fig. 20.5). 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, the probability 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

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

as given in eqn 20.4.

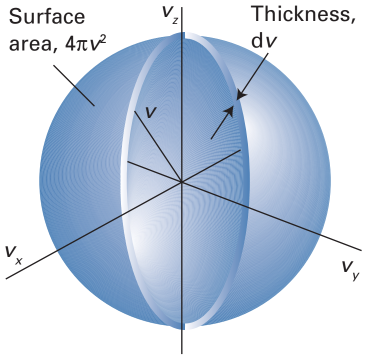

Fig. 20.5 To evaluate the probability that a molecule has a speed in the range v to $v + \mathrm{d}v$, we evaluate the total probability that the molecule will have a speed that is anywhere on the surface of a sphere of radius $v = (v_x^2 + v_y^2 + v_z^2)^{1/2}$ by summing the probabilities that it is in a volume element $\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z$ at a distance v from the origin.

Example 20.1 *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 A mean speed 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

$$\bar{c} = \int_{-\infty}^{\infty} vf(v)\mathrm{d}v$$

with $f(v)$ given in eqn 20.4.

Answer The integral required is

$$\begin{aligned}\bar{c} &= 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\int_0^{\infty} v^3\mathrm{e}^{-Mv^2/2RT}\mathrm{d}v \\ &= 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\times\tfrac{1}{2}\left(\frac{2RT}{M}\right)^2 = \left(\frac{8RT}{\pi M}\right)^{1/2}\end{aligned}$$

where we have used the standard result from tables of integrals (or software) that

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

Substitution of the data then gives

$$\bar{c} = \left(\frac{8\times(8.3141\ \mathrm{J\ K^{-1}\ mol^{-1}})\times(298\ \mathrm{K})}{\pi\times(28.02\times10^{-3}\ \mathrm{kg\ mol^{-1}})}\right)^{1/2} = 475\ \mathrm{m\ s^{-1}}$$

where we have used $1\ \mathrm{J} = 1\ \mathrm{kg\ m^2\ s^{-2}}$.

Self-test 20.1 Evaluate the root mean square speed of the molecules by integration. You will need the integral

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

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

As shown in Example 20.1, we can use the Maxwell distribution to evaluate the **mean speed**, $\bar{c}$, of the molecules in a gas:

$$\bar{c} = \left(\frac{8RT}{\pi M}\right)^{1/2} \qquad \boxed{\text{Mean speed}} \tag{20.7}$$

We can identify the **most probable speed**, c^*, by differentiating f with respect to v and looking for the value of v at which the derivative is zero (other than at $v = 0$ and $v = \infty$):

$$c^* = \left(\frac{2RT}{M}\right)^{1/2} \qquad \boxed{\text{Most probable speed}} \tag{20.8}$$

Figure 20.6 summarizes these results. Note that the mean speed is the value of v that divides the distribution into two equal areas.

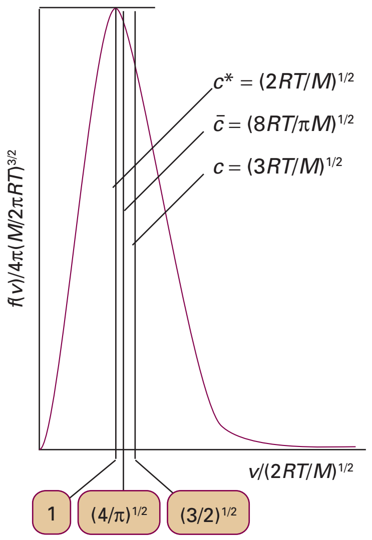

Fig. 20.6 A summary of the conclusions that can be deduced from the Maxwell distribution for molecules of molar mass M at a temperature T: c^* is the most probable speed, $\bar{c}$ is the mean speed, and c is the root mean square speed.

The **relative mean speed**, $\bar{c}_{\mathrm{rel}}$, the mean speed with which one molecule approaches another, can also be calculated from the distribution:

$$\bar{c}_{\mathrm{rel}} = 2^{1/2}\bar{c} \qquad (20.9)$$

Relative mean speed

This result is much harder to derive, but the diagram in Fig. 20.7 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:

$$\bar{c}_{\mathrm{rel}} = \left(\frac{8kT}{\pi\mu}\right)^{1/2} \qquad \mu = \frac{m_A m_B}{m_A + m_B} \qquad (20.10)$$

Relative mean speed

Note that the molecular masses (not the molar masses) and Boltzmann's constant, $k = R/N_A$, appear in this expression; the quantity μ is called the **reduced mass** of the molecules. Equation 20.10 turns into eqn 20.9 when the molecules are identical (that is, $m_A = m_B = m$, so $\mu = \frac{1}{2}m$).

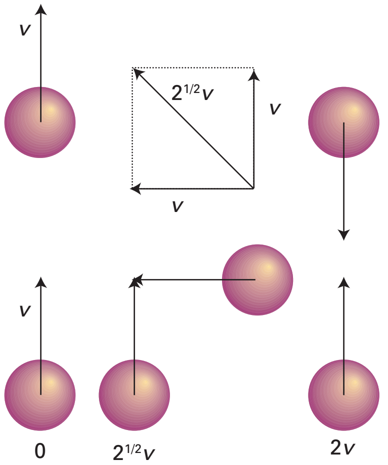

Fig. 20.7 A simplified version of the argument to show that the relative mean speed of molecules in a gas is related to the mean speed. When the molecules are moving in the same direction, the relative mean speed is zero; it is $2v$ when the molecules are approaching each other. A typical mean direction 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.

(b) The collision frequency

A qualitative picture of the events taking place in a gas was first described in Section 1.2. The kinetic model enables us to make that picture more quantitative. In particular, it enables us to calculate the frequency with which molecular collisions occur and the distance a molecule travels on average between collisions.

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*, we can use kinetic model 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

$$z = \sigma\bar{c}_{\mathrm{rel}}\mathcal{N} \qquad (20.11a)^{\circ}$$

Collision frequency

with $\mathcal{N} = N/V$ and $\bar{c}_{\mathrm{rel}}$ given in eqn 20.10. The area $\sigma = \pi d^2$ is called the **collision cross-section** of the molecules. Some typical collision cross-sections are given in Table 20.1. In terms of the pressure

$$z = \frac{\sigma\bar{c}_{\mathrm{rel}}p}{kT} \qquad (20.11b)^{\circ}$$

Collision frequency in terms of the pressure

A brief comment

The reduced mass arises whenever relative motion of two particles is encountered. It also occurs in the hydrogen atom when considering the relative motion of the electron and nucleus (Section 9.1) and in the description of the vibration of a diatomic molecule (Section 12.8).

Justification 20.3 *Using the kinetic model to calculate the collision frequency*

When a molecule travels through a gas it sweeps out a 'collision tube' of area $\sigma = \pi d^2$ and length $\lambda = \bar{c}_{\mathrm{rel}}\Delta t$ where $\bar{c}_{\mathrm{rel}}$ is the relative velocity and Δt is the interval before the first collision (Fig. 20.8). There is one molecule in this tube of volume $\sigma\lambda$, so the number density is $1/\sigma\lambda = 1/\sigma\bar{c}_{\mathrm{rel}}\Delta t$. This number density must be equal to the bulk number density, $\mathcal{N} = N/V = p/kT$, so from $p/kT = 1/\sigma\bar{c}_{\mathrm{rel}}\Delta t$ we can infer that $\Delta t = kT/\sigma\bar{c}_{\mathrm{rel}}p$. The collision frequency, z, is the inverse of the time between collisions, so $z = 1/\Delta t = \sigma\bar{c}_{\mathrm{rel}}p/kT$, as in eqn 20.11b.

Table 20.1* Collision cross-sections

	σ/nm^2
C_6H_6	0.88
CO_2	0.52
He	0.21
N_2	0.43

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

Equation 20.11a shows that, at constant volume (and therefore constant number density), the collision frequency increases with increasing temperature. The reason

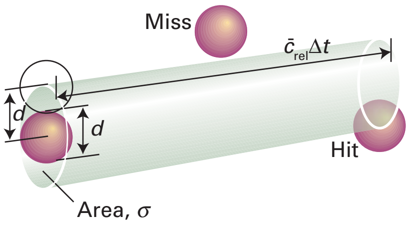

Fig. 20.8 The calculation of the collision frequency and the mean free path in the kinetic theory of gases.

for this increase is that the relative mean speed increases with temperature (eqns 20.9 and 20.10). Equation 20.11b shows 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, $z \approx 5 \times 10^9\ \mathrm{s}^{-1}$, so a given molecule collides about 5×10^9 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**, λ (lambda), the average distance a molecule travels between collisions. As implied by the derivation in *Justification 20.3*

$$\lambda = \bar{c}_{\rm rel}\Delta t = \frac{\bar{c}_{\rm rel}}{z} \qquad \text{Mean free path} \qquad (20.12)$$

Substitution of the expression for z in eqn 20.11b gives

$$\lambda = \frac{kT}{\sigma p} \qquad \text{Mean free path in terms of the pressure} \qquad (20.13)$$

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 20.13, 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 500 m s^{-1}. Each molecule makes a collision within about 1 ns, and between collisions it travels about 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.

IMPACT ON ASTROPHYSICS

I20.1 The Sun as a ball of perfect gas

The kinetic model of gases is valid when the size of the particles is negligible compared with their mean free path. It may seem absurd, therefore, to expect the kinetic model and, as a consequence, the perfect gas law, to be applicable to the dense matter of stellar interiors. In the Sun, for instance, the density at its centre is 1.50 times that of liquid water and comparable to that of water about halfway to its surface. However, we have to realize that the state of matter is that of a *plasma*, in which the electrons have been stripped from the atoms of hydrogen and helium that make up the bulk of the matter of stars. As a result, the particles making up the plasma have diameters comparable to those of nuclei, or about 10 fm. Therefore, a mean free path of only 0.1 pm satisfies the criterion for the validity of the kinetic theory and the perfect gas law. We can therefore use $pV = nRT$ as the equation of state for the stellar interior. Although the Coulombic interaction between charged particles is strong, at the high temperatures of stellar interiors the kinetic energy of the charged particles is very much greater and so 'kinetic-energy only' is a tolerable approximation.

As for any perfect gas, the pressure in the interior of the Sun is related to the mass density, $\rho = m/V$, by $p = \rho RT/M$. Atoms are stripped of their electrons in the interior of stars so, if we suppose that the interior consists of ionized hydrogen atoms, the mean molar mass is one-half the molar mass of hydrogen, or 0.5 g mol^{-1} (the mean of the molar mass of H$^+$ and e$^-$, the latter being virtually 0). Halfway to the centre of the Sun, the temperature is 3.6 MK and the mass density is 1.20 g cm^{-3} (slightly denser than water); so the pressure there works out as 7.2×10^{13} Pa, or about 720 million atmospheres.

We can combine this result with the expression for the pressure from the kinetic model (eqn 20.1). Because the total kinetic energy of the particles is $E_k = \frac{1}{2}Nmc^2$, we can write $p = \frac{2}{3}E_k/V$. That is, the pressure of the plasma is related to the *kinetic energy density*, $\rho_k = E_k/V$, the kinetic energy of the molecules in a region divided by the volume of the region, by $p = \frac{2}{3}\rho_k$. It follows that the kinetic energy density halfway to the centre of the Sun is about 0.11 GJ cm^{-3}. In contrast, on a warm day (25°C) on Earth, the (translational) kinetic energy density of our atmosphere is only 0.15 J cm^{-3}.

20.2 Collisions with walls and surfaces

Key point **The collision flux, Z_W, is the number of collisions with an area in a given time interval divided by the area and the duration of the interval.**

The key result for accounting for transport in the gas phase (and in Chapter 23 for the discussion of surface chemistry) is the rate at which molecules strike an area, which may be an imaginary area embedded in the gas, or part of a real wall. The **collision flux**, Z_W, is the number of collisions with the area in a given time interval divided by the area and the duration of the interval. The **collision frequency**, the number of hits per second, is obtained by multiplication of the collision flux by the area of interest. We show in the following *Justification* that the collision flux is

$$Z_W = \frac{p}{(2\pi mkT)^{1/2}} \qquad \boxed{\text{Collision flux}} \qquad (20.14)^\circ$$

When $p = 100$ kPa (1.00 bar) and $T = 300$ K, $Z_W \approx 3 \times 10^{23}$ cm^{-2} s^{-1} for O$_2$.

Justification 20.4 *The collision flux*

Consider a wall of area A perpendicular to the x-axis (as in Fig. 20.2). If a molecule has $v_x > 0$ (that is, it is travelling in the direction of positive x), then it will strike the wall within an interval Δt if it lies within a distance $v_x\Delta t$ of the wall. Therefore, all molecules in the volume $Av_x\Delta t$, and with positive x-component of velocities, will strike the wall in the interval Δt. The total number of collisions in this interval is therefore the volume $Av_x\Delta t$ multiplied by the number density, $\mathcal{N}$, of molecules. However, to take account of the presence of a range of velocities in the sample, we must sum the result over all the positive values of v_x weighted by the probability distribution of velocities (eqn 20.6):

$$\text{Number of collisions} = \mathcal{N}A\Delta t\int_0^\infty v_x f(v_x)\mathrm{d}x$$

The collision flux is the number of collisions divided by A and Δt, so

$$Z_W = \mathcal{N}\int_0^\infty v_x f(v_x)\mathrm{d}x$$

Exercises

20.1(a) Determine the ratios of (a) the mean speeds, (b) the mean kinetic energies of H_2 molecules and Hg atoms at 20°C.

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

20.2(a) A 1.0 dm^3 glass bulb contains 1.0×10^{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?

20.2(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.

20.3(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 m s^{-1}.

20.3(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 m s^{-1}.

20.4(a) Find an expression for the root mean square deviation of the speed of molecules in a gas from its mean value, $\Delta c = \{\langle c^2\rangle - \langle c\rangle^2\}^{1/2}$.

20.4(b) Find a relation between $\langle c^2\rangle^{1/2}$ and $\langle c^4\rangle^{1/4}$ for molecules in a gas at a temperature T.

20.5(a) At what pressure does the mean free path of argon at 25°C become comparable to the size of a 1 dm^3 vessel that contains it? Take $\sigma = 0.36$ nm^2.

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

20.6(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.)

20.6(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.)

20.7(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 μatm?

20.7(b) How many collisions per second does an N_2 molecule make at an altitude of 15 km? (See Exercise 20.6b for data.)

20.8(a) Calculate the mean free path of molecules in air using $\sigma = 0.43$ nm^2 at 25°C and (a) 10 atm, (b) 1.0 atm, (c) 1.0 μatm.

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

20.9(a) A solid surface with dimensions 2.5 mm × 3.0 mm is exposed to argon gas at 90 Pa and 500 K. How many collisions do the Ar atoms make with this surface in 15 s?

20.9(b) A solid surface with dimensions 3.5 mm × 4.0 cm is exposed to helium gas at 111 Pa and 1500 K. How many collisions do the He atoms make with this surface in 10 s?

20.10(a) An effusion cell has a circular hole of diameter 2.50 mm. If the molar mass of the solid in the cell is 260 g mol^{-1} and its vapour pressure is 0.835 Pa at 400 K, by how much will the mass of the solid decrease in a period of 2.00 h?

20.10(b) An effusion cell has a circular hole of diameter 3.00 mm. If the molar mass of the solid in the cell is 300 g mol^{-1} and its vapour pressure is 0.224 Pa at 450 K, by how much will the mass of the solid decrease in a period of 24.00 h?

20.11(a) A solid compound of molar mass 100 g mol^{-1} was introduced into a container and heated to 400°C. When a hole of diameter 0.50 mm was opened in the container for 400 s, a mass loss of 285 mg was measured. Calculate the vapour pressure of the compound at 400°C.

20.11(b) A solid compound of molar mass 200 g mol^{-1} was introduced into a container and heated to 300°C. When a hole of diameter 0.50 mm was opened in the container for 500 s, a mass loss of 277 mg was measured. Calculate the vapour pressure of the compound at 300°C.

20.12(a) A manometer was connected to a bulb containing carbon dioxide under slight pressure. The gas was allowed to escape through a small pinhole, and the time for the manometer reading to drop from 75 cm to 50 cm was 52 s. When the experiment was repeated using nitrogen (for which $M = 28.02$ g mol^{-1}) the same fall took place in 42 s. Calculate the molar mass of carbon dioxide.

20.12(b) A manometer was connected to a bulb containing nitrogen under slight pressure. The gas was allowed to escape through a small pinhole, and the time for the manometer reading to drop from 65.1 cm to 42.1 cm was 18.5 s. When the experiment was repeated using a fluorocarbon gas, the same fall took place in 82.3 s. Calculate the molar mass of the fluorocarbon.

20.13(a) A space vehicle of internal volume 3.0 m^3 is struck by a meteor and a hole of radius 0.10 mm is formed. If the oxygen pressure within the vehicle is initially 80 kPa and its temperature 298 K, how long will the pressure take to fall to 70 kPa?

20.13(b) A container of internal volume 22.0 m^3 was punctured, and a hole of radius 0.050 mm was formed. If the nitrogen pressure within the vehicle is initially 122 kPa and its temperature 293 K, how long will the pressure take to fall to 105 kPa?

20.14(a) Calculate the flux of energy arising from a temperature gradient of 2.5 K m^{-1} in a sample of argon in which the mean temperature is 273 K.

20.14(b) Calculate the flux of energy arising from a temperature gradient of 3.5 K m^{-1} in a sample of hydrogen in which the mean temperature is 260 K.

20.15(a) Use the experimental value of the thermal conductivity of neon (Table 20.2) to estimate the collision cross-section of Ne atoms at 273 K.

20.15(b) Use the experimental value of the thermal conductivity of nitrogen (Table 20.2) to estimate the collision cross-section of N_2 molecules at 298 K.

20.16(a) In a double-glazed window, the panes of glass are separated by 5.0 cm. What is the rate of transfer of heat by conduction from the warm room (25°C) to the cold exterior (−10°C) through a window of area 1.0 m^2? What power of heater is required to make good the loss of heat?

20.16(b) Two sheets of copper of area 1.50 m^2 are separated by 10.0 cm. What is the rate of transfer of heat by conduction from the warm sheet (50°C) to the cold sheet (−10°C). What is the rate of loss of heat?

20.17(a) Use the experimental value of the coefficient of viscosity for neon (Table 20.2) to estimate the collision cross-section of Ne atoms at 273 K.

20.17(b) Use the experimental value of the coefficient of viscosity for nitrogen (Table 20.2) to estimate the collision cross-section of the molecules at 273 K.

20.18(a) Calculate the inlet pressure required to maintain a flow rate of 9.5×10^5 dm^3 h^{-1} of nitrogen at 293 K flowing through a pipe of length 8.50 m and diameter 1.00 cm. The pressure of gas as it leaves the tube is 1.00 bar. The volume of the gas is measured at that pressure.

Chapter 1

E1.1(a)	(a) 24 atm (b) 22 atm
E1.2(a)	(a) 3.42 bar (b) 3.38 atm
E1.3(a)	30 lb in^{-2}
E1.4(a)	4.20×10^{-2} atm
E1.5(a)	0.50 m^3
E1.6(a)	102 kPa
E1.7(a)	8.3147 J K^{-1} mol^{-1}
E1.8(a)	S_8
E1.9(a)	6.2 kg
E1.10(a)	(a) (i) 0.762 (ii) 0.238 (iii) 0.752 bar (iv) 0.235 bar
	(b) (i) 0.782 (ii) 0.208 (iii) 0.0099 bar (iv) 0.772 bar (v) 0.205
E1.11(a)	169 g mol^{-1}
E1.12(a)	−273°C
E1.13(a)	(a) (i) 1.0 atm (ii) 8.2×10^2 atm
	(b) (i) 1.0 atm (ii) 1.8×10^3 atm
E1.14(a)	$a = 7.61 \times 10^{-2}$ kg m^5 s^{-2} mol^{-2}, $b = 2.26 \times 10^{-5}$ m^3 mol^{-1}
E1.15(a)	(a) 0.88 (b) 1.2 dm^3 mol^{-1}
E1.16(a)	140 atm
E1.17(a)	(a) 50.7 atm (b) 35.2 atm, 0.695
E1.18(a)	(a) 0.67, 0.33 (b) 2.0 atm, 1.0 atm (c) 3.0 atm
E1.19(a)	32.9 cm^3 mol^{-1}, 1.33 dm^6 atm mol^{-2}, 0.118 nm
E1.20(a)	(a) 1.41×10^3 K (b) 0.139 nm
E1.21(a)	(a) $T = 3.64 \times 10^3$ K, $p = 8.7$ atm (b) $T = 2.60 \times 10^3$ K, $p = 4.5$ atm
	(c) $T = 46.7$ K, $p = 0.18$ atm
E1.22(a)	0.66

Chapter 20

E20.1(a) (a) 9.975

E20.2(a) (a) 72 K (b) $94\bar{6}\ \mathrm{m\,s^{-1}}$ (c) the temperature would not be different

E20.3(a) 9.06×10^{-3}

E20.4(a) $\left(3-\frac{8}{\pi}\right)^{1/2}\left(\frac{RT}{M}\right)^{1/2}, \left(1-\frac{8}{\pi}\right)^{1/2} c$

E20.5(a) 0.0652 Pa

E20.6(a) 0.97 μm

E20.7(a) $397\ \mathrm{m\,s^{-1}}$ (a) $5.0 \times 10^{10}\ \mathrm{s^{-1}}$ (b) $5.0 \times 10^{9}\ \mathrm{s^{-1}}$ (c) $5.0 \times 10^{3}\ \mathrm{s^{-1}}$

E20.8(a) (a) 6.7 nm (b) 67 nm (c) 6.7 cm

E20.9(a) 1.9×10^{20}

E20.10(a) 104 mg

E20.11(a) 415 Pa

E20.12(a) $42.4\ \mathrm{g\,mol^{-1}}$

E20.13(a) 1.3 days

E20.14(a) $-0.013\ \mathrm{J\,m^{-2}\,s^{-1}}$

E20.15(a) $0.0562\ \mathrm{nm^2}$

E20.16(a) 17 W

E20.17(a) $0.142\ \mathrm{nm^2}$

E20.18(a) $p_1 = 205\ \mathrm{kPa}, \frac{\mathrm{d}V}{\mathrm{d}t} = \frac{\pi R^4}{16\eta p_0 l}(p_1^2 - p_2^2)$ Poiseuille's formula

E20.19(a) (a) $12\bar{7}$ μP (b) $13\bar{2}$ μP (c) $24\bar{3}$ μP

E20.20(a) (a) $\kappa = 5.4\ \mathrm{mJ\,K^{-1}\,m^{-1}\,s^{-1}}$, $J_{\text{energy}} = -0.81\ \mathrm{W\,m^{-2}}$, Rate of energy flow $= -8.1$ mW (b) $\kappa = 29\ \mathrm{mJ\,K^{-1}\,m^{-1}\,s^{-1}}$, $J_{\text{energy}} = -4.4\ \mathrm{W\,m^{-2}}$, Rate of energy flow $= -44$ mW

E20.21(a) $5.4\ \mathrm{mJ\,m^{-1}\,s^{-1}}$