

1

The properties of gases

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

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

The perfect gas

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

1.1 The states of gases

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

The general form of an equation of state is

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

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

The perfect gas

1.1 The states of gases

1.2 The gas laws

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Real gases

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Table 1.1 Pressure units

Name	Symbol	Value
pascal	1 Pa	1 N m^{-2} , $1 \text{ kg m}^{-1} \text{ s}^{-2}$
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

Comment 1.1

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

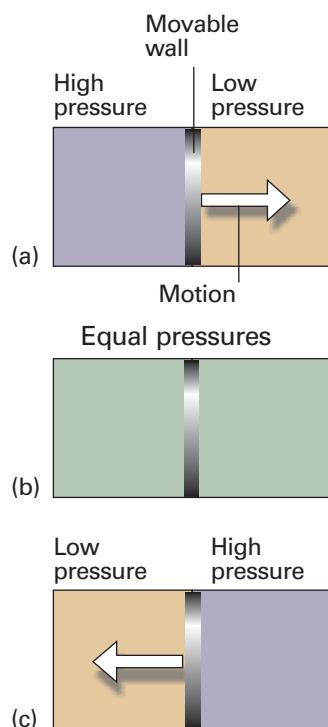


Fig. 1.1 When a region of high pressure is separated from a region of low pressure by a movable wall, the wall will be pushed into one region or the other, as in (a) and (c). However, if the two pressures are identical, the wall will not move (b). The latter condition is one of mechanical equilibrium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

(a) Pressure

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

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

$$1 \text{ Pa} = 1 \text{ N m}^{-2} \quad [1.2a]$$

In terms of base units,

$$1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2} \quad [1.2b]$$

Several other units are still widely used (Table 1.1); of these units, the most commonly used are atmosphere (1 atm = 1.01325×10^5 Pa exactly) and bar (1 bar = 10^5 Pa). A pressure of 1 bar is the **standard pressure** for reporting data; we denote it p° .

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

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

(b) The measurement of pressure

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

exerted by the atmosphere. It follows that the height of the mercury column is proportional to the external pressure.

Example 1.1 Calculating the pressure exerted by a column of liquid

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

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

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

$$F = mg = \rho Ahg$$

The pressure at the base of the column is therefore

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

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

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

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).

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

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

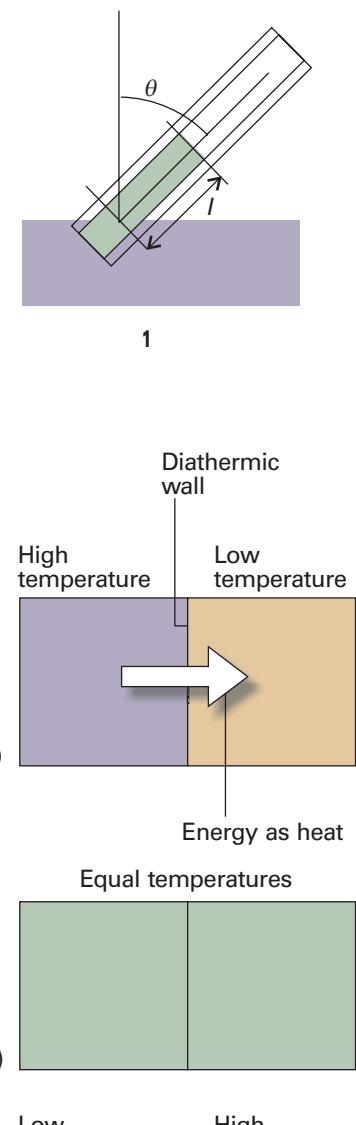


Fig. 1.2 Energy flows as heat from a region at a higher temperature to one at a lower temperature if the two are in contact through a diathermic wall, as in (a) and (c). However, if the two regions have identical temperatures, there is no net transfer of energy as heat even though the two regions are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

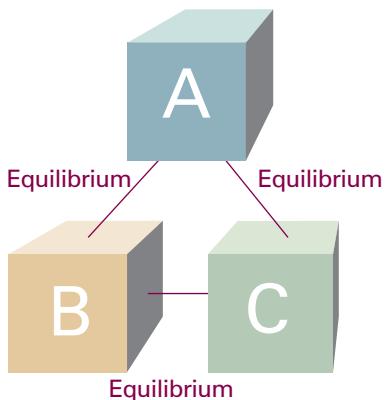


Fig. 1.3 The experience summarized by the Zeroth Law of thermodynamics is that, if an object A is in thermal equilibrium with B and B is in thermal equilibrium with C, then C is in thermal equilibrium with A.

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.

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

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

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

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

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

Illustration 1.1 Converting temperatures

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

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

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

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

1.2 The gas laws

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

(a) The perfect gas law

We assume that the following individual gas laws are familiar:

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

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

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

$$\text{Avogadro's principle:}^2 V = \text{constant} \times n \text{ at constant } p, T \quad (1.7)^{\circ}$$

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 $p \rightarrow 0$. 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 $p \rightarrow 0$. Although these relations are strictly true only at $p = 0$, they are reasonably reliable at normal pressures ($p \approx 1$ bar) and are used widely throughout chemistry.

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

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

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

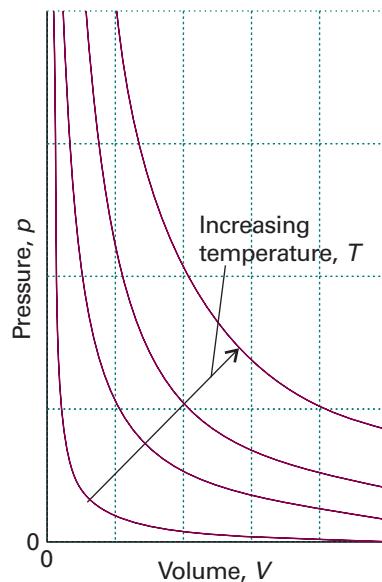


Fig. 1.4 The pressure–volume dependence of a fixed amount of perfect gas at different temperatures. Each curve is a hyperbola ($pV = \text{constant}$) and is called an **isotherm**.

 **Exploration**³ Explore how the pressure of 1.5 mol CO₂(g) varies with volume as it is compressed at (a) 273 K, (b) 373 K from 30 dm³ to 15 dm³.

Comment 1.2

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

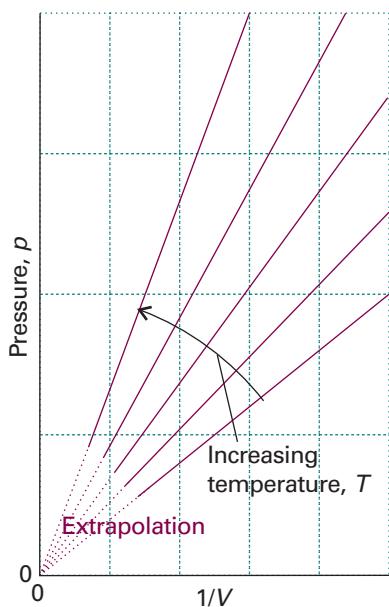


Fig. 1.5 Straight lines are obtained when the pressure is plotted against $1/V$ at constant temperature.

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

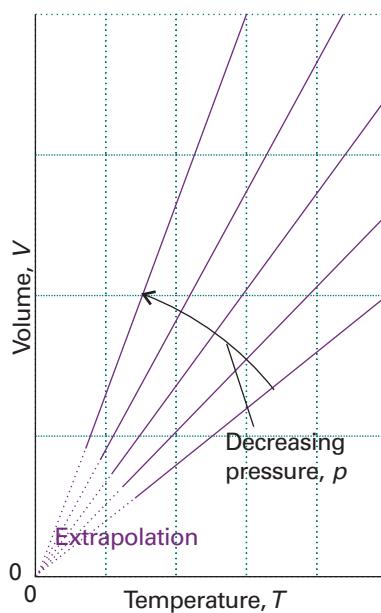


Fig. 1.6 The variation of the volume of a fixed amount of gas with the temperature at constant pressure. Note that in each case the isobars extrapolate to zero volume at $T = 0$, or $\theta = -273^{\circ}\text{C}$.

Exploration Explore how the volume of 1.5 mol $\text{CO}_2(\text{g})$ in a container maintained at (a) 1.00 bar, (b) 0.50 bar varies with temperature as it is cooled from 373 K to 273 K.

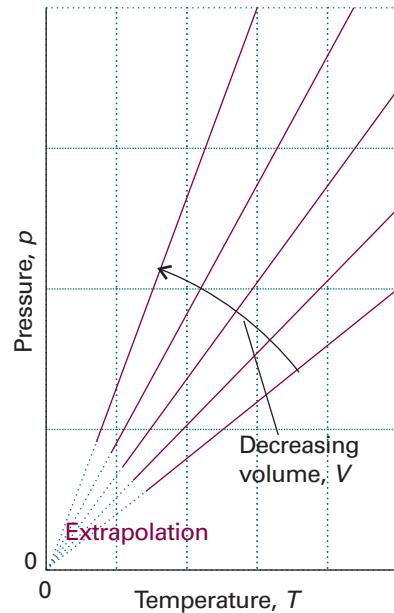


Fig. 1.7 The pressure also varies linearly with the temperature at constant volume, and extrapolates to zero at $T = 0$ (-273°C).

Exploration Explore how the pressure of 1.5 mol $\text{CO}_2(\text{g})$ in a container of volume (a) 30 dm^3 , (b) 15 dm^3 varies with temperature as it is cooled from 373 K to 273 K.

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

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

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

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

$$pV = nRT \tag{1.8}^{\circ}$$

is the **perfect gas equation**. It is the approximate equation of state of any gas, and becomes increasingly exact as the pressure of the gas approaches zero. A gas that obeys eqn 1.8 exactly under all conditions is called a **perfect gas** (or *ideal gas*). A **real gas**, an actual gas, behaves more like a perfect gas the lower the pressure, and is described exactly by eqn 1.8 in the limit of $p \rightarrow 0$. 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.

Molecular interpretation 1.1 The kinetic model of gases

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

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

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

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

$$pV = \frac{1}{3}nMc^2 \quad (1.9)^{\circ}$$

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

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

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

$$pV = \text{constant}$$

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

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

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

Table 1.2 The gas constant

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

Comment 1.3

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

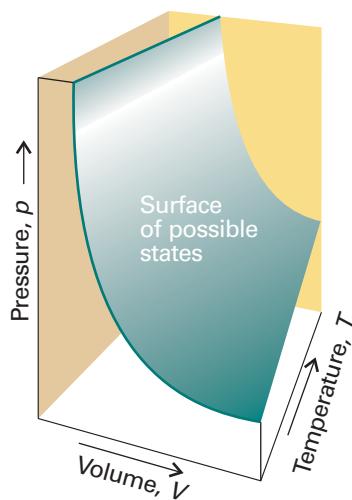


Fig. 1.8 A region of the p, V, T surface of a fixed amount of perfect gas. The points forming the surface represent the only states of the gas that can exist.

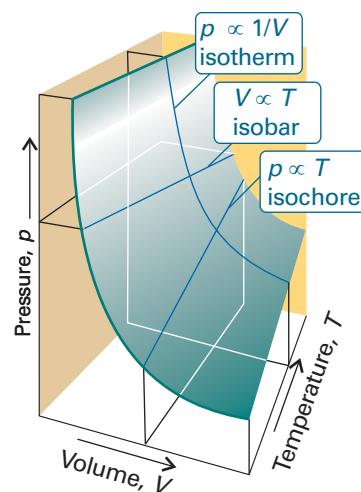


Fig. 1.9 Sections through the surface shown in Fig. 1.8 at constant temperature give the isotherms shown in Fig. 1.4 and the isobars shown in Fig. 1.6.

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

Example 1.2 Using the perfect gas equation

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

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

$$\frac{p_1 V_1}{n_1 T_1} = \frac{p_2 V_2}{n_2 T_2} \quad (1.12)^o$$

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

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

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

2

Substitution of the data then gives

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

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

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

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

IMPACT ON ENVIRONMENTAL SCIENCE

11.1 The gas laws and the weather

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

Table 1.3 The composition of dry air at sea level

Component	Percentage	
	By volume	By mass
Nitrogen, N ₂	78.08	75.53
Oxygen, O ₂	20.95	23.14
Argon, Ar	0.93	1.28
Carbon dioxide, CO ₂	0.031	0.047
Hydrogen, H ₂	5.0×10^{-3}	2.0×10^{-4}
Neon, Ne	1.8×10^{-3}	1.3×10^{-3}
Helium, He	5.2×10^{-4}	7.2×10^{-5}
Methane, CH ₄	2.0×10^{-4}	1.1×10^{-4}
Krypton, Kr	1.1×10^{-4}	3.2×10^{-4}
Nitric oxide, NO	5.0×10^{-5}	1.7×10^{-6}
Xenon, Xe	8.7×10^{-6}	1.2×10^{-5}
Ozone, O ₃ ; summer	7.0×10^{-6}	1.2×10^{-5}
winter	2.0×10^{-6}	3.3×10^{-6}

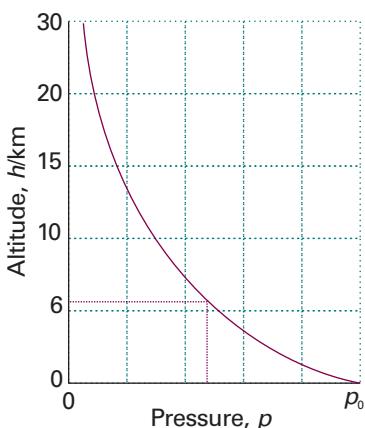


Fig. 1.10 The variation of atmospheric pressure with altitude, as predicted by the barometric formula and as suggested by the 'US Standard Atmosphere', which takes into account the variation of temperature with altitude.

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

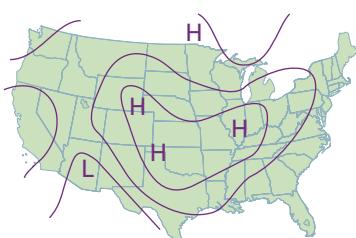


Fig. 1.11 A typical weather map; in this case, for the United States on 1 January 2000.

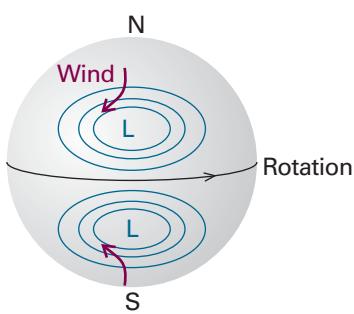


Fig. 1.12 The flow of air ('wind') around regions of high and low pressure in the Northern and Southern hemispheres.

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

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

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

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

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

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

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

(b) Mixtures of gases

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

$$p_J = x_J p$$

[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:

$$x_J = \frac{n_J}{n} \quad n = n_A + n_B + \dots \quad [1.14]$$

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

$$p_A + p_B + \dots = (x_A + x_B + \dots) p = p \quad (1.15)$$

This relation is true for both real and perfect gases.

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

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

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

Example 1.3 Calculating partial pressures

The mass percentage composition of dry air at sea level is approximately N₂: 75.5; O₂: 23.2; Ar: 1.3. What is the partial pressure of each component when the total pressure is 1.00 atm?

Method We expect species with a high mole fraction to have a proportionally high partial pressure. Partial pressures are defined by eqn 1.13. To use the equation, we need the mole fractions of the components. To calculate mole fractions, which are defined by eqn 1.14, we use the fact that the amount of molecules J of molar mass M_J in a sample of mass m_J is $n_J = m_J/M_J$. The mole fractions are independent of the total mass of the sample, so we can choose the latter to be 100 g (which makes the conversion from mass percentages very easy). Thus, the mass of N₂ 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 N₂, O₂, and Ar are 75.5 g, 23.2 g, and 1.3 g, respectively, are

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

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

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

These three amounts work out as 2.69 mol, 0.725 mol, and 0.033 mol, respectively, for a total of 3.45 mol. The mole fractions are obtained by dividing each of the

above amounts by 3.45 mol and the partial pressures are then obtained by multiplying the mole fraction by the total pressure (1.00 atm):

	N ₂	O ₂	Ar
Mole fraction:	0.780	0.210	0.0096
Partial pressure/atm:	0.780	0.210	0.0096

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

Self-test 1.4 When carbon dioxide is taken into account, the mass percentages are 75.52 (N₂), 23.15 (O₂), 1.28 (Ar), and 0.046 (CO₂). What are the partial pressures when the total pressure is 0.900 atm? [0.703, 0.189, 0.0084, 0.00027 atm]

Real gases

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

1.3 Molecular interactions

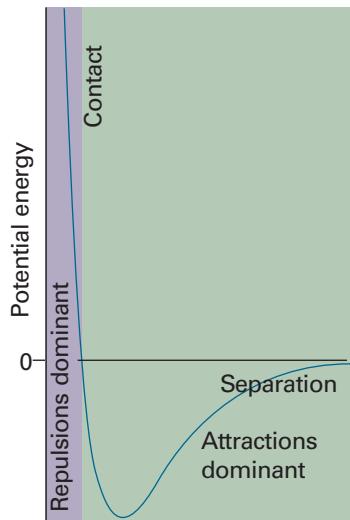


Fig. 1.13 The variation of the potential energy of two molecules on their separation. High positive potential energy (at very small separations) indicates that the interactions between them are strongly repulsive at these distances. At intermediate separations, where the potential energy is negative,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

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

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

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

(a) The compression factor

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

$$Z = \frac{V_m}{V_m^o} \quad [1.16]$$

Because the molar volume of a perfect gas is equal to RT/p , an equivalent expression is $Z = RT/pV_m^o$, which we can write as

$$pV_m = RTZ \quad (1.17)$$

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

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

(b) Virial coefficients

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

$$pV_m = RT(1 + B'p + C'p^2 + \dots) \quad (1.18)$$

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

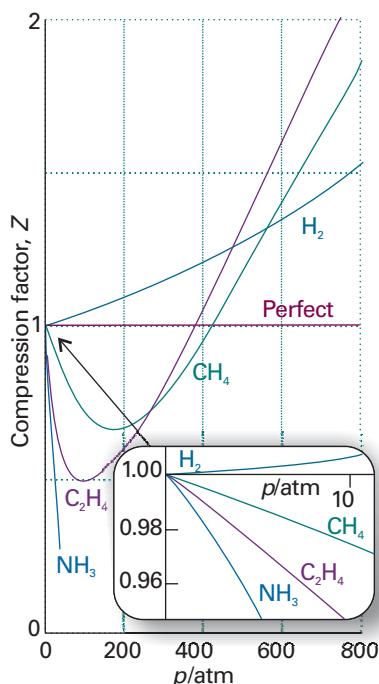


Fig. 1.14 The variation of the compression factor, Z , with pressure for several gases at 0°C . A perfect gas has $Z = 1$ at all pressures. Notice that, although the curves approach 1 as $p \rightarrow 0$, they do so with different slopes.

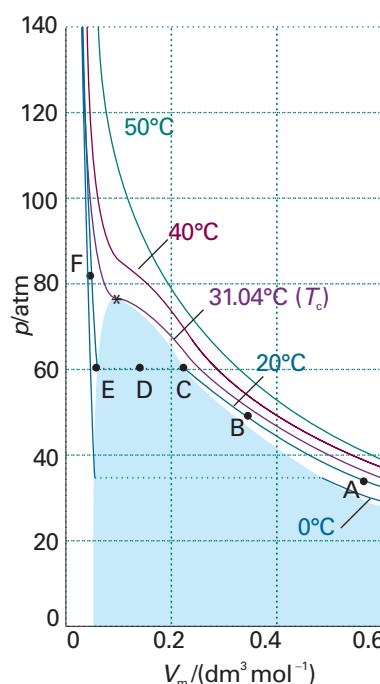


Fig. 1.15 Experimental isotherms of carbon dioxide at several temperatures. The ‘critical isotherm’, the isotherm at the critical temperature, is at 31.04°C . The critical point is marked with a star.

Comment 1.4

Series expansions are discussed in Appendix 2.

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

	Temperature	
	273 K	600 K
Ar	-21.7	11.9
CO ₂	-149.7	-12.4
N ₂	-10.5	21.7
Xe	-153.7	-19.6

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

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

$$pV_m = RT \left(1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots \right) \quad (1.19)$$

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

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

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

$$\frac{dZ}{dp} = B' + 2pC' + \dots \rightarrow B' \quad \text{as} \quad p \rightarrow 0 \quad (1.20a)$$

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

$$\frac{dZ}{d(1/V_m)} \rightarrow B \text{ as } V_m \rightarrow \infty, \quad \text{corresponding to} \quad p \rightarrow 0 \quad (1.20b)$$

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

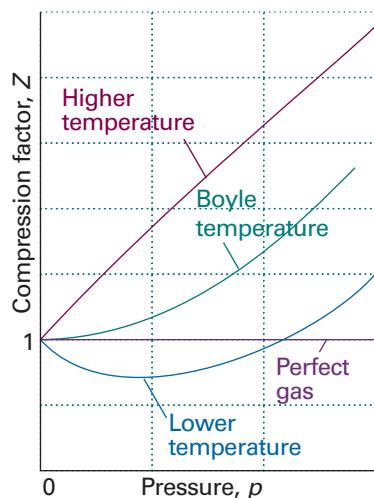


Fig. 1.16 The compression factor, Z , approaches 1 at low pressures, but does so with different slopes. For a perfect gas, the slope is zero, but real gases may have either positive or negative slopes, and the slope may vary with temperature. At the Boyle temperature, the slope is zero and the gas behaves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

Synoptic Table 1.5* Critical constants of gases

	p_c/atm	$V_c/(cm^3 \text{ mol}^{-1})$	T_c/K	Z_c	T_B/K
Ar	48.0	75.3	150.7	0.292	411.5
CO ₂	72.9	94.0	304.2	0.274	714.8
He	2.26	57.8	5.2	0.305	22.64
O ₂	50.14	78.0	154.8	0.308	405.9

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

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

(c) Condensation

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

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

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

(d) Critical constants

The isotherm at the temperature T_c (304.19 K, or 31.04°C for CO₂) plays a special role in the theory of the states of matter. An isotherm slightly below T_c behaves as we have already described: at a certain pressure, a liquid condenses from the gas and is distinguishable from it by the presence of a visible surface. If, however, the compression takes place at T_c itself, then a surface separating two phases does not appear and the volumes at each end of the horizontal part of the isotherm have merged to a single point, the **critical point** of the gas. The temperature, pressure, and molar volume at the critical point are called the **critical temperature**, T_c , **critical pressure**, p_c , and **critical molar volume**, V_c , of the substance. Collectively, p_c , V_c , and T_c are the **critical constants** of a substance (Table 1.5).

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

1.4 The van der Waals equation

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

The **van der Waals equation** is

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

Comment 1.5

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

Synoptic Table 1.6* van der Waals coefficients

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

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

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

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad (1.21b)$$

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

Justification 1.1 The van der Waals equation of state

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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 $\text{dm}^3 \text{ mol}^{-1}$]

(a) The reliability of the equation

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

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

Table 1.7 Selected equations of state

Equation	Reduced form*	Critical constants			
		p_c	V_c	T_c	
Perfect gas	$p = \frac{RT}{V_m}$				
van der Waals	$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$	$p = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2}$	$\frac{a}{27b^2}$	$3b$	$\frac{8a}{27bR}$
Berthelot	$p = \frac{RT}{V_m - b} - \frac{a}{TV_m^2}$	$p = \frac{8T_r}{3V_r - 1} - \frac{3}{T_r V_r^2}$	$\frac{1}{12} \left(\frac{2aR}{3b^3} \right)^{1/2}$	$3b$	$\frac{2}{3} \left(\frac{2a}{3bR} \right)^{1/2}$
Dieterici	$p = \frac{RT e^{-a/RTV_m}}{V_m - b}$	$p = \frac{e^2 T_r e^{-2/T_r V_r}}{2V_r - 1}$	$\frac{a}{4e^2 b^2}$	$2b$	$\frac{a}{4bR}$
Virial	$p = \frac{RT}{V_m} \left\{ 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \dots \right\}$				

* Reduced variables are defined in Section 1.5.

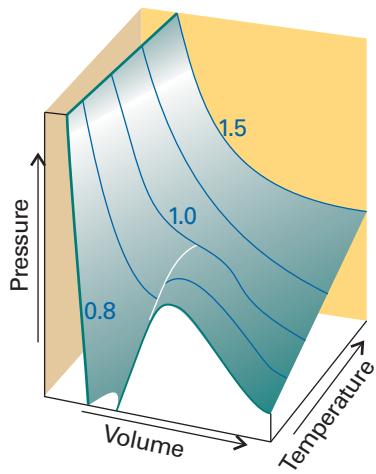


Fig. 1.17 The surface of possible states allowed by the van der Waals equation. Compare this surface with that shown in Fig. 1.8.

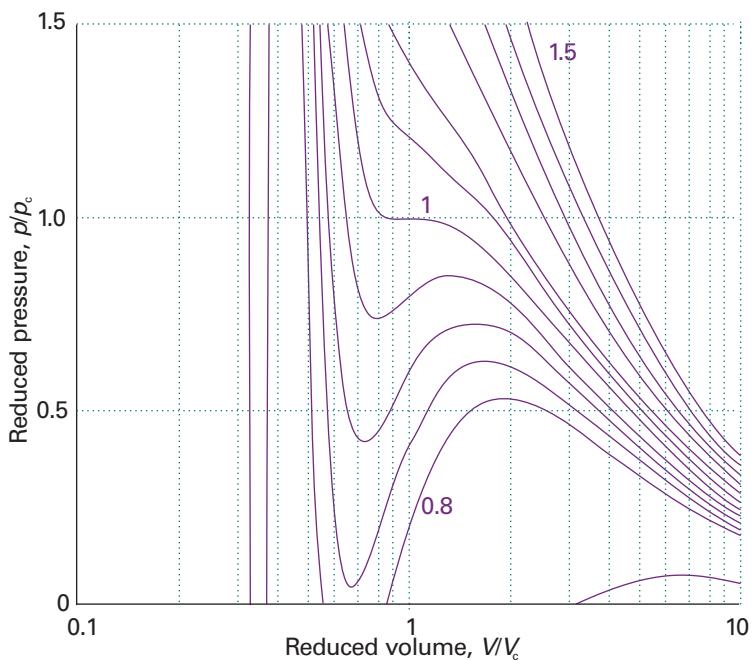
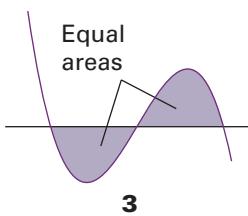


Fig. 1.18 Van der Waals isotherms at several values of T/T_c . Compare these curves with those in Fig. 1.15. The van der Waals loops are normally replaced by horizontal straight lines. The critical isotherm is the isotherm for $T/T_c = 1$.

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

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



(b) The features of the equation

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

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

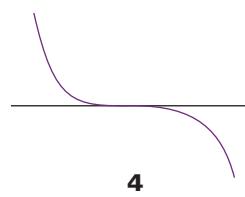
When the temperature is high, RT may be so large that the first term in eqn 1.21b greatly exceeds the second. Furthermore, if the molar volume is large in the sense $V_m \gg b$, then the denominator $V_m - b \approx V_m$. Under these conditions, the equation reduces to $p = RT/V_m$, the perfect gas equation.

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

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

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

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



$$\frac{dp}{dV_m} = -\frac{RT}{(V_m - b)^2} + \frac{2a}{V_m^3} = 0$$

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

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

$$V_c = 3b \quad p_c = \frac{a}{27b^2} \quad T_c = \frac{8a}{27Rb} \quad (1.22)$$

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

$$Z_c = \frac{p_c V_c}{RT_c} = \frac{3}{8} \quad (1.23)$$

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

1.5 The principle of corresponding states

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

$$p_r = \frac{p}{p_c} \quad V_r = \frac{V_m}{V_c} \quad T_r = \frac{T}{T_c} \quad [1.24]$$

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

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

$$p_r p_c = \frac{RT_r T_c}{V_r V_c - b} - \frac{a}{V_r^2 V_c^2}$$

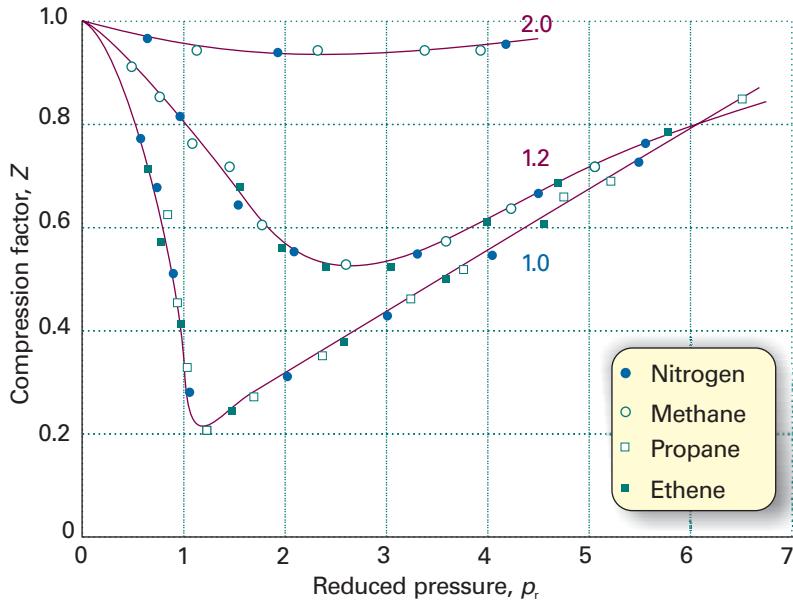


Fig. 1.19 The compression factors of four of the gases shown in Fig. 1.14 plotted using reduced variables. The curves are labelled with the reduced temperature $T_r = T/T_c$. The use of reduced variables organizes the data on to single curves.

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

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

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

which can be reorganized into

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

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

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

Checklist of key ideas

- 1. A gas is a form of matter that fills any container it occupies.
- 2. An equation of state interrelates pressure, volume, temperature, and amount of substance: $p = f(T, V, n)$.
- 3. The pressure is the force divided by the area to which the force is applied. The standard pressure is $p^\circ = 1$ bar (10^5 Pa).
- 4. Mechanical equilibrium is the condition of equality of pressure on either side of a movable wall.
- 5. Temperature is the property that indicates the direction of the flow of energy through a thermally conducting, rigid wall.
- 6. A diathermic boundary is a boundary that permits the passage of energy as heat. An adiabatic boundary is a boundary that prevents the passage of energy as heat.
- 7. Thermal equilibrium is a condition in which no change of state occurs when two objects A and B are in contact through a diathermic boundary.
- 8. The Zeroth Law of thermodynamics states that, if A is in thermal equilibrium with B, and B is in thermal equilibrium with C, then C is also in thermal equilibrium with A.
- 9. The Celsius and thermodynamic temperature scales are related by $T/K = \theta/^\circ\text{C} + 273.15$.
- 10. A perfect gas obeys the perfect gas equation, $pV = nRT$, exactly under all conditions.
- 11. Dalton's law states that the pressure exerted by a mixture of gases is the sum of the partial pressures of the gases.
- 12. The partial pressure of any gas is defined as $p_j = x_j p$, where $x_j = n_j/n$ is its mole fraction in a mixture and p is the total pressure.
- 13. In real gases, molecular interactions affect the equation of state; the true equation of state is expressed in terms of virial coefficients B, C, \dots : $pV_m = RT(1 + B/V_m + C/V_m^2 + \dots)$.
- 14. The vapour pressure is the pressure of a vapour in equilibrium with its condensed phase.
- 15. The critical point is the point at which the volumes at each end of the horizontal part of the isotherm have merged to a single point. The critical constants p_c , V_c , and T_c are the pressure, molar volume, and temperature, respectively, at the critical point.
- 16. A supercritical fluid is a dense fluid phase above its critical temperature and pressure.
- 17. The van der Waals equation of state is an approximation to the true equation of state in which attractions are represented by a parameter a and repulsions are represented by a parameter b : $p = nRT/(V - nb) - a(n/V)^2$.
- 18. A reduced variable is the actual variable divided by the corresponding critical constant.
- 19. According to the principle of corresponding states, real gases at the same reduced volume and reduced temperature exert the same reduced pressure.

Further reading

Articles and texts

- J.L. Pauley and E.H. Davis, *P-V-T* isotherms of real gases: Experimental versus calculated values. *J. Chem. Educ.* **63**, 466 (1986).
- M. Ross, Equations of state. In *Encyclopedia of applied physics* (ed. G.L. Trigg), **6**, 291. VCH, New York (1993).
- A. J. Walton, *Three phases of matter*. Oxford University Press (1983).

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

Sources of data and information

- J.H. Dymond and E.B. Smith, *The virial coefficients of pure gases and mixtures*. Oxford University Press (1980).
- A.D. McNaught and A. Wilkinson, *Compendium of chemical terminology*. Blackwell Scientific, Oxford (1997).

Discussion questions

- 1.1** Explain how the perfect gas equation of state arises by combination of Boyle's law, Charles's law, and Avogadro's principle.
- 1.2** Explain the term 'partial pressure' and explain why Dalton's law is a limiting law.
- 1.3** Explain how the compression factor varies with pressure and temperature and describe how it reveals information about intermolecular interactions in real gases.

- 1.4** What is the significance of the critical constants?
- 1.5** Describe the formulation of the van der Waals equation and suggest a rationale for one other equation of state in Table 1.7.
- 1.6** Explain how the van der Waals equation accounts for critical behaviour.

Exercises

1.1(a) (a) Could 131 g of xenon gas in a vessel of volume 1.0 dm³ 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 dm³ 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 dm³. The final pressure and volume of the gas are 5.04 bar and 4.65 dm³, 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 dm³. The final pressure and volume of the gas are 1.97 bar and 2.14 dm³, 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 dm³ 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 m³ of natural gas in a year to heat a home. Assume that natural gas is all methane, CH₄, 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 m³ 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 dm³ 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 O₂.

p/atm	0.750 000	0.500 000	0.250 000
V _m /(dm ³ mol ⁻¹)	29.9649	44.8090	89.6384
ρ/(g dm ⁻³)	1.07144	0.714110	0.356975

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

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

1.9(a) Calculate the mass of water vapour present in a room of volume 400 m³ 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 m³ 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 cm³ 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 dm³ 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 dm³ (°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 C₂H₆ 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 dm³, (ii) at 1000 K in 100 cm³. Use the data in Table 1.6.

1.13(b) Calculate the pressure exerted by 1.0 mol H₂S 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 dm³, (ii) at 500 K in 150 cm³. Use the data in Table 1.6.

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

1.14(b) Express the van der Waals parameters $a = 1.32 \text{ atm dm}^6 \text{ mol}^{-2}$ and $b = 0.0436 \text{ dm}^3 \text{ mol}^{-1}$ 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 m³. 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, $a = 1.352 \text{ dm}^6 \text{ atm mol}^{-2}$, $b = 0.0387 \text{ dm}^3 \text{ mol}^{-1}$.

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, $a = 1.364 \text{ dm}^6 \text{ atm mol}^{-2}$, $b = 3.19 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}$.

1.17(a) Suppose that 10.0 mol C₂H₆(g) is confined to 4.860 dm³ 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, $a = 5.507 \text{ dm}^6 \text{ atm mol}^{-2}$, $b = 0.0651 \text{ dm}^3 \text{ mol}^{-1}$.

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 dm³ contains 2.0 mol H₂ and 1.0 mol N₂ 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 dm³ contains 1.5 mol H₂ and 2.5 mol N₂ 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 $p_c = 45.6 \text{ atm}$, $V_c = 98.7 \text{ cm}^3 \text{ mol}^{-1}$, and $T_c = 190.6 \text{ K}$. 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 $p_c = 48.20 \text{ atm}$, $V_c = 148 \text{ cm}^3 \text{ mol}^{-1}$, and $T_c = 305.4 \text{ K}$. 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 Cl₂ molecule regarded as a sphere.

1.20(b) Use the van der Waals parameters for hydrogen sulfide to calculate approximate values of (a) the Boyle temperature of the gas and (b) the radius of a H₂S molecule regarded as a sphere ($a = 4.484 \text{ dm}^6 \text{ atm mol}^{-2}$, $b = 0.0434 \text{ dm}^3 \text{ mol}^{-1}$).

1.21(a) Suggest the pressure and temperature at which 1.0 mol of (a) NH₃, (b) Xe, (c) He will be in states that correspond to 1.0 mol H₂ at 1.0 atm and 25°C.

1.21(b) Suggest the pressure and temperature at which 1.0 mol of (a) H₂S, (b) CO₂, (c) Ar will be in states that correspond to 1.0 mol N₂ at 1.0 atm and 25°C.

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

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

Problems*

Numerical problems

1.1 Recent communication with the inhabitants of Neptune have revealed that they have a Celsius-type temperature scale, but based on the melting point (0°N) and boiling point (100°N) of their most common substance, hydrogen. Further communications have revealed that the Neptunians know about perfect gas behaviour and they find that, in the limit of zero pressure, the value of pV is 28 dm³ atm at 0°N and 40 dm³ atm at 100°N. What is the value of the absolute zero of temperature on their temperature scale?

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

p/kPa	12.223	25.20	36.97	60.37	85.23	101.3
$\rho/(\text{kg m}^{-3})$	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
$10^3\alpha/(\text{°C})^{-1}$	3.6717	3.6697	3.6665	3.6643

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

1.4 The molar mass of a newly synthesized fluorocarbon was measured in a gas microbalance. This device consists of a glass bulb forming one end of a beam, the whole surrounded by a closed container. The beam is pivoted, and the balance point is attained by raising the pressure of gas in the container, so increasing the buoyancy of the enclosed bulb. In one experiment, the balance point was reached when the fluorocarbon pressure was 327.10 Torr; for the same setting of the pivot, a balance was reached when CHF₃ ($M = 70.014 \text{ g mol}^{-1}$) was introduced at 423.22 Torr. A repeat of the experiment with a different setting of the pivot required a pressure of 293.22 Torr of the fluorocarbon and 427.22 Torr of the CHF₃. What is the molar mass of the fluorocarbon? Suggest a molecular formula.

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

1.6 A vessel of volume 22.4 dm³ contains 2.0 mol H₂ and 1.0 mol N₂ at 273.15 K initially. All the H₂ reacted with sufficient N₂ to form NH₃. Calculate the partial pressures and the total pressure of the final mixture.

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

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

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

1.9 Calculate the volume occupied by 1.00 mol N₂ using the van der Waals equation in the form of a virial expansion at (a) its critical temperature, (b) its Boyle temperature, and (c) its inversion temperature. Assume that the pressure is 10 atm throughout. At what temperature is the gas most perfect? Use the following data: $T_c = 126.3 \text{ K}$, $a = 1.352 \text{ dm}^6 \text{ atm mol}^{-2}$, $b = 0.0387 \text{ dm}^3 \text{ mol}^{-1}$.

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

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

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

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

Theoretical problems

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

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

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

1.17 A scientist proposed the following equation of state:

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

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

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

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

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

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

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

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

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

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

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

Applications: to environmental science

1.25 Atmospheric pollution is a problem that has received much attention. Not all pollution, however, is from industrial sources. Volcanic eruptions can be a significant source of air pollution. The Kilauea volcano in Hawaii emits 200–300 t of SO₂ per day. If this gas is emitted at 800°C and 1.0 atm, what volume of gas is emitted?

1.26 Ozone is a trace atmospheric gas that plays an important role in screening the Earth from harmful ultraviolet radiation, and the abundance of ozone is commonly reported in *Dobson units*. One Dobson unit is the thickness, in thousandths of a centimetre, of a column of gas if it were collected as a pure gas at 1.00 atm and 0°C. What amount of O₃ (in moles) is found in a column of atmosphere with a cross-sectional area of 1.00 dm² if the abundance is 250 Dobson units (a typical mid-latitude value)? In the seasonal Antarctic ozone hole, the column abundance drops below 100 Dobson units; how many moles of ozone are found in such a column of air above a 1.00 dm² area? Most atmospheric ozone is found between 10 and 50 km above the surface of the earth. If that ozone is spread uniformly through this portion of the atmosphere, what is the average molar concentration corresponding to (a) 250 Dobson units, (b) 100 Dobson units?

1.27 The barometric formula relates the pressure of a gas of molar mass M at an altitude h to its pressure p_0 at sea level. Derive this relation by showing that

the change in pressure dp for an infinitesimal change in altitude dh where the density is ρ is $dp = -\rho g dh$. Remember that ρ depends on the pressure. Evaluate (a) the pressure difference between the top and bottom of a laboratory vessel of height 15 cm, and (b) the external atmospheric pressure at a typical cruising altitude of an aircraft (11 km) when the pressure at ground level is 1.0 atm.

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

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

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