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

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \qquad (1C.5b)$$

The constants a and b are called the **van der Waals coefficients**. As can be understood from the following *Justification*, a represents the strength of attractive interactions and b that of the repulsive interactions between the molecules. They are characteristic of each gas but independent of the temperature (Table 1C.3). Although a and b are not precisely defined molecular properties, they correlate with physical properties such as critical temperature, vapour pressure, and enthalpy of vaporization that reflect the strength of intermolecular interactions. Correlations have also been sought where intermolecular forces might play a role. For example, the potency of certain general anaesthetics shows a correlation in the sense that a higher activity is observed with lower values of a (Fig. 1C.5).

Table 1C.3* 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

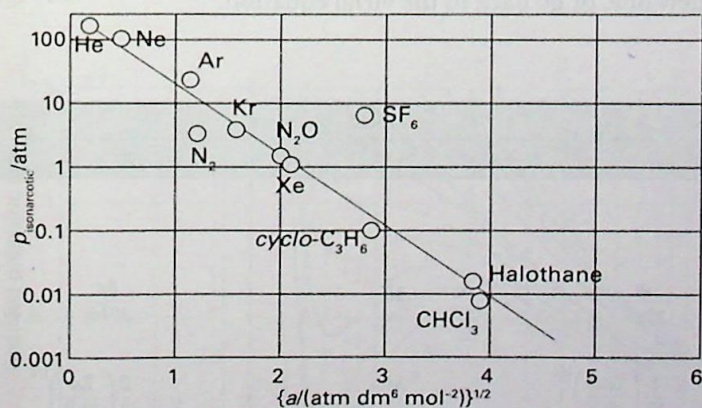* More values are given in the *Resource section*.

Figure 1C.5 The correlation of the effectiveness of a gas as an anaesthetic and the van der Waals parameter a. (Based on R.J. Wulf and R.M. Featherstone, *Anesthesiology* **18**, 97 (1957).) The isonarcotic pressure is the pressure required to bring about the same degree of anaesthesia.

Justification 1C.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. To calculate the excluded volume we note that the closest distance of two hard-sphere molecules of radius r, and volume $V_{molecule} = \frac{4}{3}\pi r^3$, is $2r$, so the volume excluded is $\frac{4}{3}\pi(2r)^3$ or $8V_{molecule}$. The volume excluded per molecule is one-half this volume, or $4V_{molecule}$, so $b \approx 4V_{molecule}N_A$.

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 interaction, which act with a strength proportional to the molar concentration, n/V, of molecules in the sample. Therefore, because both the frequency and the force of the collisions are reduced by the attractive interactions, the pressure is reduced in proportion to the square of this concentration. If the reduction of pressure is written as $a(n/V)^2$, where a is a positive constant characteristic of each gas, the combined effect of the repulsive and attractive forces is the van der Waals equation of state as expressed in eqn 1C.5.

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 that represent attractions and repulsions, respectively, rather than as precisely defined molecular properties.

Example 1C.1 Using the van der Waals equation to estimate a molar volume

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

Method We need to find an expression for the molar volume by solving the van der Waals equation, eqn 1C.5b. To do

so, we multiply both sides of the equation by $(V_m - b)V_m^2$, to obtain

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

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

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

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

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

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

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

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

The acceptable root is $x = 0.366$ (Fig. 1C.6), which implies that $V_m = 0.366\,dm^3\,mol^{-1}$. For a perfect gas under these conditions, the molar volume is $0.410\,dm^3\,mol^{-1}$.
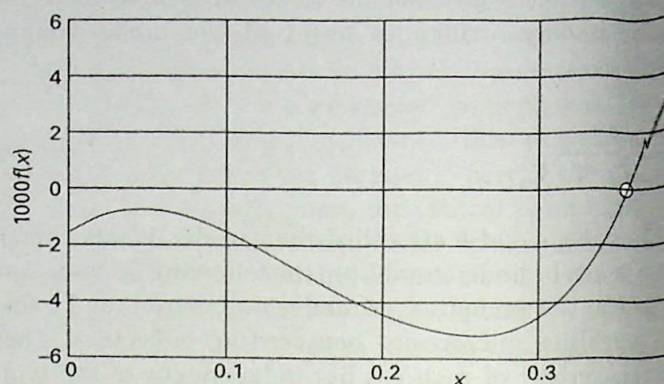

Figure 1C.6 The graphical solution of the cubic equation for V in *Example* 1C.1.

Self-test 1C.4 Calculate the molar volume of argon at 100 and 100 atm on the assumption that it is a van der Waals gas.

Answer: 0.298 dm³ mol

(b) The features of the equation

We now examine to what extent the van der Waals equation predicts the behaviour of real gases. It is too optimistic expect a single, simple expression to be the true equation state of all substances, and accurate work on gases must ne to the virial equation, use tabulated values of the coefficie at various temperatures, and analyse the systems numerica The advantage of the van der Waals equation, however, is t it is analytical (that is, expressed symbolically) and allows to draw some general conclusions about real gases. When equation fails we must use one of the other equations of st that have been proposed (some are listed in Table 1C.4), inv a new one, or go back to the virial equation.

Table 1C.4 Selected equations of state

	Equation	Reduced form*	Critical constants		
			p_c	V_c	T_c
Perfect gas	$p = \dfrac{nRT}{V}$				
van der Waals	$p = \dfrac{nRT}{V-nb} - \dfrac{n^2a}{V^2}$	$p_r = \dfrac{8T_r}{3V_r - 1} - \dfrac{3}{V_r^2}$	$\dfrac{a}{27b^2}$	$3b$	$\dfrac{8a}{27bR}$
Berthelot	$p = \dfrac{nRT}{V-nb} - \dfrac{n^2a}{TV^2}$	$p_r = \dfrac{8T_r}{3V_r - 1} - \dfrac{3}{T_rV_r^2}$	$\dfrac{1}{12}\left(\dfrac{2aR}{3b^3}\right)^{1/2}$	$3b$	$\dfrac{2}{3}\left(\dfrac{2a}{3bR}\right)^{1/2}$
Dieterici	$p = \dfrac{nRTe^{-aRTV/n}}{V-nb}$	$p_r = \dfrac{T_re^{2(1-1/T_rV_r)}}{2V_r - 1}$	$\dfrac{a}{4e^2b^2}$	$2b$	$\dfrac{a}{4bR}$
Virial	$p = \dfrac{nRT}{V}\left\{1 + \dfrac{nB(T)}{V} + \dfrac{n^2C(T)}{V^2} + \cdots\right\}$				

* Reduced variables are defined in Section 1C.2(c). Equations of state are sometimes expressed in terms of the molar volume, $V_m = V/n$.

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. 1C.2. Some calculated isotherms are shown in Fig. 1C.7 and Fig. 1C.8. 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 (1). The van der Waals coefficients, such as those in Table 1C.3, are found by fitting the calculated curves to the experimental curves.
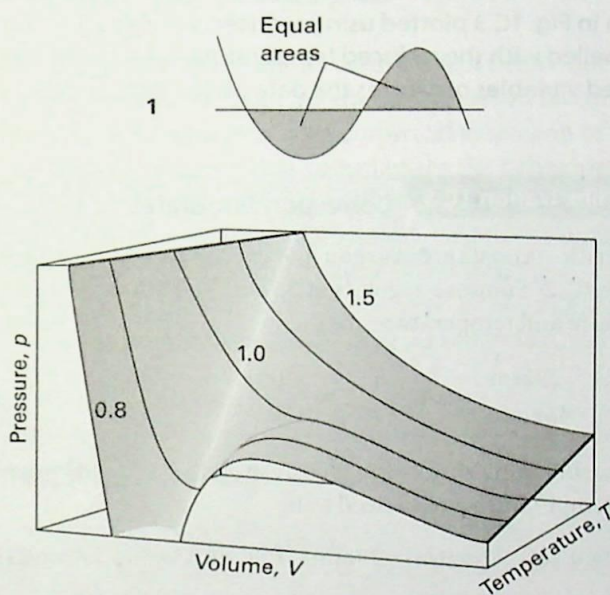

Figure 1C.7 The surface of possible states allowed by the van der Waals equation. Compare this surface with that shown in Fig. 1C.8.
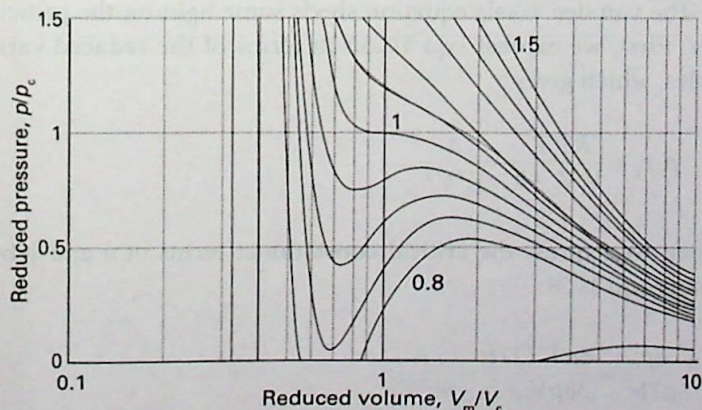

Figure 1C.8 van der Waals isotherms at several values of T/T_c. Compare these curves with those in Fig. 1C.2. The van der Waals loops are normally replaced by horizontal straight lines. The critical isotherm is the isotherm for $T/T_c=1$.

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 1C.5b 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 the attractive and repulsive effects are in balance.

The van der Waals loops occur when both terms in eqn 1C.5b have similar magnitudes. The first term arises from the kinetic energy of the molecules and their repulsive interactions; the second represents the effect of the attractive interactions.

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

For $T < T_c$, the calculated isotherms oscillate, and each one passes through a minimum followed by a maximum. These extrema converge as $T \rightarrow T_c$ and coincide at $T = T_c$; at the critical point the curve has a flat inflexion (2). From the properties of curves, we know that an inflexion of this type occurs when both the first and second derivatives are zero. Hence, we can find the critical constants by calculating these derivatives and setting them equal to zero at the critical point:
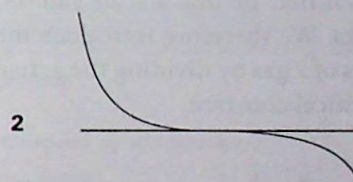
$$\frac{dp}{dV_m} = -\frac{RT}{(V_m - b)^2} + \frac{2a}{V_m^3} = 0$$

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

The solutions of these two equations (and using eqn 1C.5b to calculate p_c from V_c and T_c) are

$$V_c = 3b \qquad p_c = \frac{a}{27b^2} \qquad T_c = \frac{8a}{27Rb} \qquad (1C.6)$$

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

$$Z_c = \frac{p_c V_c}{RT_c} = \frac{3}{8} \qquad (1C.7)$$

for all gases that are described by the van der Waals equation near the critical point. We see from Table 1C.2 that although $Z_c < \frac{3}{8} = 0.375$, it is approximately constant (at 0.3) and the discrepancy is reasonably small.

Brief illustration 1C.4 Criteria for perfect gas behaviour

For benzene $a = 18.57$ atm dm^6 mol^{-2} (1.882 Pa m^6 mol^{-2}) and $b = 0.1193$ dm^3 mol^{-1} (1.193 × 10^{-4} m^3 mol^{-1}); its normal boiling point is 353 K. Treated as a perfect gas at $T = 400$ K and $p = 1.0$ atm, benzene vapour has a molar volume of $V_m = RT/p = 33$ dm mol^{-1}, so the criterion $V_m \gg b$ for perfect gas behaviour is satisfied. It follows that $a/V_m^2 \approx 0.017$ atm, which is 1.7 per cent of 1.0 atm. Therefore, we can expect benzene vapour to deviate only slightly from perfect gas behaviour at this temperature and pressure.

Self-test 1C.5 Can argon gas be treated as a perfect gas at 400 K and 3.0 atm?

Answer: Yes

(c) 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:

$$V_r = \frac{V_m}{V_c} \quad p_r = \frac{p}{p_c} \quad T_r = \frac{T}{T_c} \quad \text{Definition} \quad \text{Reduced variables} \quad (1C.8)$$

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. 1C.9). 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. 1C.3, 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.
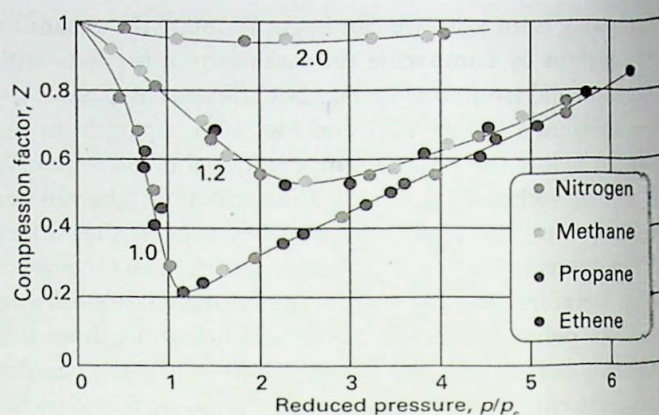

Figure 1C.9 The compression factors of four of the gases shown in Fig. 1C.3 plotted using reduced variables. The curve are labelled with the reduced temperature $T_r = T/T_c$. The use reduced variables organizes the data on to single curves.

Brief illustration 1C.5 Corresponding states

The critical constants of argon and carbon dioxide are given Table 1C.2. Suppose argon is at 23 atm and 200 K, its reduc pressure and temperature are then

$$p_r = \frac{23\,\text{atm}}{48.0\,\text{atm}} = 0.48 \quad T_r = \frac{200\,\text{K}}{150.7\,\text{K}} = 1.33$$

For carbon dioxide to be in a corresponding state, its press and temperature would need to be

$$p = 0.48 \times (72.9\,\text{atm}) = 35\,\text{atm} \quad T = 1.33 \times 304.2\,\text{K} = 405\,\text{K}$$

Self-test 1C.6 What would be the corresponding state ammonia?

Answer: 53 atm, 5.

The van der Waals equation sheds some light on the principle. First, we express eqn 1C.5b in terms of the reduced ables, which gives

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

Then we express the critical constants in terms of a and using eqn 1C.8:

$$\frac{a p_r}{27 b^2} = \frac{8 a T_r / 27 b}{3 b p V_r - b} - \frac{a}{9 b^2 V_r^2}$$

which can be reorganized into

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

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. 1C.8 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 (like those in Table 1C.4). 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. 1C.9 instead of Fig. 1C.3).

Checklist of concepts

☐ 1. The extent of deviations from perfect behaviour is summarized by introducing the **compression factor**.

☐ 2. The **virial equation** is an empirical extension of the perfect gas equation that summarizes the behaviour of real gases over a range of conditions.

☐ 3. The isotherms of a real gas introduce the concepts of **vapour pressure** and **critical behaviour**.

☐ 4. A gas can be liquefied by pressure alone only if its temperature is at or below its **critical temperature**.

☐ 5. The **van der Waals equation** is a model equation of state for a real gas expressed in terms of two parameters, one (a) corresponding to molecular attractions and the other (b) to molecular repulsions.

☐ 6. The van der Waals equation captures the general features of the behaviour of real gases, including their critical behaviour.

☐ 7. The properties of real gases are coordinated by expressing their equations of state in terms of **reduced variables**.

Checklist of equations

Property	Equation	Comment	Equation number
Compression factor	$Z = V_m / V_m^\circ$	Definition	1C.1
Virial equation of state	$pV_m = RT(1 + B/V_m + C/V_m^2 + \cdots)$	B, C depend on temperature	1C.3
van der Waals equation of state	$p = nRT/(V - nb) - a(n/V)^2$	a parameterizes attractions, b parameterizes repulsions	1C.5
Reduced variables	$X_r = X/X_c$	$X = p$, V_m, or T	1C.8