

Attractive forces are ineffective when the molecules are far apart (well to the right in Fig. 1C.1). 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.

The consequences of these interactions are shown by shapes of experimental isotherms (Fig. 1C.2). 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.

Consider what happens when we compress (reduce the volume of) a sample of gas initially in the state marked A in Fig. 1C.2 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

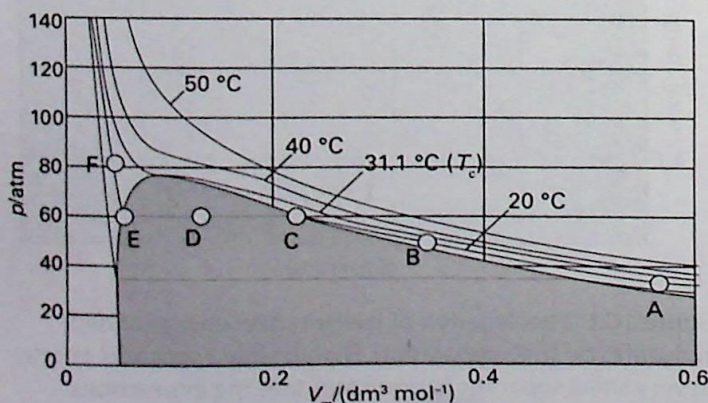


Figure 1C.2 Experimental isotherms of carbon dioxide at several temperatures. The 'critical isotherm', the isotherm at the critical temperature, is at 31.1 °C.

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 the 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.

### (a) The compression factor

As a first step in making these observations quantitative we introduce the **compression factor**,  $Z$ , the ratio of the measured molar volume of a gas,  $V_m = V/n$ , to the molar volume of a perfect gas,  $V_m^\circ$ , at the same pressure and temperature:

$$Z = \frac{V_m}{V_m^\circ} \quad \text{Definition Compression factor (1C.1)}$$

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

$$pV_m = RTZ \quad \text{(1C.2)}$$

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. 1C.3. 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.

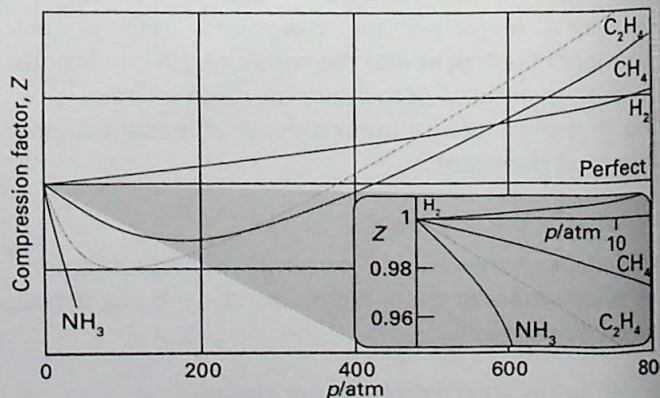


Figure 1C.3 The variation of the compression factor,  $Z$ , with pressure for several gases at 0 °C. A perfect gas has  $Z=1$  at all pressures. Notice that, although the curves approach 1 as  $p \rightarrow 0$ , they do so with different slopes.

**Brief illustration 1C.1** The compression factor

The molar volume of a perfect gas at 500 K and 100 bar is  $V_m^\circ = 0.416 \text{ dm}^3 \text{ mol}^{-1}$ . The molar volume of carbon dioxide under the same conditions is  $V_m = 0.366 \text{ dm}^3 \text{ mol}^{-1}$ . It follows that at 500 K

$$Z = \frac{0.366 \text{ dm}^3 \text{ mol}^{-1}}{0.416 \text{ dm}^3 \text{ mol}^{-1}} = 0.880$$

The fact that  $Z < 1$  indicates that attractive forces dominate repulsive forces under these conditions.

**Self-test 1C.1** The mean molar volume of air at 60 bar and 400 K is  $0.9474 \text{ dm}^3 \text{ mol}^{-1}$ . Are attractions or repulsions dominant?

Answer: Repulsions

**(b) Virial coefficients**

Now we relate  $Z$  to the experimental isotherms in Fig. 1C.2. 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  $pV_m = RT$  is in fact the first term in an expression of the form

$$pV_m = RT(1 + B'p + C'p^2 + \dots) \quad (1C.3a)$$

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

$$pV_m = RT \left( 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots \right) \quad \text{Virial equation of state} \quad (1C.3b)$$

These two expressions are two versions of the **virial equation of state**.<sup>1</sup> By comparing the expression with eqn 1C.2 we see that the term in parentheses in eqn 1C.3b is just the compression factor,  $Z$ .

The coefficients  $B, C, \dots$ , which depend on the temperature, are the second, third, ... **virial coefficients** (Table 1C.1); 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  $C/V_m^2 \ll B/V_m$ . The values of the virial coefficients of a gas are determined from measurements of its compression factor.

<sup>1</sup> The name comes from the Latin word for force. The coefficients are sometimes denoted  $B_2, B_3, \dots$ .

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

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

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

**Brief illustration 1C.2** The virial equation of state

To use eqn 1C.3b (up to the  $B$  term), to calculate the pressure exerted at 100 K by 0.104 mol O<sub>2</sub>(g) in a vessel of volume 0.225 dm<sup>3</sup>, we begin by calculating the molar volume:

$$V_m = \frac{V}{n_{\text{O}_2}} = \frac{0.225 \text{ dm}^3}{0.104 \text{ mol}} = 2.16 \text{ dm}^3 \text{ mol}^{-1} = 2.16 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$$

Then, by using the value of  $B$  found in Table 1C.1 of the *Resource section*,

$$\begin{aligned} p &= \frac{RT}{V_m} \left( 1 + \frac{B}{V_m} \right) \\ &= \frac{(8.3145 \text{ J mol}^{-1} \text{ K}^{-1}) \times (100 \text{ K})}{2.16 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}} \left( 1 - \frac{1.975 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}}{2.16 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}} \right) \\ &= 3.50 \times 10^5 \text{ Pa, or } 350 \text{ kPa} \end{aligned}$$

where we have used  $1 \text{ Pa} = 1 \text{ J m}^{-3}$ . The perfect gas equation of state would give the calculated pressure as 385 kPa, or 10 per cent higher than the value calculated by using the virial equation of state. The deviation is significant because under these conditions  $B/V_m \approx 0.1$  which is not negligible relative to 1.

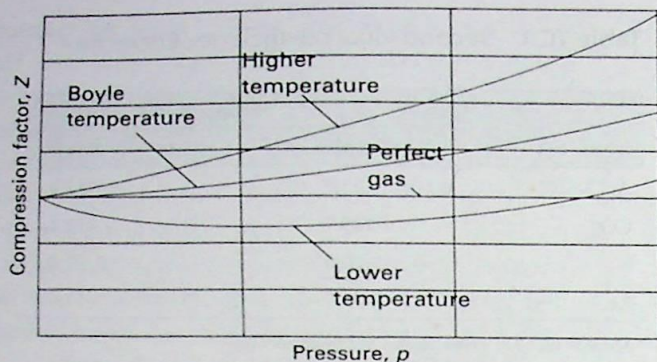
**Self-test 1C.2** What pressure would 4.56 g of nitrogen gas in a vessel of volume 2.25 dm<sup>3</sup> exert at 273 K if it obeyed the virial equation of state?

Answer: 104 kPa

An important point is 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 1C.3a we obtain

$$\frac{dZ}{dp} = B' + 2pC' + \dots \rightarrow B' \text{ as } p \rightarrow 0 \quad (1C.4a)$$

However,  $B'$  is not necessarily zero, so the slope of  $Z$  with respect to  $p$  does not necessarily approach 0 (the perfect gas



**Figure 1C.4** 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.

value), as we can see in Fig. 1C.4. 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,

$$\frac{dZ}{d(1/V_m)} \rightarrow B \text{ as } V_m \rightarrow \infty \quad (1C.4b)$$

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 (as in Fig. 1C.4). 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 1C.4b,  $Z$  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 1C.3 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 1C.2.

### (c) Critical constants

The isotherm at the temperature  $T_c$  (304.19 K, or 31.04 °C for  $\text{CO}_2$ ) plays a special role in the theory of the states of matter.

**Table 1C.2\*** Critical constants of gases

	$p_c/\text{atm}$	$V_c/(\text{cm}^3 \text{ mol}^{-1})$	$T_c/\text{K}$	$Z_c$	$T_B/\text{K}$
Ar	48.0	75.3	150.7	0.292	411.5
$\text{CO}_2$	72.9	94.0	304.2	0.274	714.8
He	2.26	57.8	5.2	0.305	22.64
$\text{O}_2$	50.14	78.0	154.8	0.308	405.9

\* More values are given in the Resource section.

An isotherm slightly below  $T_c$  behaves as we have already described: at a certain pressure, a liquid condenses from gas and is distinguishable from it by the presence of a visible surface. If, however, the compression takes place at  $T_c$ , 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 1C.2).

At and above  $T_c$ , the sample has a single phase which occupies the entire volume of the container. Such a phase is, by definition, a gas. Hence, the liquid phase of a substance does not form above the critical temperature. The single phase that fills the entire volume when  $T > T_c$  may be much denser than normally consider typical of gases, and the name **supercritical fluid** is preferred.

### Brief illustration 1C.3 The critical temperature

The critical temperature of oxygen 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.

**Self-test 1C.3** Under which conditions can liquid nitrogen be formed by the application of pressure?

Answer: At  $T < 120$  K.

## 1C.2 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'.

### (a) Formulation of the equation

The van der Waals equation is

$$p = \frac{nRT}{V - nb} - a \frac{n^2}{V^2} \quad \text{Van der Waals equation of state} \quad (1C.5)$$

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

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

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 <sub>2</sub>	3.610	4.29
He	0.0341	2.38
Xe	4.137	5.16

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

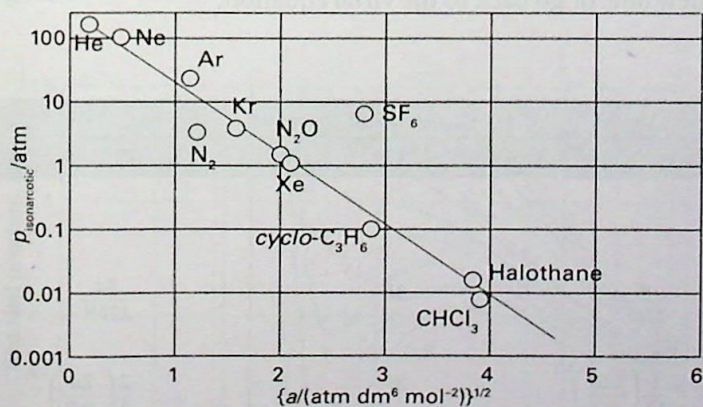


Figure 1C.5 The correlation of the effectiveness of a gas as an anaesthetic and the van der Waals parameter  $a$ . (Based on R.J. Wulf and R.M. Featherstone, *Anesthesiology* 18, 97 (1957).) The isonarcotic pressure is the pressure required to bring about the same degree of anaesthesia.

### 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  $V_{\text{molecule}} = \frac{4}{3}\pi r^3$ , 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  $b = 4V_{\text{molecule}}N_A$ .

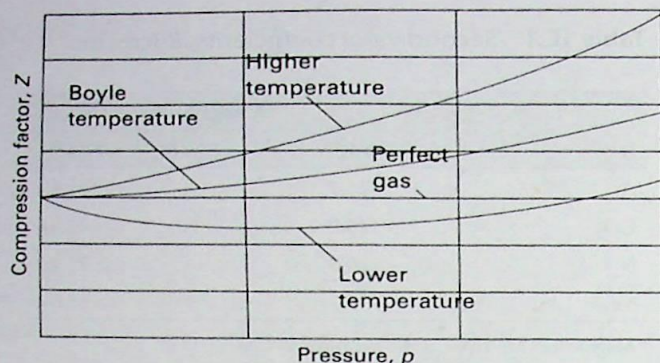
The pressure depends on both the frequency of collisions with the walls and the force of each collision. Both the frequency of the collisions and their force are reduced by the attractive interaction, which act with a strength proportional to the molar concentration,  $n/V$ , of molecules in the sample. 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<sub>2</sub> 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



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Van der Waals equation of state (1C.2)