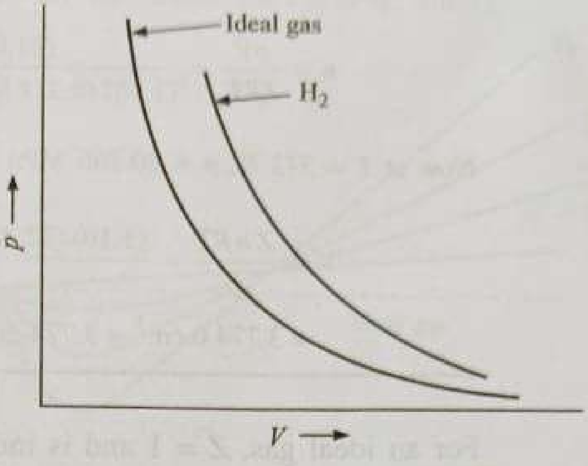
high temperatures, gases obey the laws of Boyle, Charles and Avogadro approximately, but as the pressure is increased or the temperature is decreased, a marked departure from ideal behaviour is observed. Figure 1.8.1 shows, for example, the type of deviation that occurs in Boyle's law for H_2 at room temperature.



ig. 1.8.1 Plot of *p* ersus *V* of hydrogen, s compared to that f an ideal gas

The curve for the real gas has a tendency to coincide with that of an ideal gas at low pressures when the volume is large. At higher pressures, however, deviations are observed.

ompression actor

The deviations can be displayed more clearly, by plotting the ratio of the observed molar volume V_m to the ideal molar volume $V_{m,\text{ideal}}$ (= RT/p) as a function of pressure at constant temperature. This ratio is called the compression factor Z and can be expressed as

$$Z = \frac{V_m}{V_{m,\text{ideal}}} = \frac{p}{RT}V_m \qquad (1.8.1)$$

---

cample 1.8.1

At 273.15 K and under a pressure of 10.132 5 MPa, the compression factor of O_2 is 0.927. Calculate the mass of O_2 necessary to fill a gas cylinder of 100 dm^3 capacity under the given conditions.

lution

From the given data, we have

$$T = 273.15 \text{ K}, \quad Z = 0.927, \quad p = 10.132\ 5 \text{ MPa}$$

Thus, the molar volume of O_2 is

$$V_m = \frac{ZRT}{p} = \frac{(0.927)(8.314 \text{ MPa cm}^3 \text{ K}^{-1} \text{ mol}^{-1})(273.15 \text{ K})}{10.132\ 5 \text{ MPa}}$$
$$= 207.77 \text{ cm}^3 \text{ mol}^{-1}$$

The mass of this molar volume will be equal to the molar mass of oxygen, i.e. 207.77 cm^3 weighs 0.032 kg. Thus, the mass of oxygen required to fill a gas cylinder of 100 dm^3 (i.e. 10^5 cm^3) under the given condition is

$$\left(\frac{0.032 \text{ kg}}{207.77 \text{ cm}^3}\right)(10^5 \text{ cm}^3) = 15.40 \text{ kg}$$

.2 The compression factor ($Z = pV/nRT$) for N_2 at 223 K and 81.06 MPa is 1.95 and at 373 K and 20.265 MPa it is 1.10. A certain mass of N_2 occupies a volume of 1.0 dm^3 at 223 K and 81.06 MPa. Calculate the amount of the gas and the volume occupied by the same quantity of N_2 at 373 K and 20.265 MPa.

For T = 223 K, p = 81.06 MPa, Z = 1.95 and $V = 1.0\ dm^3 = 10^3\ cm^3$, we have

$$n = \frac{pV}{ZRT} = \frac{(81.06\ \text{MPa})\,(10^3\ \text{cm}^3)}{(1.95)\,(8.314\ \text{MPa cm}^3\ \text{K}^{-1}\ \text{mol}^{-1})\,(223\ \text{K})} = 22.42\ \text{mol}$$

Now at T = 373 K, p = 20.265 MPa, Z = 1.10, the volume occupied would be

$$V = \frac{ZnRT}{p} = \frac{(1.10)\,(22.42\ \text{mol})\,(8.314\ \text{MPa cm}^3\ \text{K}^{-1}\ \text{mol}^{-1})\,(373\ \text{K})}{(20.265\ \text{MPa})}$$

$$= 3\,774.0\ \text{cm}^3 = 3.774\ \text{dm}^3$$

n

s

For an ideal gas, $Z = 1$ and is independent of pressure and temperature. For a real gas, $Z = f(T, p)$, a function of both temperature and pressure. Figure 1.8.2 shows a graph between Z and p for some gases at 273.15 K, the pressure range in this graph is very large. It can be noted that:

(1) Z is always greater than 1 for H_2.

(2) For N_2, $Z < 1$ in the lower pressure range and is greater than 1 at higher pressures. It decreases with increase of pressure in the lower pressure region, passes through a minimum at some pressure and then increases continuously with pressure in the higher pressure region.

(3) For CO_2, there is a large dip in the beginning. In fact, for gases which are easily liquefied, Z dips sharply below the ideal line in the low pressure region.

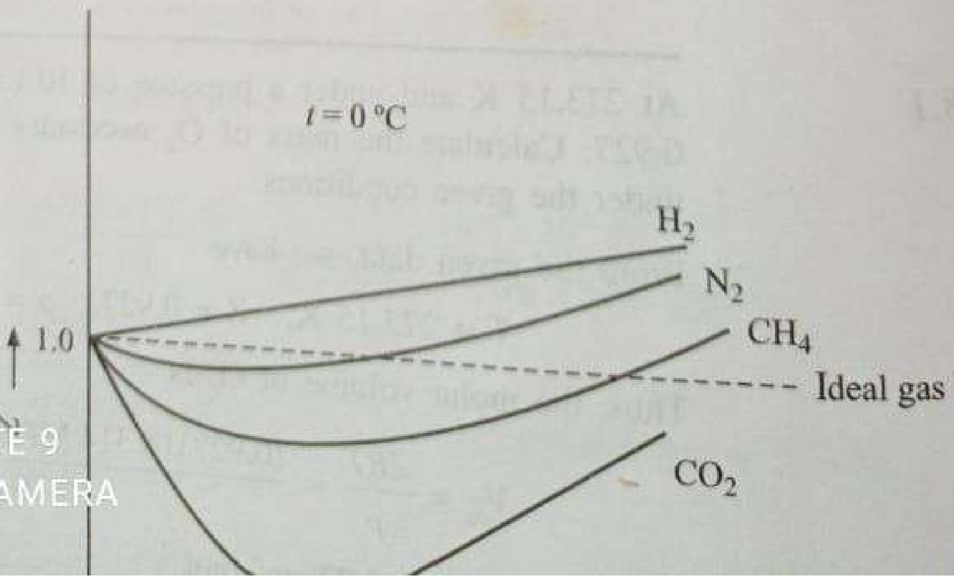


Figure 1.8.2 gives an impression that the nature of deviations depend upon the nature of the gas. In fact, it is not so. The determining factor is the temperature relative to the critical temperature (*see* p. 36) of the particular gas; near the critical temperature, the pV curves are like those for CO_2, but when far away, the curves are like those for H_2 (Fig. 1.8.3).

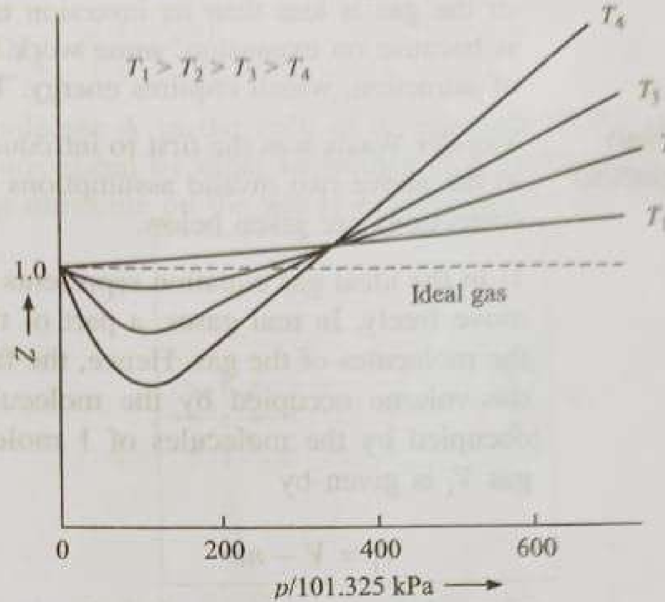


Fig. 1.8.3 Plots of Z versus p of a single gas at various temperatures

Provided the pressure is of the order of 1 bar or less, and the temperature is not too near the point of liquefaction, the observed deviations from the ideal gas laws are not more than a few per cent. Under these conditions, therefore, the equation $pV = nRT$ and related expressions may be used.

1.9 VAN DER WAALS EQUATION OF STATE FOR A REAL GAS

Causes of Deviations from Ideal Behaviour The ideal gas laws can be derived from the kinetic theory of gases which is based on the following two important assumptions:

(i) The volume occupied by the molecules is negligible in comparison to the total volume of the gas.

(ii) The molecules exert no forces of attraction upon one another.

It is because neither of these assumptions can be regarded as applicable to real gases that the latter show departure from the ideal behaviour.

Evidence for Molecular Volume The molecules of a gas, however, do occupy a certain volume as can be seen from the fact that gases can be liquefied and solidified at low temperatures and high pressures. On decreasing the temperature of a gas, the thermal energy of molecules is decreased and the effect of applying high pressure is to bring the molecules closer to one another, thereby increasing the forces of attraction amongst them. Both these factors favour liquefaction and solidification. In the solid state, however, there is a considerable resistance to any further attempt at compression. It is, therefore, apparent that the molecules of a gas must have an appreciable volume, which is probably of the same order as that occupied by the same number of molecules in the solid state.

Evidence for Molecular Attractions

The molecules in gases also have weak forces of attraction (called van der Waals attraction) amongst themselves, as otherwise, the gases could never be liquefied and solidified. This is also supported by the fact that when a compressed gas is passed through a porous plug of silk or cotton in adiabatic condition, the emerging gas is found to be cooler than the entering gas provided the temperature of the gas is less than its inversion temperature (Joule-Thomson effect).[†] This is because on expansion, some work has to be done against the internal forces of attraction, which requires energy. This energy comes from the system itself.

Derivation of Van der Waals Equation

Van der Waals was the first to introduce systematically the correction terms due to the above two invalid assumptions in the ideal gas equation $p_iV_i = nRT$. His corrections are given below.

Correction for Volume

V_i in the ideal gas equation represents an ideal volume where the molecules can move freely. In real gases, a part of the total volume is, however, occupied by the molecules of the gas. Hence, the free volume V_i is the total volume V minus the volume occupied by the molecules. If b represents the *effective volume* occupied by the molecules of 1 mole of a gas, then for the amount n of the gas V_i is given by

$$V_i = V - nb \tag{1.9.1}$$

where b is called the *excluded volume* or *co-volume*. The numerical value of b is four times the actual volume occupied by the gas molecules. This can be shown as follows.

Expression of Excluded Volume

If we consider only bimolecular collisions, then the volume occupied by the sphere of radius $2r$ represents the excluded volume per pair of molecules as shown in Fig. 1.9.1.

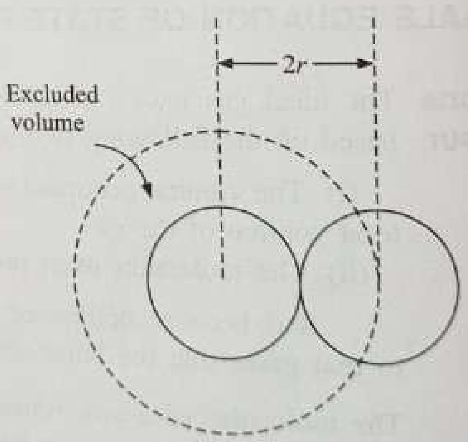


Fig. 1.9.1 Excluded volume per pair of molecules

Thus, excluded volume per pair of molecules

$$= \frac{4}{3}\pi(2r)^3 = 8\left(\frac{4}{3}\pi r^3\right)$$

[†] See Section 2.9 of Volume 2 of this series of book

Excluded volume per molecule

$$= \frac{1}{2}\left[8\left(\frac{4}{3}\pi r^3\right)\right] = 4\left(\frac{4}{3}\pi r^3\right) = 4\ \text{(volume occupied by a molecule)}$$

Since b represents excluded volume per mole of the gas, it is obvious that

$$b = N_\text{A}\left[4\left(\frac{4}{3}\pi r^3\right)\right] \tag{1.9.2}$$

Correction for Forces of Attraction

Consider a molecule A in the bulk of a vessel as shown in Fig. 1.9.2. This molecule is surrounded by other molecules in a symmetrical manner, with the result that this molecule on the whole experiences no net force of attraction.

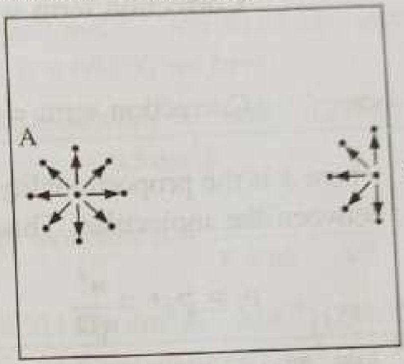


Fig. 1.9.2 Arrangement of molecules within and near the surface of a vessel

Now, consider a molecule B near the side of the vessel, which is about to strike one of its sides, thus contributing towards the total pressure of the gas. There are molecules only on one side of the vessel, i.e. towards its centre, with the result that this molecule experiences a net force of attraction towards the centre of the vessel. This results in decreasing the velocity of the molecule, and hence its momentum. Thus, the molecule does not contribute as much force as it would have, had there been no forces of attraction. Thus, the pressure of a real gas would be smaller than the corresponding pressure of an ideal gas, i.e.

$$p_\text{i} = p + \text{correction term} \tag{1.9.3}$$

This correction term depends upon two factors:

(i) *The number of molecules per unit volume of the vessel* Larger the number, larger the net force of attraction with which the molecule B is dragged behind. This results in a greater decrease in the velocity of the molecule B and hence a greater decrease in the rate of change of momentum. Consequently, the correction term also has a large value. If n is the amount of the gas present in the volume V of the container, the number of molecules per unit volume of the container is given as

$$N' = \frac{nN_\text{A}}{V} \quad \text{or} \quad N' \propto \frac{n}{V}$$

Thus, the correction term is given as:

$$\text{Correction term} \propto \frac{n}{V} \tag{1.9.4a}$$

(ii) *The number of molecules striking the side of the vessel per unit time*. Larger this number, larger the decrease in the rate of change of momentum. Consequently, the correction term also has a larger value. Now, the number of molecules striking the side of vessel in a unit time also depends upon the number of molecules present in unit volume of the container, and hence in the present case:

$$\text{Correction term} \propto \frac{n}{V} \tag{1.9.4b}$$

Taking both these factors together, we have

$$\text{Correction term} \propto \left(\frac{n}{V}\right)\left(\frac{n}{V}\right)$$

or

$$\text{Correction term} = a\frac{n^2}{V^2} \tag{1.9.5}$$

where a is the proportionality constant and is a measure of the forces of attraction between the molecules. Thus

$$p_i = p + a\frac{n^2}{V^2} \tag{1.9.6}$$

The unit of the term an^2/V^2 is the same as that of the pressure. Thus, the SI unit of a is Pa m^6 mol^{-2}. It may be conveniently expressed in kPa dm^6 mol^{-2}.

**xpression of
an der Waals
quation of State**

When the expressions as given by Eqs (1.9.1) and (1.9.6) are substituted in the ideal gas equation $p_iV_i = nRT$, we get

$$\left(p + \frac{n^2a}{V^2}\right)(V - nb) = nRT \tag{1.9.7}$$

This equation is applicable to real gases and is known as the *van der Waals equation*.

**alues of Van der
aals Constants**

The constants a and b in van der Waals equation are called van der Waals constants and their values depend upon the nature of the gas (Table 1.9.1). They

Table 1.9.1 Van der Waals Constants

Gas	a / kPa dm^6 mol^{-2}	b / dm^3 mol^{-1}	Gas	a / kPa dm^6 mol^{-2}	b / dm^3 mol^{-1}
H_2	21.764	0.026 61	CH_4	228.285	0.042 78
He	3.457	0.023 70	C_2H_6	556.173	0.063 80
N_2	140.842	0.039 13	C_3H_8	877.880	0.084 45
O_2	137.802	0.031 83	C_4H_{10}(n)	1 466.173	0.122 6
Cl_2	657.903	0.056 22	C_4H_{10}(iso)	1 304.053	0.114 2
NO	135.776	0.027 89	C_5H_{12}(n)	1 926.188	0.146 0
NO_2	535.401	0.044 24	CO	150.468	0.039 85
H_2O	553.639	0.030 49	CO_2	363.959	0.042 67

are characteristics of the gas. The values of these constants are determined by the critical constants of the gas. Actually, the so-called constants vary to some extent with temperature and this shows that the van der Waals equation is not a complete solution of the behaviour of real gases.

Example 1.9.1 Calculate the pressure exerted by 22 g of carbon dioxide in 0.5 dm^3 at 298.15 K using: (a) the ideal gas law and (b) van der Waals equation. Given:

$$a = 363.76 \text{ kPa dm}^6 \text{ mol}^{-2} \quad \text{and} \quad b = 42.67 \text{ cm}^3 \text{ mol}^{-1}$$

Solution

$$\text{Amount of } CO_2 = \frac{22 \text{ g}}{44 \text{ g mol}^{-1}} = 0.5 \text{ mol}$$

$$V = 0.5 \text{ dm}^3 \qquad T = 298.15 \text{ K}$$

$$a = 363.76 \text{ kPa dm}^6 \text{ mol}^{-2} \quad b = 42.67 \text{ cm}^3 \text{ mol}^{-1} = 0.042\,67 \text{ dm}^3 \text{ mol}^{-1}$$

(**a**) From the ideal gas law, $p = nRT/V$, we have

$$p = \frac{(0.5 \text{ mol})\,(8.314 \text{ kPa dm}^3 \text{ K}^{-1} \text{ mol}^{-1})\,(298.15 \text{ K})}{(0.5 \text{ dm}^3)} = 2.479 \times 10^3 \text{ kPa}$$

(**b**) From the van der Waals equation, $p = \dfrac{nRT}{V - nb} - \dfrac{n^2 a}{V^2}$, we have

$$p = \frac{(0.5 \text{ mol})\,(8.314 \text{ kPa dm}^3 \text{ K}^{-1} \text{ mol}^{-1})\,(298.15 \text{ K})}{0.5 \text{ dm}^3 - (0.5 \text{ mol})\,(0.042\,67 \text{ dm}^3 \text{ mol}^{-1})} - \frac{(0.5 \text{ mol})^2 (363.76 \text{ kPa dm}^6 \text{ mol}^{-2})}{(0.5 \text{ dm}^3)^2}$$

$$= 2\,589.31 \text{ kPa} - 363.76 \text{ kPa} = 2\,225.55 \text{ kPa}$$

Example 1.9.2 Two van der Waals gases have the same value of b but different a values. Which of these would occupy greater volume under identical conditions? If the gases have the same a value but different values of b which would be more compressible?

Solution If two gases have same value of b but different values of a, then the gas having a larger value a will occupy lesser volume. This is because the gas with a larger value of a will have a larger force of attraction, and hence lesser distance between its molecules.

If two gases have the same value of a but different values of b, then the smaller the value of b, larger will be the compressibility because the gas with the smaller value of b will occupy lesser volume and hence will be more compressible.

Example 1.9.3 Calculate molecular diameter d of helium from its van der Waals constant b ($b = 24 \text{ cm}^3 \text{ mol}^{-1}$).

Solution Since $b = 4 \times$ volume occupied by the molecules in 1 mole of a gas

or

$$b = 4N_A\left(\frac{4}{3}\pi r^3\right)$$

therefore

$$r = \left(\frac{3b}{16N_A\pi}\right)^{1/3} = \left\{\frac{3 \times 24 \text{ cm}^3 \text{ mol}^{-1}}{16(6.022 \times 10^{23} \text{ mol}^{-1})(3.14)}\right\}^{1/3}$$

$$= 1.335 \times 10^{-8} \text{ cm} = 133.5 \text{ pm}$$

$$d = 2r = 267 \text{ pm}$$

Example 1.9.4 The molar volume of helium at 10.132 5 MPa and 273 K is 0.011 075 of its molar volume at 101.325 kPa at 273 K. Calculate the radius of helium atom. The value of a may be neglected.

Solution The van der Waals equation after neglecting a reduces to

$$p(V_m - b) = RT$$

Substituting the given data, we have

at 101.325 kPa:

$$(101.325\ \text{kPa})\ (V_m - b) = (8.314\ \text{kPa dm}^3\ \text{K}^{-1}\ \text{mol}^{-1})\ (273\ \text{K})$$

i.e. $$V_m - b = 22.4\ \text{dm}^3\ \text{mol}^{-1} = 22.4 \times 10^3\ \text{cm}^3\ \text{mol}^{-1} \quad (1)$$

at 10.132 5 MPa:

$$(10.132\ 5\ \text{MPa})\ (0.011\ 075\ V_m - b) = (8.314\ \text{MPa cm}^3\ \text{K}^{-1}\ \text{mol}^{-1})\ (273\ \text{K})$$

i.e. $$0.011\ 075\ V_m - b = 224.00\ \text{cm}^3\ \text{mol}^{-1} \quad (2)$$

Multiplying Eq. (1) by 0.011 075 and then subtracting Eq. (2) from it, we get

$$b - 0.011\ 075\ b = (248.08 - 224)\ \text{cm}^3\ \text{mol}^{-1}$$

$$b = \frac{24.08\ \text{cm}^3\ \text{mol}^{-1}}{0.988\ 925} = 24.35\ \text{cm}^3\ \text{mol}^{-1}$$

Since $$b = \left(\frac{4}{3}\pi r^3\right)(4N_A)$$

we have $$r = \left(\frac{3b}{16\pi N_A}\right)^{1/3} = \left(\frac{3 \times 24.35\ \text{cm}^3\ \text{mol}^{-1}}{16 \times 3.14 \times 6.022 \times 10^{23}\ \text{mol}^{-1}}\right)^{1/3}$$

$$= 1.34 \times 10^{-8}\ \text{cm} = 134\ \text{pm}$$

Applicability of the van der Waals Equation Since the van der Waals equation is applicable to real gases, it is worth considering how far this equation can explain the experimental behaviour of real gases, as represented by Fig. 1.8.2. The van der Waals equation for 1 mole of a gas is

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT \quad (1.9.8)$$

At low pressure When pressure is low, the volume is sufficiently large and b can be ignored in comparison to V_m in Eq. (1.9.8). Thus, we have

$$\left(p + \frac{a}{V_m^2}\right)V_m = RT \quad \text{or} \quad pV_m + \frac{a}{V_m} = RT$$

or $$Z = 1 - \frac{a}{V_m RT} \quad (1.9.9)$$

From the above equation it is clear that in the low pressure region, Z is less than 1. On increasing the pressure in this region, the value of the term

(a/V_mRT) increases as V is inversely proportional to p. Consequently, Z decreases with increase of p.

At high pressure When p is large, V_m will be small and one cannot ignore b in comparison to V_m. However, the term a/V_m^2 may be considered negligible in comparison to p in Eq. (1.9.8). Thus,

$$p(V_m - b) = RT$$

or
$$Z = 1 + \frac{pb}{RT} \tag{1.9.10}$$

Here Z is greater than 1 and it increases linearly with pressure. This explains the nature of the graph in the high pressure region.

At high temperature and low pressure If temperature is high, V_m will also be sufficiently large and thus the term a/V_m^2 will be negligibly small. At this stage, b may also be negligible in comparison to V_m. Under these conditions, Eq. (1.9.8) reduces to an ideal gas equation of state:

$$pV_m = RT$$

Hydrogen and helium The value of a is extremely small for these gases as they are difficult to liquefy. Thus, we have the equation of state as $p(V_m - b) = RT$, obtained from the van der Waals equation by ignoring the term a/V_m^2. Hence, Z is always greater than 1 and it increases with increase of p.

The van der Waals equation is a distinct improvement over the ideal gas law. It gives qualitative reasons for the deviations from ideal behaviour. However, the generality of the equation is lost as it contains two constants, the values of which depend upon the nature of the gas.

1.10 OTHER EQUATIONS OF STATE FOR REAL GASES

Berthelot's Equation The van der Waals equation is one of the many equations of state suggested in order to account for the behaviour of real gases. There are two other simple equations of state which involve just two arbitrary constants. The first of these, due to Berthelot, is

$$\left(p + \frac{n^2a}{TV^2}\right)(V - nb) = nRT \tag{1.10.1}$$

where a and b are constants called the *Berthelot's constants* (different from va der Waals constants) and are characteristics of the gas.

Dieterici's Equation The second equation, due to Dieterici, is

$$\{p \exp(na/VRT)\}\ (V - nb) = nRT \qquad (1.1$$

Virial Equation

All these three equations of state can be expressed approximately in one common form, called the *virial equation of state*, which has the following form for 1 mole of a gas

$$Z = \frac{pV_{\mathrm{m}}}{RT} = 1 + B\frac{1}{V_{\mathrm{m}}} + C\frac{1}{V_{m}^{2}} + D\frac{1}{V_{m}^{3}} + \cdots \tag{1.10.3}$$

where B, C, . . . are temperature dependent constants known as second, third, etc., virial coefficients. These coefficients must be evaluated experimentally at each different temperature.

The second virial coefficient B may be obtained from the experimental data. Rearranging the virial equation, we get

$$V_{\mathrm{m}}\left(\frac{pV_{\mathrm{m}}}{RT} - 1\right) = B + \frac{C}{V_m} + \cdots$$

Thus, extrapolating the graph between $V_m\{(pV_m/RT) - 1\}$ versus $1/V_m$ to $1/V_{\mathrm{m}} = 0$ gives the value of B, i.e.

$$B = \lim_{V_{\mathrm{m}} \to \infty} V_{\mathrm{m}}\left[\frac{pV_{\mathrm{m}}}{RT} - 1\right] \tag{1.10.4}$$

The third virial coefficient C would be the slope of this plot if there were no higher terms in Eq. (1.10.3). These further terms cause the plot to be curved so that C must be evaluated from the initial slope.

Physical Significance of the Constant *B*

The second virial coefficient B has the unit of volume and may be considered to be an excluded molar volume as can be shown by using statistical mechanics. The term B can be expressed in terms of intermolecular attraction by the equation

$$B = 2\pi N_{\mathrm{A}} \int_0^{\infty} \{1 - \exp(-\Phi/kT)\} r^2 \,\mathrm{d}r \tag{1.10.5}$$

where r is the intermolecular distance, k is the Boltzmann constant and Φ is the potential of molecular interaction. As the simplest example of the use of this equation, we consider a gas made up of rigid spherical molecules of diameter d. We assume that the molecules do not interact unless they touch one another and thus $\Phi = 0$ if $r > d$. The molecules cannot penetrate one another as they are rigid; thus $\Phi = \infty$ if $r < d$. Therefore, we have

$$B = 2\pi N_{\mathrm{A}} \int_0^{d} r^2 \,\mathrm{d}r = \frac{2}{3}\pi N_{\mathrm{A}} d^3 = 4N_{\mathrm{A}}\left(\frac{4}{3}\pi r^3\right) \tag{1.10.6}$$

Hence B is the product of Avogadro constant and the volume excluded per molecule.

In general, the numerical values of the virial coefficients decrease very sharply with higher powers of volume.

Problem 1.10.1 Show that at low densities, the van der Waals equation

$$\left(p+\frac{a}{V_{\mathrm{m}}^2}\right)(V_{\mathrm{m}}-b)=RT$$

and the Dieterici's equation

$$p(V_{\mathrm{m}}-b)=RT\exp(-a/RTV_{\mathrm{m}})$$

give essentially the same value of p.

Solution At low densities, volume of the gas is large, therefore b may be ignored in comparison to V_{m}. Moreover, the term a/RTV_{m} will have small value and thus the term $\exp(-a/RTV_{\mathrm{m}})$ can be expanded as

$$\exp(-a/RTV_{\mathrm{m}})=1-\frac{a}{RTV_{\mathrm{m}}}$$

Thus, under these approximations we can write van der Waals equation as

$$\left(p+\frac{a}{V_{\mathrm{m}}^2}\right)(V_{\mathrm{m}})=RT \quad\text{or}\quad p=\frac{RT}{V_{\mathrm{m}}}-\frac{a}{V_{\mathrm{m}}^2}$$

and Dieterici's equation as

$$p=\frac{RT}{V_{\mathrm{m}}}\left(1-\frac{a}{RTV_{\mathrm{m}}}\right)=\frac{RT}{V_{\mathrm{m}}}-\frac{a}{V_{\mathrm{m}}^2}$$

Thus, we see that both van der Waals equation and Dieterici's equation reduce to the same expression of p at low densities.

1.11 REDUCTION OF VAN DER WAALS EQUATION TO VIRIAL EQUATION

Virial Equation in Volume The van der Waals equation of state for 1 mole of a gas is

(A)

$$\left(p+\frac{a}{V_{\mathrm{m}}^2}\right)(V_{\mathrm{m}}-b)=RT \quad\text{or}\quad p=\frac{RT}{V_{\mathrm{m}}-b}-\frac{a}{V_{\mathrm{m}}^2}$$

Multiplying both sides by V_{m}/RT, we get

$$\frac{pV_{\mathrm{m}}}{RT}=\frac{V_{\mathrm{m}}}{V_{\mathrm{m}}-b}-\frac{a}{V_{\mathrm{m}}RT} \quad\text{or}\quad Z=\left(1-\frac{b}{V_{\mathrm{m}}}\right)^{-1}-\frac{a}{V_{\mathrm{m}}RT}$$

(A) in Sub. in (A)

In the low pressure region, V_{m} is large and $b/V_{\mathrm{m}} \ll 1$. Thus, the expression $(1-b/V_{\mathrm{m}})^{-1}$ can be expanded into a power series in b/V_{m}:

$$\left(1-\frac{b}{V_{\mathrm{m}}}\right)^{-1}=1+\frac{b}{V_{\mathrm{m}}}+\left(\frac{b}{V_{\mathrm{m}}}\right)^2+\left(\frac{b}{V_{\mathrm{m}}}\right)^3+\cdots$$

A $p \to 0$

$Z \to 1$.

Substituting this in the expression for Z, we get

$$Z = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{V_m} + \left(\frac{b}{V_m}\right)^2 + \cdots \qquad (1.11.1)$$

Thus for the second virial coefficient, we have

$$B = b - \frac{a}{RT}$$

Third virial coefficient $C = b^2$, and so on.

Virial Equation in Pressure

An alternative form of the virial equation of state involves the expression of Z in terms of a power series in p, i.e.

$$Z = 1 + A_1 p + A_2 p^2 + \cdots \qquad (1.11.2)$$

The expressions for A_1 and A_2 can be derived as follows:

$$Z = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{V_m} + \left(\frac{b}{V_m}\right)^2 + \cdots$$

Since $Z = pV_m/RT$, therefore, $1/V_m = p/RTZ$. Hence

$$Z = 1 + \left(b - \frac{a}{RT}\right)\frac{p}{RTZ} + b^2\left(\frac{p}{RTZ}\right)^2 + \cdots \qquad (1.11.3)$$

Comparing Eqs (1.11.2) and (1.11.3), we get

$$1 + A_1 p + A_2 p^2 + \cdots = 1 + \left(b - \frac{a}{RT}\right)\frac{p}{RTZ} + \left(\frac{b}{RTZ}\right)^2 p^2 + \cdots$$

or

$$A_1 p + A_2 p^2 + \cdots = \frac{1}{RTZ}\left(b - \frac{a}{RT}\right)p + \left(\frac{b}{RT}\right)^2 \frac{p^2}{Z^2} + \cdots$$

Dividing by p, we get

$$A_1 + A_2 p + \cdots = \frac{1}{RTZ}\left(b - \frac{a}{RT}\right) + \left(\frac{b}{RT}\right)^2 \frac{p}{Z^2} + \cdots \quad \text{—} \textcircled{A}$$

In the limiting state of zero pressure, Z = 1 and this equation becomes

$$A_1 = \frac{1}{RT}\left(b - \frac{a}{RT}\right) \qquad (1.11.4)$$

which is the required expression for A_1. Thus Sub. in $\textcircled{A}$

$$A_1 + A_2 p + \cdots = A_1\left(\frac{1}{Z}\right) + \left(\frac{b}{RT}\right)^2 \frac{p}{Z^2} + \cdots$$

We repeat the procedure by subtracting A_1 from both sides of this equation, dividing by p and taking the limiting value at zero pressure. Note that $(Z - 1)/p = A_1$ at zero pressure. Then

$$A_2 p = \frac{A_1}{Z} - A_1 + \left(\frac{b}{RT}\right)^2 \frac{p}{Z^2}$$

$$\frac{A_2 p}{p} = -\left(\frac{Z-1}{Z}\right)\frac{A_1}{p} + \left(\frac{b}{RT}\right)^2 \frac{p}{Z^2 \times p}$$

As $p \to 0$.
$Z \to 1$.

$A_2 = -\left(\frac{Z-1}{p}\right)\frac{A_1}{Z} + \left(\frac{b}{RT}\right)^2 \frac{1}{Z^2}$

From eq 1.112 $\left(\frac{Z-1}{p}\right) = A_1$

$A_2 = -A_1 \times A_1 + \frac{b^2}{(RT)^2}$

$A_2 = -A_1^2 + \frac{b^2}{(RT)^2}$

$$A_2 = \left(\frac{b}{RT}\right)^2 - A_1^2 = \frac{a}{(RT)^3}\left(2b - \frac{a}{RT}\right) \qquad (1.11.5)$$

Thus, the expression for Z correct up to the third coefficient is

$$Z = 1 + \frac{1}{RT}\left(b - \frac{a}{RT}\right)p + \frac{a}{(RT)^3}\left(2b - \frac{a}{RT}\right)p^2 + \cdots \qquad (1.11.6)$$

The correct coefficient for p could have been obtained by simply replacing $1/V_m$ in Eq. (1.11.1) by the ideal value; however, this would yield incorrect values of the coefficients of higher powers of pressures.

The slope of Z versus p curve is obtained by differentiating the above virial equation in Z with respect to pressure, keeping the temperature constant, i.e.

$$\left(\frac{\partial Z}{\partial p}\right)_T = \frac{1}{RT}\left(b - \frac{a}{RT}\right) + \frac{2a}{(RT)^3}\left(2b - \frac{a}{RT}\right)p + \cdots \qquad (1.11.7)$$

At $p = 0$, all higher terms drop out and this derivative simply reduces to

$$\left(\frac{\partial Z}{\partial p}\right)_T = \frac{1}{RT}\left(b - \frac{a}{RT}\right); \qquad (p = 0) \qquad (1.11.8)$$

Comment on the Plots of Compression Factor versus Pressure

The derivative in Eq. (1.11.8) is the initial slope of the plot of Z versus p (Fig. 1.8.2). Now if $b > a/RT$, the initial slope is positive and the size effect (i.e. b factor) will dominate the behaviour of the gas. However, if $b < a/RT$, the initial slope is negative and the effect of the attractive forces (i.e. a factor) will dominate. Thus, the van der Waals equation, which includes both the effects of size and of intermolecular forces, can interpret both the positive and negative slopes of the Z versus p plots. In interpreting Fig. 1.8.2, we can say that at 0 °C, the effect of attractive forces dominate the behaviour of methane and carbon dioxide, while the molecular size effect dominates the behaviour of hydrogen.

While interpreting Fig. 1.8.3 (graph of Z versus p of the same gas at different temperatures), we can say that if the temperature is low enough, the term a/RT will be larger than b and so the initial slope of Z versus p will be negative. As the temperature rises, a/RT becomes smaller. At a sufficiently high temperature it becomes less than b, and the initial slope of Z versus p curve turns positive.

Boyle Temperature

At some intermediate temperature T_B, called *Boyle temperature*, the initial slope is zero. This is obtained from Eq. (1.11.8) by putting $b - a/RT_B = 0$, which yields

$$T_B = \frac{a}{Rb} \qquad (1.11.9)$$

At the Boyle temperature, the Z versus p line of an ideal gas is tangent to that of a real gas when p approaches zero. The latter rises above the ideal gas line only very slowly. In Eq. (1.11.6) the second term is zero at T_B and the remaining terms are small until the pressure becomes very high. Thus, at the Boyle temperature, the real gas behaves ideally over a wide range of pressure, because the effects of the size of molecules and intermolecular forces roughly compensate each other.

The Boyle temperature of some gases are given below:

$T_B(H_2) = -\,156\ ^\circ C$ $\qquad$ $T_B(N_2) = 59\ ^\circ C$

$T_B(He) = -\,249\ ^\circ C$ $\qquad$ $T_B(CH_4) = 224\ ^\circ C$

$T_B(NH_3) = 587\ ^\circ C$

Thus we can see that for H_2 and He, the temperature of 0 °C is above their respective Boyle temperatures and so they have Z values greater than unity. The other gases at 0 °C are below their respective Boyle temperatures and so they have Z values less than unity in the low pressure range.

Example 1.11.1 Given that $Z = 1.000\,54$ at 273.15 K and 101.325 kPa pressure and the Boyle temperature of the gas is 107 K, estimate the values of a and b.

Solution We are given that

$$Z = 1.000\,54, \quad T = 273.15\ \text{K}, \quad p = 101.325\ \text{kPa}, \quad \text{and} \quad T_B = 107\ \text{K}$$

From the expression

$$Z = 1 + \frac{p}{RTZ}\left(b - \frac{a}{RT}\right)$$

we have $\quad b = (Z-1)\dfrac{RTZ}{p} + \dfrac{a}{RT}$

At Boyle temperature, $T_B = a/Rb$ so that $a = RbT_B$. Therefore,

$$b = (Z-1)\frac{RTZ}{p} + \frac{RbT_B}{RT}$$

On rearranging, we get

$$b = \left(\frac{T}{T - T_B}\right)\left(\frac{Z-1}{p}\right)RTZ$$

Substituting the values, we have

$$b = \left(\frac{273.15\ \text{K}}{273.15\ \text{K} - 107\ \text{K}}\right)\left(\frac{1.000\,54 - 1}{101.325\ \text{kPa}}\right)(8.314\ \text{kPa dm}^3\ \text{K}^{-1}\ \text{mol}^{-1}) \times (273.15\ \text{K})\,(1.000\,54)$$

$$= 0.019\,9\ \text{dm}^3\ \text{mol}^{-1}$$

Also $\quad a = RbT_B = (8.314\ \text{kPa dm}^3\ \text{K}^{-1}\ \text{mol}^{-1})\,(0.019\,9\ \text{dm}^3\ \text{mol}^{-1})\,(107\ \text{K})$

$$= 17.703\ \text{kPa dm}^6\ \text{mol}^{-2}$$

Problem 1.11.1 Express Berthelot and Dieterici equations in the form of virial equation of state and derive the expressions for the second virial coefficient of these equations. Also derive the expressions for Boyle temperature.

Solution ***Berthelot's equation***

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

Multiplying by V_m/RT, we get

$$Z = \frac{pV_m}{RT} = \frac{V_m}{V_m - b} - \frac{a}{V_m RT^2} = \left(1 - \frac{b}{V_m}\right)^{-1} - \frac{a}{V_m RT^2}$$

$$= 1 + \frac{b}{V_m} + \left(\frac{b}{V_m}\right)^2 + \cdots - \frac{a}{V_m RT^2}$$

$$= 1 + \frac{1}{V_m}\left(b - \frac{a}{RT^2}\right) + \left(\frac{b}{V_m}\right)^2 + \cdots$$

The second virial coefficient and Boyle temperature are

$$B = \left(b - \frac{a}{RT^2}\right); \qquad T_B = \left(\frac{a}{Rb}\right)^{1/2}$$

Dieterici's equation

$$p = \frac{RT}{(V_m - b)} \exp(-a/V_m RT)$$

Therefore,

$$Z = \frac{pV_m}{RT} = \frac{V_m}{V_m - b} \exp(-a/V_m RT) = \left(1 - \frac{b}{V_m}\right)^{-1} \exp(-a/V_m RT)$$

$$= \left[1 + \frac{b}{V_m} + \left(\frac{b}{V_m}\right)^2 + \cdots\right]\left[1 - \frac{a}{V_m RT} + \cdots\right] = 1 + \frac{1}{V_m}\left(b - \frac{a}{RT}\right) + \cdots$$

Thus, the second virial coefficient is $(b - a/RT)$ and Boyle temperature T_B is a/Rb.

1.12 CRITICAL CONSTANTS

Andrews Isotherms In 1869, Thomas Andrews carried out an experiment in which p–V relations of carbon dioxide gas were measured at various temperatures. The types of isotherms obtained are shown in Fig. 1.12.1. Other real gases also show the same types of isotherms.

We observe from Fig. 1.12.1 the following:

(1) At high temperatures, such as T_4, the isotherms look like those of an ideal gas.

(2) At low temperatures, the curves have altogether different appearances. Consider, for example, a typical curve abcd. As the pressure increases, the volume of the gas decreases (curve a to b). At point b liquefaction commences and the volume decreases rapidly as the gas is converted to a liquid with a much higher density. This conversion takes place at constant pressure p. At the point c, liquefaction is complete and thus the line cd represents the variation of V with p of the liquid state. The steepness of the line cd is evidence of the fact that the liquid cannot be easily compressed. Thus, we note that ab represents the gaseous state, bc, liquid and vapour in equilibrium, and cd shows the liquid state only.