

2-4 EQUATIONS OF STATE OF REAL GASES

Many equations have been proposed which describe the P - v - T relations of real gases more accurately than does the equation of state of an ideal gas. Some of these are purely empirical, while others are derived from assumptions regarding molecular properties. Van der Waals*, in 1873, derived the following equation:

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT. \tag{2-8}$$

The quantities a and b are constants for any one gas but differ for different gases. Some values are listed in Table 2-1. We shall show in Chapter 10 that the term a/v^2 arises from the existence of intermolecular forces and that the term b is proportional to the volume occupied by the molecules themselves, but for the present we shall consider the equation as an empirical one.

Table 2-1 Constants a and b in van der Waals equation. P in N m^{-2} , v in $\text{m}^3 \text{ kilomole}^{-1}$, T in kelvins, $R = 8.31 \times 10^3$ $\text{J kilomole}^{-1} \text{ K}^{-1}$.

Substance	a ($\text{J m}^3 \text{ kilomole}^{-2}$)	b ($\text{m}^3 \text{ kilomole}^{-1}$)
He	3.44×10^3	0.0234
H ₂	24.8	.0266
O ₂	138	.0318
CO ₂	366	.0429
H ₂ O	580	.0319
Hg	292	.0055

At sufficiently large specific volumes, the term a/v^2 becomes negligible in comparison with P , and b becomes negligible in comparison with v . The van der Waals equation then reduces to the equation of state of an ideal gas, which any equation of state must do at large specific volumes.

Figure 2-4 is a diagram of a portion of the P - v - T surface of a van der Waals gas, and Fig. 2-5 is a projection of a number of isotherms onto the P - v plane.

* Johannes D. van der Waals, Dutch physicist (1837-1923).

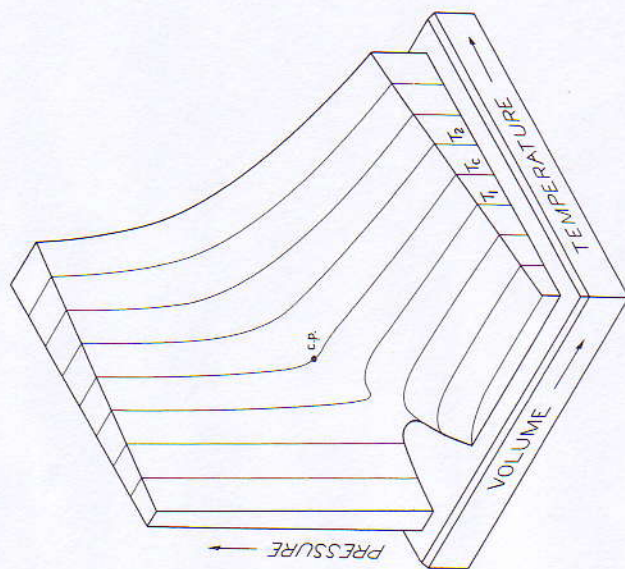


Fig. 2-4 P - v - T surface for a van der Waals gas.

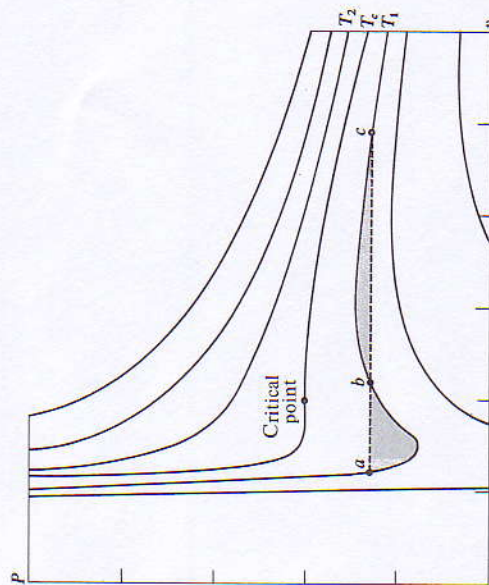


Fig. 2-5 Isotherms of a van der Waals gas.

10-1 INTERMOLECULAR FORCES

In the preceding chapter, the molecules of a gas were treated as geometrical points that exerted no forces on each other. We now wish to take such forces into account.

The force between any pair of molecules is of electrical origin; and because of the complicated structure of an atom or molecule, it is not expressible by any simple law. In general, at relatively large separations, the force is one of attraction, referred to as a van der Waals force, which decreases rapidly with increasing separation. When two molecules approach so closely that their electron clouds overlap, the force becomes one of repulsion that rises very rapidly as the separation becomes smaller. Thus the intermolecular force must have the general form of the solid curve in Fig. 10-1.

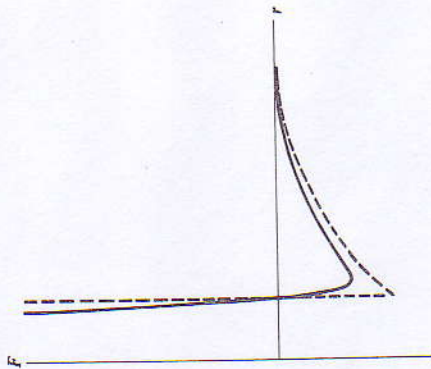


Fig. 10-1 Intermolecular forces.

The simplest approximation to this law is to treat the molecules as elastic *hard spheres*, for which the force of repulsion becomes infinite when the surfaces of the spheres come into contact. If we include a force of attraction when the molecules are not in contact, the force law has the form of the dotted curve in Fig. 10-1.

10-2 THE VAN DER WAALS EQUATION OF STATE

We have made extensive use of the van der Waals equation of state in earlier chapters, not so much because of any great accuracy of this equation in describing the properties of real gases but because it shows in a general way, through the factor a , how these properties depend on intermolecular forces of attraction, and through the factor b how they depend on molecular sizes.

The latter correction to the equation of state was actually first suggested by Clausius. He reasoned that in the derivation in Section 9-4 one should use not the actual volume V of the container, but the volume available to a single molecule, which will be somewhat less than V because of the volume occupied by the other molecules. If we represent the "unavailable" volume per mole by b , then in a gas consisting of n moles the unavailable volume is nb and we should write

$$P(V - nb) = nRT,$$

or, dividing through by n ,

$$P(v - b) = RT. \quad (10-1)$$

This equation was first written down by Hirn.* (Here, the letter v represents the molal specific volume, not the molecular speed.)

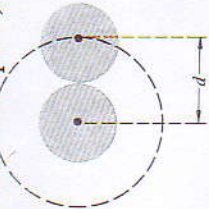


Fig. 10-2 The radius of the sphere of exclusion equals the molecular diameter d .

If the molecules are considered as hard spheres of diameter d , the minimum distance between the centers of two molecules, as shown in Fig. 10-2, is equal to d . In effect, the center of each molecule is excluded by the other from a sphere of radius d , known as the "sphere of exclusion." The volume of this sphere is $\frac{4}{3}\pi d^3/3$, and to avoid counting each pair twice, we take as the total unavailable volume, for a system of N molecules,

$$\frac{1}{2} N \times \frac{4}{3} \pi d^3.$$

The number of molecules N is the product of the number of moles n and Avogadro's number N_A , so the unavailable volume per mole, or the constant b , is

$$b = \frac{2}{3} N_A \pi d^3. \quad (10-2)$$

This is four times as great as the actual molecular volume per mole, which is

$$\frac{1}{6} N_A \pi d^3. \quad (10-3)$$

Van der Waals, in 1873, included a second correction term in the equation of state to take into account the force of attraction between molecules. Let us assume

* Gustav A. Hirn, French engineer, (1815-1890).

that these forces decrease so rapidly with distance (for example, as $1/r^6$) that they are appreciable only between a molecule and its nearest neighbors. Molecules within the body of the gas are on the average attracted equally in all directions, but those in the outermost layers experience a net inward force. A molecule approaching the wall of the container is therefore slowed down and the average force exerted on the wall, and hence the observed pressure, is somewhat smaller than it would be in the absence of attractive forces.

The reduction in pressure will be proportional both to the number of molecules per unit volume in the outer layer, $n = N/V$, and to the number per unit volume in the next layer beneath them, which is doing the attracting. Hence the pressure will be reduced by an amount proportional to n^2 , or equal to αn^2 , where α is a factor dependent on the strength of the attractive force. Since the number of molecules N equals nN_A , where n is the number of moles, then

$$\alpha n^2 = \alpha \left(\frac{N}{V} \right)^2 = \alpha N_A^2 \frac{n^2}{V^2} = \frac{\alpha N_A^2}{v^2} = \frac{a}{v^2}, \quad (10-4)$$

where the product αN_A^2 has been replaced by a . Thus the pressure P given by the Hirm equation,

$$P = \frac{RT}{v - b},$$

should be reduced by a/v^2 ; and

$$P = \frac{RT}{v - b} - \frac{a}{v^2},$$

or

$$\left(P + \frac{a}{v^2} \right) (v - b) = RT, \quad (10-5)$$

which is the van der Waals equation of state.

Since the molal specific critical volume of a van der Waals gas, v_c , is equal to $3b$, it follows from Eq. (10-2) that

$$v_c = 3b = 2N_A \pi d^3, \quad (10-6)$$

which is 12 times the total molecular volume. The value of b for a van der Waals gas therefore provides a means of estimating molecular diameters, since

$$d = \left(\frac{3b}{2\pi N_A} \right)^{1/3}. \quad (10-7)$$

Thus for helium, for which $b = 23.4 \times 10^{-3} \text{ m}^3 \text{ kilomole}^{-1}$, we have

$$d = \left(\frac{3 \times 23.4 \times 10^{-3}}{2 \times 3.14 \times 6.02 \times 10^{26}} \right)^{1/3} \approx 2.6 \times 10^{-10} \text{ m} = 2.6 \times 10^{-8} \text{ cm}.$$

Other methods of estimating molecular diameters will be described in Section 10-4. Values of a and b for several gases are given in Table 2-1.

10-3 COLLISION CROSS SECTION. MEAN FREE PATH

In deriving the expression for the pressure exerted by a gas, the molecules were treated as geometrical points which could fly freely from one wall of a container to the other without colliding with other molecules. One of the objections raised in the early development of kinetic theory was that if molecules acted in this way, a small amount of gas released in a large room would spread throughout the room practically instantaneously, whereas we know that when the stopper is removed from a bottle of perfume, a considerable time elapses before the odor can be detected even at a point only a few feet away, in the absence of air currents. It was soon realized that this relatively slow *diffusion* of one gas in another resulted from molecular collisions such as that shown in Fig. 10-3, which cause a molecule to move in an irregular, zigzag path.

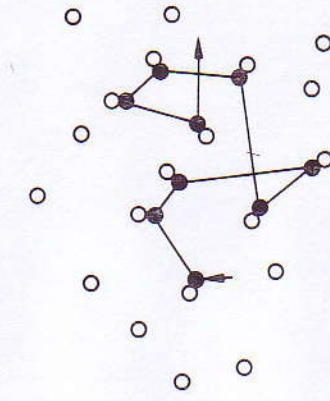


Fig. 10-3 Molecular free paths.

We again assume that a molecule is a hard sphere. Let us refer to one of the colliding molecules as the "target" molecule and to the other as the "bullet" molecule. Then a collision occurs whenever the distance between the centers of the molecules becomes equal to the molecular diameter d , as in Fig. 10-2.

Since it is only the center-to-center distance that determines a collision, it does not matter whether the target is large and the bullet small, or vice versa. We may therefore consider the bullet molecule to shrink to a point at its center, and the target molecule to occupy the entire sphere of exclusion, of radius d .

Now consider a thin layer of gas of dimensions L , L , and Δx , as in Fig. 10-4. The layer contains (equivalent) target molecules, represented by the shaded circles. We then imagine that a very large number N of bullet molecules, represented by the black dots, is projected toward the face of the layer—like pellets from a shotgun—in such a way that they are distributed at random over the face of the layer. If the thickness of the layer is so small that no target molecule can hide behind another, the layer presents to the bullet molecules the appearance of Fig. 10-4.