1

Gases and Liquids

ALL MATTER exists in one of three states of aggregation, solid, liquid, or gaseous. A solid may be defined as a body possessing both definite volume and definite shape at a given temperature and pressure. Further, to be classed as a solid the body must be crystalline, i.e., the atoms, molecules, or ions composing the body must be arranged in a definite geometric configuration characteristic of the substance in question. A liquid in bulk, on the other hand, has a definite volume but no definite shape, while a gas has neither definite shape nor volume. Liquids and gases are both termed *fluids*. A liquid, insofar as it fills the container, will always adopt the shape of the container in which it is placed, but will retain its definite volume, while a gas will always fill completely any container in which it may be confined.

The distinctions among the three states of matter are not always as clear cut as the above definitions would imply. For example, a liquid at the critical point is indistinguishable from its vapor. Again, such substances as glass or asphalt, although exhibiting many of the properties of a solid, will, under certain conditions of temperature, become plastic and exhibit properties not ascribed to pure solids. For this reason such substances are usually considered to be supercooled liquids with very high viscosity.

The particular state of aggregation of a substance is determined by

the temperature and pressure under which it exists. However, within certain limits of temperature and pressure a substance may exist in more than one state at the same time. In fact, under special conditions a substance may exist in all three states simultaneously. Thus at 4.57 mm Hg pressure and at 0.010°C, ice, water, and water vapor may all be present simultaneously, and all be stable. This subject of simultaneous existence in more than one state will be discussed more completely in various places in the book.

IDEAL AND REAL GASES

For purposes of discussion, it is convenient to classify all gases into two types, namely, (a) *ideal* gases, and (b) *nonideal* or *real* gases. An ideal gas is one that obeys certain laws which will be presented shortly, while a real gas is one that obeys these laws only at low pressures.

In ideal gases the volume occupied by the molecules themselves is negligible compared with the total volume at all pressures and temperatures, and the intermolecular attraction is extremely small under all conditions. For nonideal or real gases both of these factors are appreciable, the magnitude of each depending on the nature, the temperature, and the pressure of the gas. We can easily see that an ideal gas must be a hypothetical gas, as all actual gases must contain molecules which occupy a definite volume and exert attractions between each other. However, very often the influence of these factors becomes negligible, and the gas may then be considered to be ideal. We shall find that the latter condition will obtain in particular at low pressures and relatively high temperatures, conditions under which the "free" space within the gas is large and the attractive forces between molecules small.

GENERALIZATIONS OF IDEAL GAS BEHAVIOR

Through the study of gases there have been evolved certain laws or generalizations which are the starting point in any discussion of gas behavior. These are: (a) Boyle's law, (b) Charles's or Gay-Lussac's law, (c) Dalton's law of partial pressures, and (d) Graham's law of diffusion. Another generalization is Avogadro's principle, but this will be considered later.

BOYLE'S LAW

In 1662 Robert Boyle reported that the volume of a gas at constant temperature decreased with increasing pressure, and that, within the limits of his experimental accuracy, *the volume of any definite quantity of*

gas at constant temperature varied inversely as the pressure on the gas. This highly important generalization is known as *Boyle's law.* Expressed mathematically, this law states that at *constant temperature* $V \propto 1/P$, or that

$$V = \frac{K_1}{P}$$

where V is the volume and P the pressure of the gas, while K_1 is a proportionality factor whose value is dependent on the temperature, the weight

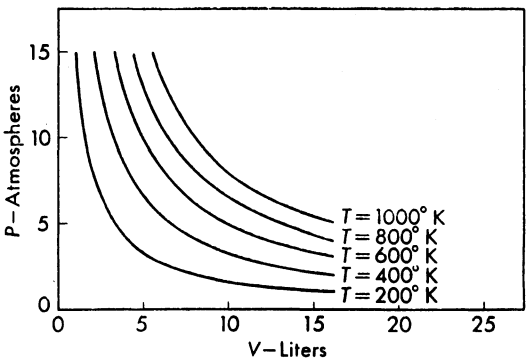

Figure 1–1. Isothermal plot of P vs. V according to Boyle's law (1 mole of gas).

of the gas, its nature, and the units in which P and V are expressed. On rearrangement this equation becomes

$$PV = K_1 \tag{1}$$

from which it follows that if in a certain state the pressure and volume of the gas are P_1 and V_1, while in another state they are P_2 and V_2, then at constant temperature

$$P_1V_1 = K_1 = P_2V_2$$

and

$$\frac{P_1}{P_2} = \frac{V_2}{V_1} \tag{2}$$

When the pressure of a gas is plotted against the volume in accordance with Eq. (1), we obtain a family of curves such as that shown in Figure 1–1. Each curve is a hyperbola with a different value of K_1. Since for a given weight of gas K_1 varies only with temperature, each curve corresponds to a different fixed temperature and is known as an *isotherm* (constant temperature plot). The higher curves correspond to the higher temperatures.

THE CHARLES OR GAY-LUSSAC LAW

Charles in 1787 observed that the gases hydrogen, air, carbon dioxide, and oxygen expanded an equal amount upon being heated from 0 to 80°C at constant pressure. However, it was Gay-Lussac in 1802 who first found that for *all* gases the increase in volume for each degree centigrade rise in temperature was equal approximately to $\frac{1}{273}$ of the volume of the gas at 0°C. A more precise value of this fraction is $\frac{1}{273.15}$. If we designate by V_0 the volume of a gas at 0°C and by V its volume at any temperature t°C, then in terms of Gay-Lussac's finding V may be written as

$$\begin{aligned} V &= V_0 + \frac{t}{273.15} V_0 \\ &= V_0\left(1 + \frac{t}{273.15}\right) \\ &= V_0\left(\frac{273.15 + t}{273.15}\right) \end{aligned} \tag{3}$$

We may define now a new temperature scale such that any temperature t on it will be given by $T = 273.15 + t$, and 0°C by $T_0 = 273.15$. Then Eq. (3) becomes simply

$$\frac{V}{V_0} = \frac{T}{T_0}$$

or generally

$$\frac{V_2}{V_1} = \frac{T_2}{T_1} \tag{4}$$

This new temperature scale, designated as the absolute or Kelvin scale of temperature, is of fundamental importance in all science. In terms of this temperature scale, Eq. (4) tells us that *the volume of a definite quantity of gas at constant pressure is directly proportional to the absolute temperature*, or that

$$V = K_2 T \tag{5}$$

where K_2 is a proportionality factor determined by the pressure, the nature and amount of gas, and the units of V. The above statement and Eq. (5) are expressions of *Charles's or Gay-Lussac's law of volumes.*

According to Eq. (5) the volume of a gas should be a straight line function of the absolute temperature at any constant pressure. Such a plot of V vs. T at selected pressures is shown in Figure 1–2. Since for a given amount of gas K_2 will have different values at different pressures, we obtain a series of straight lines, one for each constant pressure. Each constant pressure line is called an *isobar*. For every isobar the slope is the greater the lower the pressure.

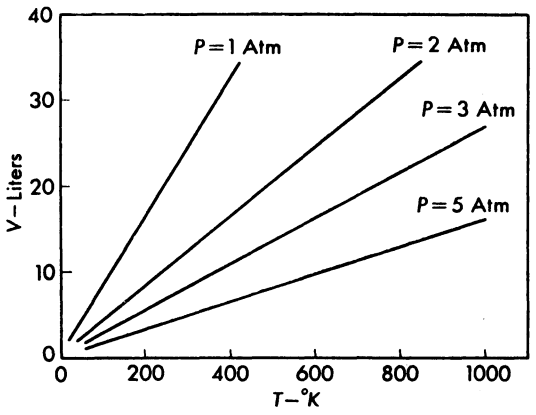

Figure 1-2. Isobaric plots of V vs. T according to Charles's law (1 mole of gas).

Equation (5) suggests also that if we were to cool a gas to 0°K (−273°C), its volume would become zero. However, no such phenomenon is ever encountered, for usually long before 0°K is approached a gas liquefies or solidifies. Again, as will be shown in the following, under such drastic conditions the equation itself cannot be considered to hold.

THE COMBINED GAS LAW

The two laws discussed give the separate variation of the volume of a gas with pressure and with temperature. To obtain the simultaneous variation of the volume with temperature and pressure, we proceed as follows. Consider a quantity of gas at P_1, V_1, and T_1, and suppose that it is desired to obtain the volume of the gas, V_2, at P_2 and T_2. First, let us compress (or expand) the gas from P_1 to P_2 at constant temperature T_1. The resulting volume V_x then will be, according to Boyle's law,

$$\frac{V_x}{V_1} = \frac{P_1}{P_2}$$

$$V_x = \frac{V_1 P_1}{P_2} \tag{6}$$

If the gas at V_x, P_2, and T_1 is heated now at constant pressure P_2 from T_1 to T_2, the final state at P_2 and T_2 will have the volume V_2 given by Charles's law, namely,

$$\frac{V_2}{V_x} = \frac{T_2}{T_1}$$

$$V_2 = \frac{V_x T_2}{T_1}$$

Substituting into this relation the value of V_x from Eq. (6), V_2 becomes

$$V_2 = \frac{V_x T_2}{T_1} = \frac{P_1 V_1 T_2}{P_2 T_1}$$

and on rearranging terms we see that

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} = \text{constant} = K \tag{7}$$

i.e., the ratio PV/T for any given state of a gas is a constant. Consequently we may drop the subscripts and write for any gas which obeys Boyle's and Charles's laws

$$PV = KT \tag{8}$$

Equation (8) is known as the *combined gas law.* It gives the complete relationship between the pressure, volume, and temperature of any gas as soon as the constant K is evaluated. That Boyle's and Charles's laws are merely special cases of Eq. (8) is easily shown. When T is constant, Eq. (8) reduces to PV = constant, or Boyle's law. Again, when P is constant, Eq. (8) becomes

$$V = \frac{K}{P} T = K_2 T$$

or Charles's law.

THE GAS CONSTANT

The numerical value of the constant K in Eq. (8) is determined by the number of moles[1] of gas involved and the units in which P and V are expressed; but it is *totally independent of the nature of the gas.* Equation (8) shows that for any given pressure and temperature an increase in the quantity of gas increases the volume, and thereby also correspondingly the magnitude of K. In other words, K is directly proportional to the number of moles of gas involved. For convenience this constant may be replaced, therefore, by the expression $K = nR$, where n is the number of moles of gas occupying volume V at P and T, while R is the *gas constant per mole.* Thus expressed, R becomes a *universal constant for all gases* and Eq. (8) takes the final form

$$PV = nRT \tag{9}$$

Equation (9) is the *ideal gas equation,* one of the most important relations in physical chemistry. It connects directly the volume, temperature, pressure, and number of moles of a gas, and permits all types of gas

[1] A *mole* is the mass of a substance in grams equal numerically to its molecular weight.

calculations as soon as the constant R is known. R may be found from the fact that 1 mole of *any* ideal gas at standard conditions, i.e., at 0°C and 1 atm pressure, occupies a volume of 22.413 liters. If we express then the *volume in liters* and the *pressure in atmospheres*, R follows from Eq. (9) as

$$R = \frac{PV}{nT} = \frac{1 \times 22.413}{1 \times 273.15} = 0.08205 \text{ liter-atm degree}^{-1} \text{ mole}^{-1}$$

This value of R can be used only when volume is taken in liters and pressure in atmospheres. For other combinations of units R will have other values. Thus, if the pressure be expressed in atmospheres while the volume in cubic centimeters, R becomes

$$R = \frac{1 \times 22{,}413}{1 \times 273.15} = 82.05 \text{ cc-atm degree}^{-1} \text{ mole}^{-1}$$

Since pressure is force per unit area and volume is area times length, it immediately follows that the units of PV/nT and hence of R are

$$\frac{PV}{nT} = R = \frac{\dfrac{\text{force}}{\text{area}} \times \text{area} \times \text{length}}{\text{moles} \times \text{degrees}} = \frac{\text{force} \times \text{length}}{\text{moles} \times \text{degrees}} = \frac{\text{work degree}^{-1}}{\text{mole}^{-1}}$$

Consequently R may be expressed in any set of units representing work or energy. Although in gas calculations in the metric system the units given above are the most useful, there is necessity in other types of calculations to employ R in some alternate energy units. These are usually ergs, joules, and calories.

To obtain R in ergs the pressure must be expressed in dynes per square centimeter and the volume in cubic centimeters. For the volume at standard conditions we have $V = 22{,}413$ cc. Again, a pressure of 1 atm is the pressure of a column of mercury 76 cm high and 1 cm^2 in cross section at 0°C. The total volume of such a column is thus 76 cc, and the mass 76×13.595, where the latter quantity is the density of mercury at 0°C. The pressure in dynes per square centimeter will be then this mass multiplied by the acceleration of gravity, 980.66 cm sec^{-2}. Inserting these values of V and P into the expression for R, we find that

$$R = \frac{(76 \times 13.595 \times 980.66)(22{,}413)}{1 \times 273.15} = 8.314 \times 10^7 \text{ ergs degree}^{-1} \text{ mole}^{-1}$$

Further, since 1 joule = 10^7 ergs, and 1 calorie = 4.184 joules, we arrive also at

$$\begin{aligned} R &= 8.314 \text{ joules degree}^{-1} \text{ mole}^{-1} \\ &= \frac{8.314}{4.184} = 1.987 \text{ cal degree}^{-1} \text{ mole}^{-1} \end{aligned}$$

It should be clearly understood that, although R may be expressed in

different units, for pressure-volume calculations involving gases *R must always be taken in the same units as those used for pressure and volume.* To facilitate calculations, Table 1–1 gives a summary of the values of R in various units.

TABLE 1–1. VALUES OF R IN VARIOUS UNITS

Pressure	Volume	Temperature	n	R
Atmospheres	liters	°K	gram-moles	0.08205 liter-atm $(°K)^{-1}$ $(g\text{-mole})^{-1}$
Atmospheres	cc	°K	gram-moles	82.05 cc-atm $(°K)^{-1}$ $(g\text{-mole})^{-1}$
Dynes/cm^2	cc	°K	gram-moles	8.314×10^7 ergs $(°K)^{-1}$ $(g\text{-mole})^{-1}$
mm Hg	cc	°K	gram-moles	62,360 cc-mm Hg $(°K)^{-1}$ $(g\text{-mole})^{-1}$
R in joules		°K	gram-moles	8.314 joules $(°K)^{-1}$ $(g\text{-mole})^{-1}$
R in calories		°K	gram-moles	1.987 cal $(°K)^{-1}$ $(g\text{-mole})^{-1}$

CALCULATIONS INVOLVING IDEAL GAS LAW

The ideal gas law may be employed to find any one of the variables P, V, T, or n from any specified set of three of these. As an illustration, suppose that we want to ascertain the volume occupied by 10.0 g of oxygen at 25.0°C and 650 mm Hg pressure. From the data we know that

$$n = \frac{10.0}{32.0} = 0.312 \text{ mole}$$
$$T = 273.2 + 25.0 = 298.2°\text{K}$$
$$P = \frac{650}{760} = 0.855 \text{ atm}$$
$$R = 0.0821 \text{ liter-atm degree}^{-1} \text{ mole}^{-1}$$

Insertion of these into Eq. (9) yields for the volume

$$V = \frac{nRT}{P} = \frac{0.312 \times 0.0821 \times 298.2}{0.855}$$
$$= 8.94 \text{ liters}$$

Similarly, from appropriately specified data the other quantities involved in the ideal gas equation may be found.

DALTON'S LAW OF PARTIAL PRESSURES

Different gases introduced into the same container interdiffuse or mix rapidly. Dalton's *law of partial pressures* states that *at constant temperature the total pressure exerted by a mixture of gases in a definite volume is*

equal to the sum of the individual pressures which each gas would exert if it occupied the same total volume alone. In other words,

$$P_{\text{total}} = P_1 + P_2 + P_3 + \cdots \tag{10}$$

where the individual pressures, P_1, P_2, P_3, etc., are termed the *partial pressures* of the respective gases. The partial pressure of each constituent may be thought of as the pressure which that constituent would exert if it were isolated in the same volume and at the same temperature as that of the mixture. In terms of the partial pressures, Dalton's law may be restated as follows: *The total pressure of a mixture of gases is equal to the sum of the partial pressures of the individual components of the mixture.*

The significance of Dalton's law and of the concept of partial pressures is best brought out by the following example. If we were to take three *1-liter* flasks filled respectively with hydrogen at 70 mm Hg pressure, carbon monoxide at 500 mm, and nitrogen at 1000 mm, all at the same temperature, and were to force all these gases into a fourth *1-liter* flask, the total pressure within the fourth flask would be

$$\begin{aligned} P &= P_{H_2} + P_{CO} + P_{N_2} \\ &= 70 + 500 + 1000 \\ &= 1570 \text{ mm Hg} \end{aligned}$$

and the pressures of the individual gases within their 1-liter flasks would be the partial pressures of these gases in the mixture.

Consider now a gaseous mixture composed of n_1 moles of one gas, n_2 moles of another gas, and n_3 moles of still a third. Let the total volume be V and the temperature T. If the conditions of pressure and temperature are not too extreme, the ideal gas laws would be valid for each gas in the mixture, and we obtain for the respective partial pressures

$$P_1 = \frac{n_1 RT}{V} \tag{11a}$$

$$P_2 = \frac{n_2 RT}{V} \tag{11b}$$

$$P_3 = \frac{n_3 RT}{V} \tag{11c}$$

According to Dalton's law the total pressure P thus becomes

$$\begin{aligned} P &= \frac{n_1 RT}{V} + \frac{n_2 RT}{V} + \frac{n_3 RT}{V} \\ &= \frac{(n_1 + n_2 + n_3) RT}{V} \\ &= \frac{n_t RT}{V} \end{aligned} \tag{12}$$

where $n_t = (n_1 + n_2 + n_3)$ = total number of moles of gas in the mixture. We see from Eq. (12), therefore, that the gas laws may be applied to mixtures as well as to pure gases, and in exactly the same way.

On division of Eqs. (11a)–(11c) by Eq. (12) it is found that

$$P_1 = \frac{n_1}{n_t} P \tag{13a}$$

$$P_2 = \frac{n_2}{n_t} P \tag{13b}$$

and

$$P_3 = \frac{n_3}{n_t} P \tag{13c}$$

Equations such as (13) are very important in chemical and chemical engineering calculations, for they relate the partial pressure of a gas to the total pressure of the mixture. Since the fractions n_1/n_t, n_2/n_t, and n_3/n_t represent the moles of a particular constituent present in the mixture divided by the total number of moles of all gases present, these quantities are called *mol fractions* and are designated by the respective symbols N_1, N_2, N_3, etc. Of necessity the sum of all the mol fractions for a system will have to be unity, namely,

$$N_1 + N_2 + N_3 + \cdots = 1 \tag{14}$$

In terms of these definitions *the partial pressure of any component in a gas mixture is equal to the mol fraction of that component multiplied by the total pressure.* This is true only when the ideal gas law applies to each constituent of the gas mixture.

AMAGAT'S LAW OF PARTIAL VOLUMES

A law similar to Dalton's is *Amagat's law of partial volumes.* This law states that *in any gas mixture the total volume may be considered to be the sum of the partial volumes of the constituents of the mixture,* i.e.,

$$V = V_1 + V_2 + V_3 + \cdots \tag{15}$$

where V is the total volume while V_1, V_2, etc., are the partial volumes. By the partial volume of a constituent is meant the volume which that constituent would occupy if present alone at the given temperature and at the *total pressure* of the mixture. By an argument similar to the one employed for partial pressures it is readily shown that, if the ideal gas laws are again applicable, then

$$V_1 = N_1 V, \qquad V_2 = N_2 V, \text{ etc.} \tag{16}$$

where V_1, V_2, etc., are the partial volumes, N_1, N_2, etc., the mol fractions, and V the total volume at any pressure and temperature.

Dalton's and Amagat's laws are equivalent and hold equally well with gases that approximate ideal behavior, i.e., with gases that are not too close to their condensation temperatures or at too elevated pressures. At high pressures and near their condensation temperatures gases begin to exhibit considerable intermolecular attractions and effects which are no longer general but are specific to the composition and nature of the substances. Under such conditions deviations appear not only from Eqs. (13) and (16), but also from Eqs. (10) and (15). In general, the law of partial volumes holds somewhat better than the law of partial pressures at high pressures and low temperatures.

GRAHAM'S LAW OF DIFFUSION

Different gases diffuse through a tube or escape from a container having a fine opening at different rates dependent on the densities or molecular weights of the gases. The law governing such diffusions was first enunciated by Graham in 1829 and bears his name. This law states that *at constant temperature and pressure the rates of diffusion of various gases vary inversely as the square roots of their densities or molecular weights.* Thus, if we let u_1 and u_2 be the rates of diffusion of two gases, and ρ_1 and ρ_2 be their respective densities, then

$$\frac{u_1}{u_2} = \frac{\sqrt{\rho_2}}{\sqrt{\rho_1}} \tag{17}$$

Again, since at the same pressure and temperature both gases must have the same molar volume V_m, we have also that

$$\frac{u_1}{u_2} = \frac{\sqrt{\rho_2 V_m}}{\sqrt{\rho_1 V_m}} = \frac{\sqrt{M_2}}{\sqrt{M_1}} \tag{18}$$

where M_1 and M_2 are the molecular weights of the two gases.

THE KINETIC THEORY OF IDEAL GASES

All the principles of gas behavior which have been discussed so far have been arrived at by experiment. The *kinetic theory of gases*, on the other hand, attempts to elucidate the behavior of gases by theoretical means in terms of a postulated "picture" of a gas and certain assumptions regarding its behavior. The theory was first proposed by Bernoulli in 1738, and was considerably elaborated and extended by Clausius, Maxwell, Boltzmann, van der Waals, and Jeans.

The kinetic theory is based on the following fundamental postulates:

1. Gases are considered to be composed of minute discrete particles called *molecules*. For any one gas all molecules are thought to be of the same mass and size but to differ in these from gas to gas.
2. The molecules within a container are believed to be in ceaseless chaotic motion during which they collide with each other and with the walls of the container.
3. The bombardment of the container walls by the molecules gives rise to the phenomenon we call *pressure*, i.e., the force exerted on the walls per unit area is the average force per unit area which the molecules exert in their collisions with the walls.
4. Inasmuch as the pressure of a gas within a container does not vary with time at any given pressure and temperature, the molecular collisions must involve no energy loss due to friction. In other words, all molecular collisions are elastic.
5. The absolute temperature is a quantity proportional to the *average* kinetic energy of all the molecules in a system.
6. At relatively low pressures the average distances between molecules are large compared with molecular diameters, and hence the attractive forces between molecules, which depend on the distance of molecular separation, may be considered negligible.
7. Finally, since the molecules are small compared with the distances between them, their volume may be considered to be negligible compared with the total volume of the gas.

Postulates 6 and 7, by ignoring the size of the molecules and the interactions between them, limit the theoretical treatment to ideal gases.

A mathematical analysis of this concept of a gas leads to fundamental conclusions that are directly verifiable by experiment. Consider a cubical container filled with n' molecules of gas, all the same, and all with molecular mass m and velocity u. This velocity u may be resolved into its three components along the x, y, and z axes, as is shown in Figure 1–3. If we

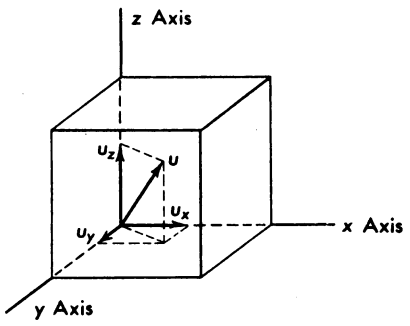

Figure 1–3. Resolution of velocity along x, y, and z axes.

designate these velocity components by u_x, u_y, u_z, then

$$u^2 = u_x^2 + u_y^2 + u_z^2 \tag{19}$$

where u is called the *root-mean-square velocity*. Each of these components may now be treated as though a single molecule of mass m were to move independently with each of the component velocities in the appropriate directions x, y, or z. The total effect of these independent motions is obtained by combining the velocities according to Eq. (19).

Suppose now that the molecule of mass m is moving in the x direction to the right with velocity u_x. It will strike the yz plane with a momentum mu_x, and, since the collision is elastic, it will rebound with velocity $-u_x$ and momentum $-mu_x$. Consequently the *change in momentum* per molecule per single collision in the x direction is $mu_x - (-mu_x) = 2\,mu_x$. Before the molecule can strike the same wall again it must travel to the opposite wall, collide with it, rebound, and return. To do this it must cover the distance $2\,l$, where l is the length of the cube edge. Hence the number of collisions with the right-hand wall which the molecule will experience per second will be $u_x/2\,l$, and thereby the change in momentum per second for the one molecule on the given wall will be

$$(2\,mu_x)\frac{u_x}{2l} = \frac{mu_x^2}{l} \tag{20}$$

But the same change in momentum will be experienced also by the same molecule at the other yz plane, so that the total change in momentum per molecule per second in the x direction is twice the quantity in Eq. (20), or

$$\text{Change in momentum/second/molecule in } x \text{ direction} = 2\frac{mu_x^2}{l} \tag{21}$$

A moment's reflection will show that analogous changes in momentum take place in the y and z directions, and that these are given by $2\,mu_y^2/l$ and $2\,mu_z^2/l$ per molecule per second. From these the

$$\begin{aligned}\text{Total change in momentum/molecule/second} &= \frac{2\,mu_x^2}{l} + \frac{2\,mu_y^2}{l} + \frac{2\,mu_z^2}{l} \\ &= \frac{2\,m}{l}(u_x^2 + u_y^2 + u_z^2) \\ &= \frac{2\,m}{l}u^2 \end{aligned} \tag{22}$$

by Eq. (19). As there are n' molecules in the cube, the change in momentum per second for all of them will be Eq. (22) multiplied by n', or

$$\text{Total change in momentum per second} = \frac{2\,n'mu^2}{l} \tag{23}$$

However, the rate of change of momentum is the acting force, f. Again, pressure is the force per unit area. Consequently,

$$P = \frac{f}{A} = \frac{2\,mn'u^2}{lA} \tag{24}$$

where P is the pressure while A is the total area over which the force is applied. For the cube in question $A = 6\,l^2$, and hence

$$P = \frac{mn'u^2}{3\,l^3} \tag{25}$$

But l^3 is the volume V of the cube, and so

$$P = \frac{mn'u^2}{3\,V}$$

or

$$PV = \frac{1}{3}\,mn'u^2 \tag{26}$$

According to Eq. (26) the product PV for any gas should equal one-third the mass of all the molecules (mn') multiplied by the square of the root-mean-square velocity. Although this equation was derived on the assumption of a cubical vessel, it can be shown that the same result is obtained no matter what shape of vessel is considered, and consequently the above deduction must be perfectly general.

DEDUCTIONS FROM KINETIC THEORY OF GASES

Boyle's Law. We have seen that one of the fundamental postulates of the kinetic theory is the direct proportionality between the kinetic energy of the molecules, i.e., $\frac{1}{2}\,mn'u^2$, and the absolute temperature, namely, that

$$\frac{1}{2}\,mn'u^2 = k_1T \tag{27}$$

where k_1 is a proportionality constant. If now Eq. (26) is multiplied and divided by 2, we have

$$PV = \frac{2}{3}\left(\frac{1}{2}\,mn'u^2\right)$$

and hence, on insertion of Eq. (27),

$$PV = \frac{2}{3}\,k_1T \tag{28}$$

At constant temperature Eq. (28) becomes thus PV = constant, which is Boyle's law.

Charles's Law. This law holds at constant pressure. If this condition is imposed on Eq. (28), we get

$$V = \left(\frac{2\,k_1}{3\,P}\right) T$$
$$= K_2 T \tag{29}$$

which is a statement of Charles's law.

Avogadro's Principle. In 1811 Avogadro enunciated the principle that *equal volumes of all gases at the same pressure and temperature contain equal numbers of molecules.* This principle is readily deducible from the kinetic theory of gases. Since the volumes and pressures are equal, $P_1V_1 = P_2V_2$ for two different gases, and hence it follows from Eq. (26) that

$$\frac{1}{3} n_1' m_1 u_1^2 = \frac{1}{3} n_2' m_2 u_2^2$$

Again, as the temperature is also constant, the average kinetic energy per molecule must be the same, or

$$\frac{1}{2} m_1 u_1^2 = \frac{1}{2} m_2 u_2^2$$

Inserting the latter relation into the preceding, we see that

$$n_1' = n_2' \tag{30}$$

which is a statement of Avogadro's principle.

The actual number of molecules in a gram-mole of any gas is an important physical constant known as *Avogadro's number*, symbol N. This constant may be arrived at by a number of methods. The best present value for this quantity is 6.0229×10^{23} molecules per gram-mole. Once this constant is available, the mass of any particular molecule can readily be computed by merely dividing the molecular weight of the substance by Avogadro's number. Thus, since the molecular weight of oxygen is 32.00, the mass of an individual molecule must be

$$m_{O_2} = \frac{32.00}{6.023 \times 10^{23}} = 5.31 \times 10^{-23} \text{ g/molecule}$$

Graham's Law of Diffusion. Graham's law also follows readily from the kinetic theory of gases. Since at constant volume and pressure for two different gases

$$\frac{1}{3} n_1' m_1 u_1^2 = \frac{1}{3} n_2' m_2 u_2^2$$

then

$$\frac{u_1^2}{u_2^2} = \frac{m_2 n_2'}{m_1 n_1'}$$

and

$$\frac{u_1}{u_2} = \sqrt{\frac{m_2 n_2'}{m_1 n_1'}} \tag{31}$$

Further, if $n_2' = n_1' = N$, then

$$\frac{u_1}{u_2} = \sqrt{\frac{m_2 N}{m_1 N}} = \sqrt{\frac{M_2}{M_1}} \tag{32}$$

Again, since at constant temperature and pressure the molar volumes are identical, we have also

$$\frac{u_1}{u_2} = \sqrt{\frac{\rho_2}{\rho_1}} \tag{33}$$

where ρ_2 and ρ_1 are the densities of the two gases. Equations (32) and (33) are identical with (17) and (18), and are, of course, statements of Graham's law.

All these deductions point to the fact that the theoretical relation $PV = \frac{1}{3} n'mu^2$ is in agreement with the empirical ideal gas law $PV = nRT$. Consequently we may write without further hesitation that

$$PV = \frac{1}{3} n'mu^2 = nRT$$

and, since $n' = nN$,

$$PV = \frac{1}{3} n(Nm)u^2 = nRT$$

$$= \frac{nMu^2}{3} = nRT \tag{34}$$

where $M = Nm$ is the molecular weight of the gas in question, and n is the number of *moles* of gas in the volume V at pressure P and temperature T.

FURTHER DEDUCTIONS FROM THE KINETIC THEORY

The value of any theory lies not only in its ability to account for known experimental facts but also in its suggestiveness of new modes of attack. In this respect the kinetic theory of gases has been very fruitful. We have seen that Eq. (26), a direct consequence and expression of the theory, gives all the laws of ideal gas behavior. At the same time, however, many other highly important relations can be deduced from it, some of which are outlined in the following.

The Velocity of Gas Molecules. According to the kinetic theory all molecules at the same temperature must have the same average kinetic energy, i.e.,

$$\frac{1}{2} m_1 u_1^2 = \frac{1}{2} m_2 u_2^2 = \frac{1}{2} m_3 u_3^2, \text{ etc.}$$

It follows, therefore, that the higher the mass of a molecule, the more

slowly must it be moving. It is of considerable interest to ascertain the actual velocity with which various molecules move. From Eq. (34) we have that

$$\frac{1}{3}nMu^2 = nRT$$

and hence

$$u = \sqrt{\frac{3RT}{M}} \tag{35a}$$

Again, since $RT = PV/n$, and $nM/V = \rho$, the density of the gas in question at temperature T and pressure P, Eq. (35a) may be written also as

$$u = \sqrt{\frac{3P}{\rho}} \tag{35b}$$

By either of these equations the root-mean-square velocity of a gas may be calculated from directly measurable quantities. In doing this, if R is expressed in ergs per degree per mole, P in dynes per square centimeter, and the density in grams per cubic centimeter, then u will be given in centimeters per second.

To calculate the velocity of hydrogen molecules at 0°C we know that $R = 8.314 \times 10^7$ ergs per mole per degree, $T = 273.15$°K, and $M = 2.016$. Hence Eq. (35a) yields for u

$$\begin{aligned} u &= \sqrt{\frac{3RT}{M}} \\ &= \sqrt{\frac{3 \times 8.314 \times 10^7 \times 273.15}{2.016}} \\ &= 184{,}000 \text{ cm/sec} \\ &= 68 \text{ miles/min} \end{aligned}$$

Since hydrogen is the lightest of all elements, this tremendously high velocity represents an upper limit for rates of molecular motion. For all other molecules the speeds will be lower in accordance with Graham's law. Thus for sulfur dioxide, with $M = 64$, the velocity at 0°C would be

$$\begin{aligned} \frac{u_{SO_2}}{68} &= \sqrt{\frac{2}{64}} \\ u_{SO_2} &= 12 \text{ miles/min} \end{aligned}$$

The Kinetic Energy of Translation. The only type of energy we have ascribed thus far to gas molecules is that due to molecular motion along three coordinate axes, i.e., *kinetic energy of translation*. The amount of this energy is again deducible from Eq. (34). Since from this equation $nRT = nMu^2/3$, and since the kinetic energy, E_k, is given by

$E_k = nMu^2/2$, then for n moles of gas

$$E_k = \frac{3}{2}\left(\frac{1}{3}nMu^2\right)$$
$$= \frac{3}{2}nRT \tag{36a}$$

and per mole

$$E_k = \frac{3}{2}RT \tag{36b}$$

Consequently, the translational energy of an ideal gas is completely independent of the nature or pressure of the gas, and depends only on the absolute temperature. At, say, 300°K all ideal gases will thus contain per mole

$$E_k = \frac{3}{2}R(300)$$
$$= 450\,R$$
$$= 895 \text{ cal}$$

or approximately 900 cal of translational kinetic energy.

The average kinetic energy per molecule follows from Eq. (36b) on division by Avogadro's number, N, namely,

$$\frac{E_k}{N} = \frac{3}{2}\frac{RT}{N} = \frac{3}{2}kT \tag{37}$$

where $k = R/N$ is called the *Boltzmann constant*, and is equal to 1.3805×10^{-16} erg per degree.

Distribution of Molecular Velocities. For convenience of treatment all molecules in a given gas and at a given temperature were considered to be composed of molecules moving with a constant root-mean-square velocity u. Actually, however, all molecules do not possess the same velocity, for as a result of collisions a redistribution of both energy and velocity takes place. Maxwell and Boltzmann, utilizing probability considerations, have in fact shown that the actual distribution of molecular velocities depends on the temperature and molecular weight of a gas, and is given by

$$\frac{dn_c}{n'} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} e^{-\frac{Mc^2}{2RT}}c^2dc \tag{38}$$

In this equation dn_c is the number of molecules out of a total n' having velocities between c and $c + dc$, while M and T are, respectively, the molecular weight and temperature of the gas. Obviously dn_c/n' is the fraction of the total number of molecules having velocities between c and $c + dc$. Equation (38) is known as the *Maxwell–Boltzmann distribution*

law for molecular velocities. If Eq. (38) is divided by dc, we get

$$p = \frac{1}{n'}\frac{dn_c}{dc} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} e^{-\frac{Mc^2}{2RT}}c^2 \qquad (38a)$$

where p may be taken as the probability of finding molecules with the velocity c.

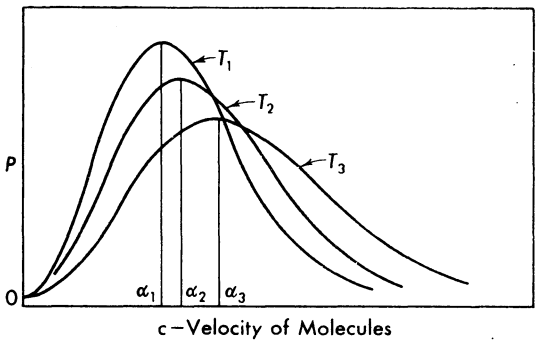

Figure 1–4. Distribution of molecular velocities in a gas.

Figure 1–4 shows schematic plots of p vs. c for several temperatures which increase in the order T_1, T_2, T_3. From these plots it may be seen that the probability of a molecule being motionless at any instant is very small. Further, for incidence of velocities greater than zero the probability increases with c, passes through a maximum, and then falls away more or less rapidly toward zero again for very high rates of motion. It is evident, therefore, that both very low and very high speeds are highly improbable, and that most of the molecules in a gas have velocities grouped about the *most probable velocity* corresponding to the peak of the curve at each temperature. The most probable velocity is in any gas not a constant, but shifts toward higher values of c with increase in temperature; i.e., at higher temperatures higher velocities are more probable than at low.

Mathematical analysis shows that the most probable velocity, α, is not equal either to the root-mean-square velocity u or the average velocity of all the molecules v. If we designate by c_1, c_2, c_3, $\cdots$ c_n the individual velocities of n' molecules in a gas, then the average velocity v is defined as

$$v = \frac{c_1 + c_2 + c_3 + \cdots c_n}{n'} \qquad (39)$$

and the root-mean-square velocity as

$$u = \sqrt{\frac{c_1^2 + c_2^2 + c_3^2 + \cdots c_n^2}{n'}} \qquad (40)$$

Kinetic theory arguments reveal that these various velocities are related by the equations

$$v = 0.921\,u \tag{41}$$

$$\alpha = \sqrt{\frac{2}{3}}u \tag{42}$$

and hence, on substitution of the value of u from Eq. (35a), we have

$$u = \sqrt{\frac{3\,RT}{M}} \tag{35a}$$

$$v = 0.921\sqrt{\frac{3\,RT}{M}} \tag{43}$$

$$\alpha = \sqrt{\frac{2\,RT}{M}} \tag{44}$$

or $$\alpha : v : u = 1 : 1.128 : 1.224$$

Since for any specific velocity c the kinetic energy of a gas per mole is $E = Mc^2/2$, we may substitute this relation into Eq. (38) to obtain the distribution of kinetic energies in a gas. The result is

$$\frac{dn_c}{n'} = \frac{2\,\pi}{(\pi RT)^{3/2}}\,e^{-\frac{E}{RT}}E^{1/2}dE \tag{45}$$

where now dn_c/n' is the fraction of the total number of molecules having kinetic energies between E and $E + dE$. Again, division of Eq. (45) by dE yields

$$p' = \frac{1}{n'}\frac{dn_c}{dE} = \frac{2\pi}{(\pi RT)^{3/2}}\,e^{-\frac{E}{RT}}E^{1/2} \tag{45a}$$

where p' is the probability for incidence of kinetic energies of translation of magnitude E. The plots of p' vs. E obtained from Eq. (45a) are very similar to those shown in Figure 4.

Frequency of Collisions and Mean Free Path. It can be shown that in a gas containing n^* identical molecules per cubic centimeter, the number of molecules with which a *single* gas molecule will collide per second is

$$\sqrt{2}\,\pi v\sigma^2 n^*$$

where v is the average molecular velocity in centimeters per second and σ the molecular diameter in centimeters. Hence the total number of colliding molecules per cubic centimeter per second, Z, must be n^* times this quantity, or

$$Z = \sqrt{2}\,\pi v\sigma^2(n^*)^2 \tag{46}$$

Further, since each collision involves two molecules, the number of molecular collisions occurring in each cubic centimeter per second, N_c,

will be one-half this number, namely,

$$N_c = \frac{Z}{2} = \frac{1}{\sqrt{2}} \pi v \sigma^2 (n^*)^2 \tag{47}$$

Another important quantity in kinetic theory considerations is the average distance a molecule traverses before colliding, or the *mean free path*, l. If a molecule has an average velocity v cm per sec, and if within this period it experiences, as we have seen, $\sqrt{2}\,\pi v \sigma^2 n^*$ collisions, then the average distance between collisions, or mean free path, must be

$$l = \frac{v}{\sqrt{2}\,\pi v \sigma^2 n^*} = \frac{1}{\sqrt{2}\,\pi \sigma^2 n^*} \tag{48}$$

The quantities N_c, Z, and l are readily calculable as soon as the molecular diameters σ are available. These are usually obtained from gas viscosity measurements in a manner to be discussed toward the end of the chapter.

APPLICABILITY OF THE IDEAL GAS LAWS

The concordance between the empirical generalizations embodied in the expression $PV = nRT$ and the deductions of the kinetic theory of gases lends considerable credence to our conception of the nature of gases and their behavior. However, there still remains the question of how completely and accurately can the expression $PV = nRT$ reproduce the actual P–V–T relations of gases. To test this point we may resort to the fact that at constant temperature the combined gas law reduces to $PV = nRT =$ constant. Hence, as long as T does not vary, the product PV for a given quantity of gas should remain the same at all pressures. A plot of PV vs. P at constant T should yield, therefore, a straight line parallel to the abscissa.

Such a plot of PV vs. P constructed from actual data for several gases at 0°C is shown in Figure 1–5. The fact immediately apparent is that PV is not constant over most of the pressure range shown. The curves are in general of two types. One, including only hydrogen and helium here, starts at the value of PV demanded by $PV = nRT$ for the temperature in question and increases continually with pressure. In every case the product PV is greater than demanded by theory. On the other hand, in the second type the plot starts again at the same point as before, but now the product PV decreases at first with pressure, passes through a

minimum characteristic of each gas and the temperature, and then increases to values which may rise appreciably above the theoretical.

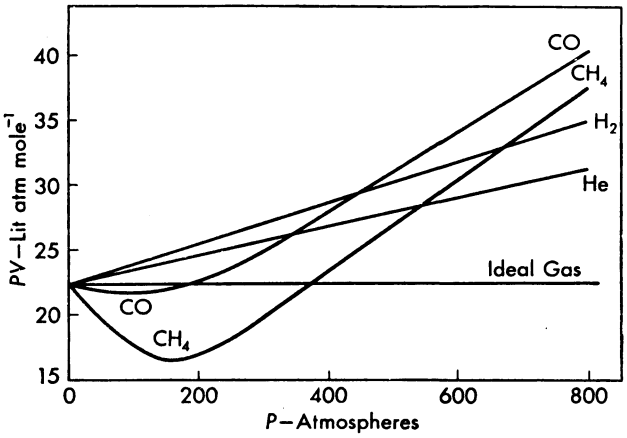

Figure 1–5. PV vs. P plot for several gases at 0°C.

Actually, both types of curves are part of a single pattern of behavior exhibited by all gases. To show this, it is convenient to employ a quantity z, called the *compressibility factor*, which is defined as

$$z = \frac{PV}{nRT} \tag{49}$$

For an ideal gas $z = 1$ at all temperatures and pressures. In the case of actual gases the compressibility factor may vary with both of these variables, and hence its deviation from a value of unity is an index of deviation from ideal behavior.

From the experimental P–V–T data for a gas z may be calculated by means of Eq. (49), and its variation with temperature and pressure observed. Figure 1–6 shows a plot of z vs. P for nitrogen at various constant temperatures. Inspection of this plot reveals that all the isotherms start with $z = 1$ at $P = 0$, and change with pressure in a manner dependent on the temperature. However, there is one temperature, in this case 51°C, at which z remains close to unity over an appreciable pressure range. In fact, between $P = 0$ and $P = 100$ atm z changes only from 1.00 to 1.02. Beyond 100 atm z rises quite rapidly with increasing pressure and attains values considerably above $z = 1$. This temperature at which a real gas obeys the ideal gas law over an appreciable pressure range is called the *Boyle temperature* or *Boyle point.* The Boyle temperature is also a dividing line in the types of isotherms exhibited by the gas. Above the Boyle point the gas shows only positive deviations from ideality, and hence all values

of z are greater than unity. Below the Boyle temperature, however, the values of z first decrease with increasing pressure, go through a minimum, and then increase to values which may climb appreciably above $z = 1$. It should also be observed that the lower the temperature the lower the minima, and that they occur at pressures which vary with the temperature.

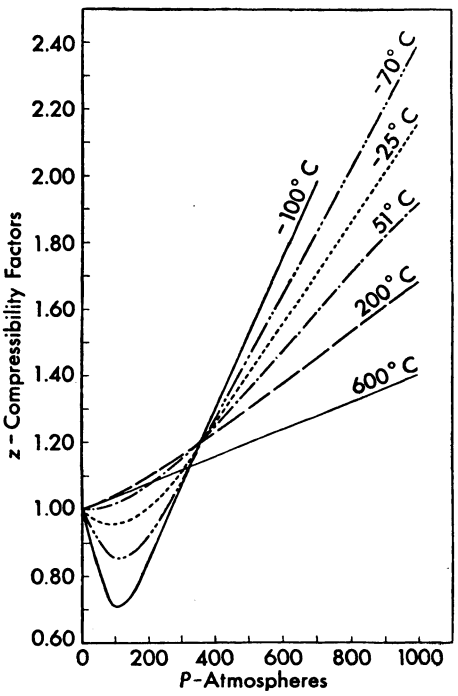

Figure 1–6. Compressibility factors for nitrogen.

The plots shown in Figure 1–6 are typical of the P–V–T behavior of *all* gases when data covering wide ranges of pressure and temperature are considered. The only differences observed are in the Boyle temperatures and in the positions of the isotherms on the plots, since these are dependent in each instance on the gas in question. Nevertheless, it is always found that above the Boyle temperature only positive deviations from ideality are observed. Below the Boyle temperature, on the other hand, increase of pressure causes the z values first to decrease below $z = 1$, to go through a minimum, and then to increase to values which eventually go appreciably above $z = 1$.

In terms of the above discussion a glance at Figure 1–5 should suffice to indicate that at 0°C hydrogen and helium are already above their Boyle

temperatures, whereas carbon monoxide and methane are still below theirs. It is also to be expected that at sufficiently low temperatures hydrogen and helium should exhibit minima in their z vs. P plots, while at higher temperatures carbon monoxide and methane should show plots similar to those of hydrogen and helium at 0°C. Such is actually the case, as may be seen from the compressibility factor plot for methane given in Figure 1–7.

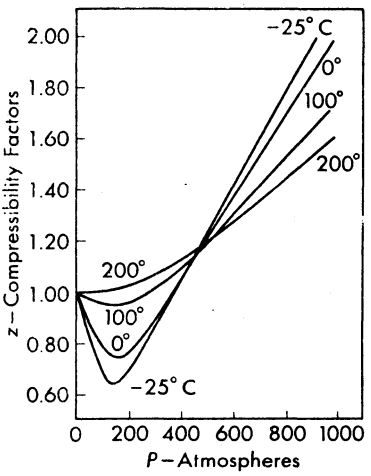

Figure 1–7. Compressibility factors for methane.

The highly individualistic behavior exhibited by various gases indicates that in order to represent their P–V–T relations equations of state, i.e., equations involving P, V, and T, would be required which would contain not only these variables but also terms making allowance for the specific forces operative in each gas. However, P–V–T studies on gases at low pressures do show that when the pressures are lowered gases begin to approximate more closely the ideal gas law, and, furthermore, the lower the pressure the better is the agreement between the observed PV product and that calculated from the combined gas law. At these low pressures all gases lose their individualistic behavior and merge to obey the simple and general expression obtained from the kinetic theory of gases. For this reason the expression $PV = nRT$ is considered to be a *limiting law* only, a law which gases obey strictly only when they are diluted highly enough so that the volume of the molecules themselves is negligible compared with the total volume, and the intermolecular attractive forces are too feeble to exercise any influence on the pressure of the gas. It may be concluded, therefore, that a gas becomes more ideal as the pressure is lowered and will become completely ideal as the pressure approaches zero. This conclusion is confirmed by the fact that, as P

approaches zero, the compressibility factors at all temperatures go to $z = 1$.

How far this concordance between the ideal gas law and observation will extend into the range of higher pressures depends on the nature of the gas and the temperature. For gases which are permanent at ordinary temperatures, i.e., which are above their critical temperatures,[2] such as hydrogen, nitrogen, oxygen, and helium, this concordance may extend within 5 per cent or so up to pressures as high as 50 atm. On the other hand, with easily condensible gases, such as carbon dioxide, sulfur dioxide, chlorine, and methyl chloride, discrepancies as large as 2 or 3 per cent may appear at 1 atm pressure. The use of the ideal gas law for such gases is considerably limited, therefore, when fairly precise calculations are required. In any case, before using the ideal gas law at any appreciable pressure it is always advisable to consider the nature of the gas in question and how far it is above its critical temperature. The greater this distance, the wider in general will be the pressure range over which calculations can be made within a given accuracy.

USE OF COMPRESSIBILITY FACTORS

When the compressibility factors of a gas are known under various conditions, they may be employed quite readily for making exact gas calculations. For instance, suppose that the volume of 10 moles of methane is required at 100 atm pressure and 0°C. At this pressure and temperature $z = 0.783$, and hence, according to Eq. (49),

$$\begin{aligned} V &= \frac{znRT}{P} \\ &= \frac{0.783 \times 10 \times 0.08205 \times 273.2}{100} \\ &= 1.754 \text{ liters} \end{aligned}$$

The experimentally observed volume is 1.756 liters. Again, suppose that a certain quantity of methane occupies a volume of 0.138 liter under a pressure of 300 atm at 200°C, and the volume is required at 600 atm at 0°C. For 300 atm at 200°C, $z_2 = 1.067$, while for 600 atm at 0°C, $z_1 = 1.367$. Since for the lower temperature we have $P_1V_1 = z_1nRT_1$ while for the higher one $P_2V_2 = z_2nRT_2$, then

$$\frac{P_1V_1}{P_2V_2} = \frac{z_1nRT_1}{z_2nRT_2} = \frac{z_1T_1}{z_2T_2} \tag{50}$$

[2] The critical temperature is the highest temperature at which a gas may be liquefied.

and hence on substitution of the given values we get

$$V_1 = \left(\frac{z_1 T_1}{z_2 T_2}\right)\left(\frac{P_2 V_2}{P_1}\right)$$
$$= \left(\frac{1.367 \times 273.2}{1.067 \times 473.2}\right)\left(\frac{300 \times 0.138}{600}\right)$$
$$= 0.051 \text{ liter}$$

THE VAN DER WAALS EQUATION OF STATE

Because of the deviation of real gases from the ideal gas law, many attempts have been made to set up equations of state which will reproduce more satisfactorily the P–V–T relations of gases. Of these equations one of the earliest and best known is that of van der Waals.

The van der Waals equation differs from the ideal gas law in that it makes allowance both for the volume occupied by the molecules themselves and for the attractive forces between them. To make correction for the finite dimensions of the molecules, let b be the effective volume of the molecules in *one* mole of gas and V be the total volume of n moles of gas. In this total volume, that occupied by the molecules themselves thus will be nb, and hence the volume available for compression will be not V but $(V - nb)$. Since the latter is the "free space," it should be substituted for V in the ideal gas law. It may be anticipated that b will be characteristic and different for each gas.

The second factor for cognizance is the attractive force operative between molecules. Consider the wall of a container which is being bombarded by gaseous molecules. When the gas molecules are not constrained by attractions for each other, they will bombard the wall with the full force due to their outward motion. If, however, under the same conditions a molecule moving outward is subjected by molecular attraction to an inward "pull," it will not strike the wall with as high a force as if it were not "dragged back" by the other molecules within the gas. Consequently, the pressure resulting from the bombardment will be lessened by an amount P'. The observed pressure, P, will thus be less than the ideal pressure, P_i, by the amount P', or

$$P = P_i - P'$$

Since in the expression $P_i V = nRT$ the pressure P_i refers to the ideal pressure, we must substitute for it its value from the expression given above, or $P_i = (P + P')$. If we combine this corrected pressure with the expression for the corrected volume we obtain

$$(P + P')(V - nb) = nRT \qquad \textbf{(51)}$$

van der Waals indicated that the magnitude of the pressure correction P' for n moles of gas present in volume V is given by

$$P' = \frac{n^2a}{V^2}$$

where a is a constant characteristic of each gas and independent of pressure and temperature. It is for each gas a measure of the magnitude of the intermolecular attractive forces within the gas. If this expression for P' is substituted in Eq. (51), we get

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT \tag{52}$$

This is the celebrated equation of state which was first developed by van der Waals in 1873 and which bears his name.

In applying van der Waals' equation care must be exercised in the choice of appropriate units for the constants a and b. Since n^2a/V^2 represents a pressure, the units of a must be pressure $\times$ (volume)^2/(mole)^2, i.e., atm-liter^2 mole^{-2}, or atm-cc^2 mole^{-2}. In any event, the units used must be the same as those of P and V, and this applies also to R. In turn, b is a volume and must correspond to the units of V.

The use of the equation can be illustrated with an example. Suppose it is desired to calculate by van der Waals' equation the pressure at which 2 moles of ammonia will occupy a volume of 5 liters at 27°C. For ammonia, $a = 4.17$ atm-liter^2 mole^{-2}, while $b = 0.0371$ liter per mole. Hence,

$$\begin{aligned} P &= \frac{nRT}{V - nb} - \frac{n^2a}{V^2} \\ &= \frac{2(0.0821)300.2}{5 - 2(0.0371)} - \frac{(2)^2 \times 4.17}{(5)^2} \\ &= 9.33 \text{ atm} \end{aligned}$$

The corresponding pressure calculated from the ideal gas law is 9.86 atm.

Table 1–2 lists the van der Waals constants for a number of gases. Such gases as carbon disulfide, ammonia, sulfur dioxide, chloroform, etc., which are easily condensible, have relatively high values of a, indicating strong intermolecular attractions. On the other hand, for the permanent gases such as argon, carbon monoxide, helium, and hydrogen, the a values are considerably lower, and hence in these the intermolecular forces are considerably weaker.

The van der Waals equation is much more accurate than the ideal gas law and is valid over a much wider pressure range, as may be seen from Table 1–3. However, under extreme conditions, such as temperatures near the critical and at very high pressures, its predictions deviate considerably in many instances from experimentally observed values. It is very doubtful whether it is justifiable to consider a and b as constants

TABLE 1–2. VAN DER WAALS CONSTANTS FOR VARIOUS GASES
(a in atm-liter^2 mole^{-2}; b in liter mole^{-1})

Gas	Formula	a	b
Ammonia	NH_3	4.17	0.0371
Argon	Ar	1.35	0.0322
Carbon dioxide	CO_2	3.59	0.0427
Carbon disulfide	CS_2	11.62	0.0769
Carbon monoxide	CO	1.49	0.0399
Carbon tetrachloride	CCl_4	20.39	0.1383
Chlorine	Cl_2	6.49	0.0562
Chloroform	$CHCl_3$	15.17	0.1022
Ethane	C_2H_6	5.49	0.0638
Ethylene	C_2H_4	4.47	0.0571
Helium	He	0.034	0.0237
Hydrogen	H_2	0.244	0.0266
Hydrogen bromide	HBr	4.45	0.0443
Methane	CH_4	2.25	0.0428
Neon	Ne	0.211	0.0171
Nitric oxide	NO	1.34	0.0279
Nitrogen	N_2	1.39	0.0391
Oxygen	O_2	1.36	0.0318
Sulfur dioxide	SO_2	6.71	0.0564
Water	H_2O	5.46	0.0305

TABLE 1–3. COMPARISON OF IDEAL GAS LAW AND VAN DER WAALS' EQUATION AT 100°C

	Hydrogen				Carbon Dioxide			
Observed P (atm)	P Calc. Ideal	% Deviation	P Calc. van der Waals	% Deviation	P Calc. Ideal	% Deviation	P Calc. van der Waals	% Deviation
50	48.7	−2.6	50.2	+0.4	57.0	+14.0	49.5	−1.0
75	72.3	−3.6	75.7	+0.9	92.3	+17.3	73.3	−2.3
100	95.0	−5.0	100.8	+0.8	133.5	+33.5	95.8	−4.2

independent of pressure and temperature. In fact, in order to fit the equation to experimental data with a relatively high order of fidelity, it is necessary to choose different values of a and b over different ranges of pressure and temperature.

OTHER EQUATIONS OF STATE

A large number of other equations of state have been proposed to represent the P–V–T relations of gases. Some of these are based to some extent

on theoretical considerations, while other are entirely empirical. We shall consider now several of the more important of these equations.

The Kamerlingh Onnes Equation of State. This empirical equation expresses PV as a power series of the pressure at any given temperature, namely,

$$PV_m = A + BP + CP^2 + DP^3 + \cdots \tag{53}$$

P is the pressure, generally in atmospheres, and V_m is the *molar* volume in liters or cubic centimeters. The coefficients A, B, C, etc., are known respectively as the first, second, third, etc., *virial coefficients.* At very low pressures only the first of these coefficients is significant, and it is equal to RT. At higher pressures, however, the others as well are important and must be considered. In general the order of significance of the coefficients is their order in the equation. These coefficients, although constant at any given temperature, change in value as the temperature is changed. Of necessity the first virial coefficient A is always positive and increases with temperature. The second coefficient, on the other hand, is negative at low temperatures, passes through zero, and becomes increasingly positive as the temperature is raised. The temperature at which $B = 0$ is the *Boyle temperature,* for at this temperature Boyle's law is valid over a fairly wide pressure range.

By using a sufficient number of terms this equation can be fitted to experimental data with a high order of accuracy. The virial coefficients for several gases are shown in Table 1–4. With these it is possible to calculate PV up to 1000 atm.

TABLE 1–4. VIRIAL COEFFICIENTS OF SOME GASES
(P in atm, V_m in liters mole^{-1})

t°C	A	$B \times 10^2$	$C \times 10^5$	$D \times 10^8$	$E \times 10^{11}$
			Nitrogen		
−50	18.312	−2.8790	14.980	−14.470	4.657
0	22.414	−1.0512	8.626	−6.910	1.704
100	30.619	0.6662	4.411	−3.534	0.9687
200	38.824	1.4763	2.775	−2.379	0.7600
			Carbon Monoxide		
−50	18.312	−3.6878	17.900	−17.911	6.225
0	22.414	−1.4825	9.823	−7.721	1.947
100	30.619	0.4036	4.874	−3.618	0.9235
200	38.824	1.3163	3.052	−2.449	0.7266
			Hydrogen		
−50	18.312	1.2027	1.164	−1.741	1.022
0	22.414	1.3638	0.7851	−1.206	0.7354
500	63.447	1.7974	0.1003	−0.1619	0.1050

The Berthelot Equation. The high-pressure form of this equation is rather difficult to handle. For low pressures the equation reduces to

$$PV = nRT\left[1 + \frac{9\,PT_c}{128\,P_cT}\left(1 - \frac{6\,T_c^2}{T^2}\right)\right] \tag{54}$$

where P, V, R, T, and n have the same meaning as in the ideal gas law, while P_c and T_c are the critical pressure and critical temperature respectively.[3] For pressures of about an atmosphere and below this equation is very accurate, and it is consequently very useful in calculating the molecular weights of gases from their densities. Its use will be illustrated in that connection.

TABLE 1–5. BEATTIE-BRIDGEMAN CONSTANTS FOR SOME GASES*
(For P in atm, V in liters mole^{-1})

Gas	A_0	a	B_0	b	c
He	0.0216	0.05984	0.01400	0	0.004×10^4
Ne	0.2125	0.2196	0.02060	0	0.101×10^4
Ar	1.2907	0.02328	0.03931	0	5.99×10^4
H_2	0.1975	−0.00506	0.02096	−0.04359	0.050×10^4
N_2	1.3445	0.02617	0.05046	−0.00691	4.20×10^4
O_2	1.4911	0.02562	0.04624	0.004208	4.80×10^4
Air	1.3012	0.01931	0.04611	−0.01101	4.34×10^4
CO_2	5.0065	0.07132	0.10476	0.07235	66.00×10^4
CH_4	2.2769	0.01855	0.05587	−0.01587	12.83×10^4
$(C_2H_5)_2O$	31.278	0.12426	0.45446	0.11954	33.33×10^4

* *J. Am. Chem. Soc.*, **50**, 3136 (1928). See also Maron and Turnbull, *Ind. Eng. Chem.*, **33**, 408 (1941).

The Beattie-Bridgeman Equation of State. This equation of state involving five constants may be stated in two forms, one explicit in pressure, the other in molar volume V_m, namely,

$$P = \frac{RT}{V_m} + \frac{\beta}{V_m^2} + \frac{\gamma}{V_m^3} + \frac{\delta}{V_m^4} \tag{55}$$

$$V_m = \frac{RT}{P} + \frac{\beta}{RT} + \frac{\gamma P}{(RT)^2} + \frac{\delta P^2}{(RT)^3} \tag{56}$$

where

$$\beta = RTB_0 - A_0 - \frac{Rc}{T^2} \tag{57a}$$

$$\gamma = -RTB_0b + A_0a - \frac{RcB_0}{T^2} \tag{57b}$$

$$\delta = \frac{RB_0bc}{T^2} \tag{57c}$$

In these relations T is again the absolute temperature and R the gas constant, while A_0, B_0, a, b, and c are constants characteristic of each gas.

[3] See page 47.

Of the two forms, Eqs. (55) and (56), the first is the more accurate, for the second was deduced from it with certain approximations.

This equation is applicable over wide ranges of temperature and pressure with excellent accuracy. Volumes and pressures calculated by it agree with experiment to 0.3 per cent or less up to pressures of 100 atm and temperatures as low as −150°C. With lower accuracy the equation may be extended to considerably higher pressures. Beattie-Bridgeman constants for a number of gases are given in Table 1–5.

MOLECULAR WEIGHTS OF GASES

The molecular weight of a gas is an important quantity essential for all types of calculations. It should be clearly realized that chemical analysis alone is insufficient to establish the molecular weight of a substance. Chemical analysis merely establishes the elements entering into the composition of a molecule and their proportions, but it does not tell us how many atoms of each substance are involved. For instance, chemical analysis of ethane shows that it is composed of carbon and hydrogen in the proportion of three atoms of hydrogen for each atom of carbon. From this alone we should be tempted to write the formula as CH_3. Actually, however, density measurements on the gas show that the formula is not CH_3 but a multiple of it, $(CH_3)_2$ or C_2H_6; i.e., the molecule is composed of two atoms of carbon and six atoms of hydrogen. In brief, chemical analysis can yield only the composition and empirical formula. Physicochemical measurements, on the other hand, can establish the molecular weight, and they can give us then the multiple by which the empirical formula weight must be multiplied in order to arrive at the actual molecular weight of the substance.

Until 1961 all molecular weights were based on the arbitrarily assumed standard of 16.0000 for the chemical atomic weight of oxygen. In that year the International Union of Pure and Applied Chemistry adopted a new atomic weight system based on the most abundant isotope of carbon, namely, C^{12}, as being 12.0000. On this new basis the chemical atomic weight of oxygen is changed to 15.9994. Since it has been proved that the oxygen molecule contains two atoms, it follows immediately that the molecular weight of oxygen must be 31.9988. Knowing the molecular weight of oxygen, the molecular weights of all other gases may be determined by physicochemical methods through application of the Avogadro hypothesis.

The Avogadro hypothesis states that under the same conditions of temperature and pressure equal volumes of all ideal gases contain the same number of molecules. If we were to determine, then, the volume that a mole of oxygen occupies under a specified set of conditions, this

would be also the volume that a mole of any other gas would occupy under the same conditions; and the weight of this volume would yield directly the molecular weight of the gas. Since by Avogadro's hypothesis the two volumes would contain the same number of molecules, the molecular weights would be in the same proportion as the actual masses of the individual molecules.

In physical chemistry the unit of mass commonly employed is the gram, and the gram-mole is the weight of a substance in grams corresponding to the molecular weight.[4] For oxygen the gram-mole is 31.9988 grams. Further, by direct measurement it has been found that the density of oxygen at standard conditions, i.e., 1 atm pressure and 273.15°K, is 1.4276 grams per liter when corrected for nonideality of the gas. Since density is mass per unit volume, it follows that the molar volume of oxygen under the conditions specified must be

$$\frac{31.9988}{1.4276} = 22.413 \text{ liters}$$

As this is also the molar volume of any other ideal gas at standard conditions, the problem of determining the exact molecular weight of any other gas reduces itself to the determination of the weight of 22.413 liters of the gas at 1 atm pressure and 273.15°K after correction for nonideal behavior.

Actually, it is not necessary or convenient to make measurements under the above conditions. Measurements may be made under any desired conditions, and the molecular weight may be calculated conveniently from these. The procedure followed for obtaining exact molecular weights will be presented later in the chapter. At present we shall concern ourselves with the determination of approximate molecular weights which, along with the chemical analysis, are generally sufficient to establish the molecular weight of a substance. For the latter purpose we employ the ideal gas law as follows: If we let W be the weight of gas under consideration, then $n = W/M$, and

$$PV = nRT = \frac{W}{M} RT$$

or

$$M = \frac{WRT}{PV} \tag{58}$$

Therefore, to obtain the molecular weight of any gas we need only determine the temperature and pressure at which a weight of gas W occupies the volume V, substitute these quantities in Eq. (58), and solve for M. Equation (58) may be expressed also in terms of the density of the gas ρ.

[4] Similarly, a pound-mole is the weight of a substance in pounds corresponding to the molecular weight.

Since $\rho = W/V$,

$$M = \frac{\rho RT}{P} \tag{59}$$

and the molecular weight follows from the density of the gas at any given temperature and pressure. Most methods for determining the molecular weights of gases are based on these equations.

REGNAULT'S METHOD FOR DETERMINATION OF MOLECULAR WEIGHTS

This method is employed to determine the molecular weights of substances which are gaseous at room temperature. The procedure in outline is as follows: A dry glass bulb of 300- to 500-cc capacity fitted with a stopcock is evacuated and weighed. It is then filled at a definite temperature and pressure with the gas whose molecular weight is to be determined and weighed again. The difference in weights represents the weight of gas W in the flask. The volume of the flask is determined by filling it with water or mercury, whose densities are known, and again weighing. From the data thus obtained the molecular weight may be calculated by Eq. (58).

For more precise work a larger bulb is used to increase the mass of gas and a similar bulb is employed as a counterpoise. The observed weights are also reduced to vacuo.

DUMAS' METHOD FOR DETERMINATION OF VAPOR DENSITIES

This method is used to determine the molecular weights in the vapor phase of readily volatile liquids. A retort-shaped bulb, having a small opening drawn to a capillary, is first weighed full of air. A sample of several cubic centimeters of the liquid in question is drawn into the bulb by cooling it with the tip below the surface of the liquid, and the bulb is then immersed in a bath whose temperature is above the boiling point of the liquid. The boiling is permitted to proceed until the vapors of boiling liquid have expelled all the air from the bulb, and the liquid in the flask has completely vaporized. The flask is then sealed, cooled to room temperature, and weighed. The volume of the bulb is determined as in Regnault's method. The pressure of the vapor when the bulb is sealed is the same as atmospheric, while the temperature is that of the bath. The weight of vapor, after corrections for buoyancy, is obtained from the equation

$$W_{\text{vapor}} = W_{(\text{bulb+vapor})} - W_{(\text{bulb+air})} + W_{\text{air}} \tag{60}$$

W_{air} is obtained by multiplying the volume of the flask by the density of the air. Knowing P, V, T, and W_{vapor}, the molecular weight of the liquid in the vapor phase may be calculated as before.

THE VICTOR MEYER METHOD FOR VAPOR DENSITIES

This method serves the same purpose as the Dumas method for the determination of vapor densities but is considerably simpler and more flexible. A sketch of the apparatus is shown in Figure 1–8. It consists of

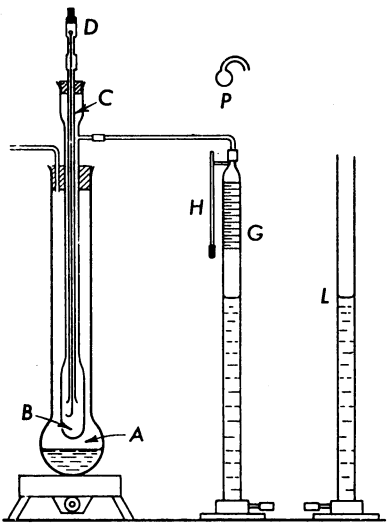

Figure 1–8. Victor Meyer apparatus.

an inner tube B, approximately 50 cm long, which is surrounded by a jacket A, partly filled as indicated with a liquid whose boiling point is at least 30 degrees higher than that of the substance to be studied. The function of the outer jacket is to keep the temperature of the inner tube constant by boiling the liquid in A throughout a run. Inside the inner tube, in turn, is another tube C, open at the bottom, down which passes a metal or glass rod, anchored with rubber tubing at the top in the manner shown and fitted with a hook at the bottom. The outlet from B communicates with a gas burette G, filled either with water, in which case correction for the aqueous pressure must be applied, or preferably mercury. L is a leveling bulb to permit adjustment of gas pressure in G to that of the atmosphere.

The liquid whose molecular weight is to be determined is enclosed in a small glass ampoule with finely drawn tip, P. This ampoule is first weighed empty. Next, enough of the liquid is drawn in to yield 40 to 60 cc of vapor, and the bulb is sealed carefully in a flame and weighed again. The difference between the first and second weighings gives the

weight of the liquid W to be vaporized. This ampoule then is hung on a hook projecting from C, and the entire apparatus assembled as shown in the figure.

To make a measurement, the liquid in A is brought to boiling and kept there for the entire run. When thermal equilibrium has been established, the levels in G and L are equalized and the burette reading is taken. Next the ampoule is smashed by pulling upward on the rod at D so as to bring the neck of the ampoule up against the bottom of C. With the bulb broken the liquid vaporizes, and the vapors generated displace air from the bottom of B into the gas burette G. The volume of air thus displaced is equal to the volume of the vapors formed at the temperature of the inner tube. Once in the gas burette the air cools to room temperature, and its volume can be measured by again reading the burette. Provided the levels in G and L are equalized, the pressure of this air is the same as that of the atmosphere outside the burette, while the temperature is that read on the thermometer H. The volume of displaced air thus obtained, i.e., final minus initial burette readings, is equal to the volume which the vapors of the liquid would occupy if they could be cooled to the temperature of the room and atmospheric pressure. Having measured in this manner the weight of liquid W, and its volume as a *vapor* at room temperature T and barometric pressure P, the density of the vapor and its molecular weight may readily be calculated from the observed data.

DETERMINATION OF EXACT MOLECULAR WEIGHTS

The molecular weights calculated from the ideal gas law are, even with good data, only approximate. The reason is that already at atmospheric pressure the ideal gas law fails to represent accurately the behavior of the vapors. If an exact molecular weight is desired, this must be obtained from either a more precise gas equation or by special treatment of the ideal gas law.

When the constants a and b of a substance are known, use of van der Waals' equation will give better concordance between observed and calculated values of the molecular weight. For the purpose at hand, however, the Berthelot equation is more convenient and gives good results. It can be used, of course, only when the critical temperature and pressure of the substance are available. Since $n = W/M$, Eq. (54) gives for M

$$M = \left(\frac{W}{V}\right)\left(\frac{RT}{P}\right)\left[1 + \frac{9\,PT_c}{128\,P_cT}\left(1 - \frac{6\,T_c^2}{T^2}\right)\right] \tag{61}$$

Further, since $W/V = \rho$, Eq. (61) may also be written as

$$M = \frac{\rho RT}{P}\left[1 + \frac{9\,PT_c}{128\,P_cT}\left(1 - \frac{6\,T_c^2}{T^2}\right)\right] \tag{62}$$

from which the density follows when M is known or vice versa.

The higher accuracy of the Berthelot equation can be illustrated with the following data on methyl chloride. For methyl chloride, $T_c = 416.2°K$, $P_c = 65.8$ atm, while the density at standard conditions is 2.3076 g per liter. Hence, by Eq. (62),

$$M = \frac{2.3076 \times 0.08205 \times 273.2}{1}\left[1 + \frac{9 \times 1 \times 416.2}{128 \times 65.8 \times 273.2}\left(1 - 6\,\frac{(416.2)^2}{(273.2)^2}\right)\right]$$

$$= 50.62 \text{ g mole}^{-1}$$

as against the theoretically calculated 50.49. Using the same data and the ideal gas law, the molecular weight obtained is 51.71.

A means of obtaining exact molecular weights is the method of *limiting densities*. This method, which gives excellent results, is based upon the fact that as zero pressure is approached the ideal gas laws become exact for all gases. The densities of a gas or vapor are determined at a given temperature at atmospheric pressure and at several other pressures below one atmosphere. The ratio ρ/P is then plotted against P. If the vapor or gas were ideal, this ratio would be the same at all pressures, for

$$P = \frac{\rho}{M} RT$$

and

$$\frac{\rho}{P} = \frac{M}{RT} = \text{constant} \tag{63}$$

However, since this is not true for real gases, the ratio ρ/P changes with decreasing pressure. Fortunately the plot is practically linear and can be extrapolated to zero pressure without any difficulty. At zero pressure the limiting ratio ρ/P is that for the ideal gas, and so

$$\left(\frac{\rho}{P}\right)_{P=0} = \frac{M}{RT}$$

and

$$M = RT\left(\frac{\rho}{P}\right)_{P=0} \tag{64}$$

This method can be illustrated with the data on hydrogen bromide given in Table 1–6, while the plot of ρ/P vs. P is shown in Fig. 1–9. The

TABLE 1–6. DENSITIES OF HBr AT VARIOUS PRESSURES (0°C)

P (atm)	ρ (g/liter)	ρ/P
1	3.6444	3.6444
⅔	2.4220	3.6330
⅓	1.2074	3.6222
0	—	3.6108 (extp'd)

extrapolated value of ρ/P is 3.6108 g per liter per atm at 0°C. Hence the molecular weight of hydrogen bromide is

$$M = 3.6108 \times 0.082054 \times 273.15 = 80.93 \text{ g mole}^{-1}$$

The value calculated from atomic weights is 80.92.

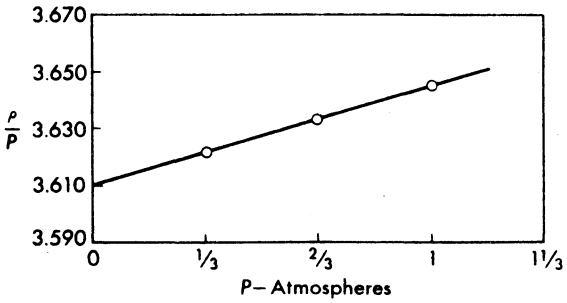

Figure 1–9. Plot of ρ/P vs. P for HBr at 0°C.

RESULTS OF VAPOR DENSITY MEASUREMENTS

The measurement of the vapor densities of a large number of substances shows that the molecular weight of these substances in the gas phase over a certain temperature interval is what would be expected from their simple formula. Among these may be mentioned ammonia, carbon dioxide, hydrogen, nitrogen, carbon monoxide, methyl chloride, methyl fluoride, ethyl ether, methyl ether, carbon tetrachloride, chloroform, carbon disulfide, acetone. There are other substances, however, which exhibit a highly anomalous behavior. These may be segregated into two groups: (a) those which exhibit vapor densities, and consequently molecular weights, higher than would be expected on the basis of their simple formulas, and (b) those which exhibit vapor densities lower than expected from their simple formulas. All these abnormalities are very much greater than can be accounted for by either experimental uncertainty or deviation from ideal behavior.

The substances exhibiting abnormally high vapor densities are considered to be associated in the vapor phase, i.e., the molecules are considered to be composed of more than a single structural unit. In line with this view is the fact that the calculated molecular weight is usually a whole-number multiple of the simple formula. Thus aluminum chloride is shown in the vapor phase to be $(AlCl_3)_2$ or Al_2Cl_6, ferric chloride Fe_2Cl_6, beryllium chloride Be_2Cl_4, and gallium chloride Ga_2Cl_6. Sulfur is another substance which shows different stages of association in the gas phase at different temperatures.

Substances exhibiting abnormally low vapor densities break down or dissociate in the vapor phase under the influence of heat into simpler molecules, leading thereby to a greater number of particles and a lower density for any given pressure. Thus the vapor of ammonium chloride contains ammonia and hydrogen chloride as a result of the reaction

$$NH_4Cl = NH_3 + HCl$$

Similarly, PCl_5 dissociates in the vapor phase into PCl_3 and Cl_2, while N_2O_4 dissociates into two molecules of NO_2. In any instance the extent of dissociation is a function of the temperature and pressure. At sufficiently high temperatures these substances may be completely dissociated, while at sufficiently low temperatures they may behave almost normally. In fact, practically all substances can be shown to be abnormal if the temperature is made high enough. Even such a stable compound as carbon dioxide dissociates above 2000°C to some extent into carbon monoxide and oxygen. Similarly, aluminum chloride at 400°C is Al_2Cl_6, at 500°C it is a mixture of Al_2Cl_6 and $AlCl_3$, while at 1100°C it is all $AlCl_3$. If heated further, $AlCl_3$ will actually dissociate into aluminum and chlorine. Hence when we speak of the molecular weight of a substance in the gas phase, it is very important to keep in mind the temperature to which reference is made.

HEAT CAPACITY OF GASES

The specific heat of any substance is defined as the quantity of heat required to raise the temperature of unit weight of the substance 1 degree of temperature. In terms of calories and degrees centigrade, the specific heat is the number of calories of heat required to raise the temperature of 1 g of a substance 1°C. Chemical calculations are most frequently made on a molar basis, and for that reason it is more convenient to deal with the *heat capacity* per mole. The heat capacity per mole is the amount of heat required to raise the temperature of 1 mole of a substance 1°C. It is equal, of necessity, to the specific heat per gram multiplied by the molecular weight of the substance.

Two types of heat capacities are recognized, depending on whether the substance is heated at constant volume or at constant pressure. When a substance is heated at constant volume, all of the energy supplied goes to increase the internal energy of the substance, and we speak then of the *heat capacity at constant volume*, C_v. On the other hand, when a substance is heated at constant pressure, energy must be supplied not only to increase its internal energy, but also to make possible expansion of th substance against the confining atmospheric pressure. The *heat capacity at constant pressure*, C_p, must therefore be larger than that at constant

volume by the amount of work which must be performed in the expansion accompanying 1 degree rise in temperature. In liquids and solids, where volume changes on heating are small, this difference between C_p and C_v is usually slight. With gases, however, where the volume changes with temperature are always large, the difference $C_p - C_v$ is always significant and cannot be disregarded.

Some important deductions concerning the specific heats of gases can be made from the kinetic theory of gas behavior. According to equation (36b), the kinetic energy of translation of an ideal gas per mole is

$$E_k = \frac{3}{2} RT$$

If this is the only type of energy the gas possesses (monatomic gas), the energy difference of the gas ($E_{k_2} - E_{k_1}$) between two temperatures T_2 and T_1 is

$$\Delta E = E_{k_2} - E_{k_1} = \frac{3}{2} R(T_2 - T_1)$$

When the temperature difference $T_2 - T_1 = 1$, ΔE becomes the energy required to raise the translational energy of 1 mole of gas 1 degree without involving any external work, or, in other words, the heat capacity per mole at constant volume C_v. Hence we may write

$$\begin{aligned} C_v &= \frac{3}{2} R = \frac{3}{2} \times 1.987 \\ &= 2.98 \text{ cal degree}^{-1} \text{ mole}^{-1} \end{aligned} \qquad (65)$$

The kinetic theory predicts, therefore, that C_v for any ideal gas *containing only translational energy* should be approximately 3 cal per mole, and, further, that this heat capacity should be constant and independent of temperature.

A similar prediction can be arrived at with respect to the heat capacity at constant pressure, C_p. In view of the preceding considerations it follows that

$$C_p = C_v + w \qquad \text{cal degree}^{-1} \text{ mole}^{-1} \qquad (66)$$

where w is the work which must be performed against a confining pressure P when 1 mole of an ideal gas is expanded from a volume V_1 at T_1 to a volume V_2 at $T_2 = T_1 + 1$. The value of w can be obtained from the relation

$$w = \int_{V_1}^{V_2} P dV \qquad (67)$$

which will be discussed in greater detail in Chapter 3. If we now differentiate $PV = RT$ at constant pressure, we have $PdV = RdT$, and on

substitution of RdT for PdV in Eq. (67), we see that

$$w = \int_{V_1}^{V_2} PdV = \int_{T_1}^{T_2} RdT$$
$$= R(T_2 - T_1)$$

For $T_2 - T_1 = 1$ this reduces to $w = R$ per mole, and hence for an ideal gas

$$C_p = C_v + R \quad \text{cal degree}^{-1}\ \text{mole}^{-1} \tag{68}$$

Equation (68) is valid for all ideal gases, and permits the simple conversion of C_p to C_v or vice versa. Inserting the values of C_v from Eq. (65) and of R, we see that for any ideal gas *involving only translational energy* C_p should be

$$C_p = \frac{5}{2} R$$
$$= 4.97 \text{ cal degree}^{-1}\ \text{mole}^{-1} \tag{69}$$

Consequently, like C_v, C_p should be constant and independent of temperature for all gases. Again, the ratio C_p/C_v, commonly designated by γ, should also be a constant equal to

$$\gamma = \frac{C_p}{C_v} = \frac{5/2\ R}{3/2\ R}$$
$$= 1.67 \tag{70}$$

In Table 1–7 are listed values of C_p, C_v, $C_p - C_v$, and γ for various gases at 15°C. It will be observed, first of all, that the requirement $C_p - C_v = R = 1.99$ cal per mole is met fairly well by practically all the gases in the table. Second, the predictions of the kinetic theory that $C_p = 4.97$ and $C_v = 2.98$ cal per mole are borne out by the heat capacities of a group of gases which includes, besides argon and helium, also krypton, xenon, and a number of metallic vapors. However, for all the other gases in the table the prediction is not valid. Inspection of the table reveals that the various gases can be divided into classes based upon their values of γ. The first group, comprising gases that obey the kinetic theory, has the expected $\gamma = 1.67$. The others, in turn, may be grouped as those with γ equal approximately to 1.4, 1.3, and lower. Further, the decrease in γ is always associated with an increase in the complexity of the molecules involved. Thus argon and helium with $\gamma = 1.67$ are monatomic, i.e., the molecules contain a single atom of the element. Again, the substances with γ equal to about 1.4, such as oxygen, nitrogen, and chlorine, are diatomic, those with γ equal to about 1.3 triatomic, while all others with

γ still lower are more complex. Finally, all substances exhibiting γ values lower than 1.67 also have values of C_p and C_v considerably greater than the predicted $C_p = \frac{5}{2} R$ and $C_v = \frac{3}{2} R$.

TABLE 1-7. HEAT CAPACITIES OF GASES AT 15°C
(Cal mole^{-1} degree^{-1})

Gas	Formula	C_p	C_v	$C_p - C_v$	γ
Argon	Ar	5.00	3.01	1.99	1.66
Helium	He	4.99	3.00	1.99	1.66
Carbon monoxide	CO	6.94	4.95	1.99	1.40
Chlorine	Cl_2	8.15	6.02	2.13	1.35
Hydrogen	H_2	6.83	4.84	1.99	1.41
Hydrogen chloride	HCl	7.07	5.01	2.06	1.41
Nitrogen	N_2	6.94	4.94	2.00	1.40
Oxygen	O_2	6.96	4.97	1.99	1.40
Carbon dioxide	CO_2	8.75	6.71	2.04	1.30
Hydrogen sulfide	H_2S	8.63	6.54	2.09	1.32
Nitrous oxide	N_2O	8.82	6.77	2.05	1.30
Sulfur dioxide	SO_2	9.71	7.53	2.18	1.29
Acetylene	C_2H_2	9.97	7.91	2.06	1.26
Ethylene	C_2H_4	10.07	8.01	2.06	1.26
Ethane	C_2H_6	11.60	9.51	2.09	1.22

These high heat capacities suggest that the fundamental assumption made, that the only energy present in a gas is kinetic energy of translation, is not always correct. A monatomic molecule can execute only translational motion along the coordinate axes, and for such a gas the deductions of the kinetic theory are valid. A more complex molecule, however, may be subject not only to translational motion as a unit, but to rotation and vibration as well. If we think of a diatomic molecule simply as a "dumbbell" held together by an elastic spring, then the two atoms may execute vibrations with respect to each other along their line of centers. Further, the molecule as a whole may undergo rotation about axes perpendicular to the line joining the centers of mass of these molecules. These extra motions involve additional terms for the energy of the gas; and if these motions are subject to temperature variation, as they are, additional terms will appear in the heat capacity equation for the gas. A more detailed discussion of rotational and vibrational energies of gas molecules will be given in Chapters 16 and 18.

THEORY OF NONIDEAL GASES

The theory of nonideal gases reduces itself essentially to the theory of intermolecular or van der Waals forces. Although we are not prepared at present to discuss the nature of these forces,[5] it is nevertheless of importance to summarize briefly the results obtained. Theoretical arguments show that the interaction energy, E', between a pair of molecules is given by

$$E' = -\frac{A}{r^6} + \frac{B}{r^n} \tag{71}$$

and the force of interaction by

$$f' = \frac{A}{r^7} - \frac{B}{r^{(n+1)}} \tag{72}$$

where A and B are constants characteristic of the molecules involved, r is their distance of separation, and n is a constant whose value may range from 9 to 12. In these equations the first term on the right represents attraction, while the second represents repulsion between the molecules. From these equations it is evident that the forces between molecules are short-range in character, and that they increase very rapidly as the distance between molecules is made small.

The consideration of molecular interactions has made possible the theoretical explanation of the second virial coefficient and, less successfully, of the third virial. However, we do not have as yet a theory which can account completely for the P–V–T behavior of gases over very wide ranges of temperature and pressure.

LIQUIDS

From the standpoint of kinetic theory, a liquid may be considered as a continuation of the gas phase into the region of small volumes and very high molecular attractions. The cohesive forces in a liquid must be stronger than those in a gas even at high pressures, for they are high enough to keep the molecules confined to a definite volume. Still, the molecules within the liquid must not be thought of as rigidly fixed. They have some freedom of motion, but this motion is considerably restricted, and hence the mean free path is much shorter than in the gas phase.

Our knowledge of the nature of the liquid state is still very incomplete.

[5] See Chapter 16.

Because of the proximity of molecules to each other, effects frequently manifest themselves in liquids which, if present, are of only secondary significance in gases. Thus we encounter clustering, association, and in general orientation of the molecules into some, even though not very pronounced, order. At best, the situation within a liquid is very complex, and the progress made in unraveling the multitudinous effects has been rather slow.

CRITICAL PHENOMENA IN LIQUIDS

If a liquid, such as water, is sealed in an evacuated tube, a certain amount will evaporate to form vapor. This vapor will exert a pressure just as any gas does, and, provided the temperature is maintained constant, an equilibrium will be established between the liquid and vapor phases. The vapor pressure established is characteristic for each liquid and is a constant at any given temperature; it is known as the *saturated vapor pressure* of the liquid. The saturated vapor pressure increases continuously with temperature. Thus, at 25°C the vapor pressure of water is 23.76 mm Hg, while at 100°C it is 760 mm Hg. As the water in the sealed tube is heated further, more and more water evaporates and the pressure continues to increase. At all times there is a definite line of demarcation, or meniscus, between the liquid and vapor phases. When we reach the temperature of 374°C, however, the meniscus becomes indefinite, fades into the vapor, and disappears. At this temperature the physical properties of liquid and vapor become identical, and no distinction can be observed between the two. A liquid in this condition is said to be at the *critical point.* The temperature, saturated vapor pressure, and molar volume corresponding to this point are designated the *critical temperature, critical pressure,* and *critical volume* respectively. Their values, which are constant and characteristic for each substance, are known as the *critical constants.* For water the critical constants are: t_c = 374.4°C, P_c = 219.5 atm, and V_c = 58.7 cc per mole.

On heating the sealed tube even slightly above the critical temperature, no evidence can be found of the presence of liquid. The whole mass is gaseous and remains in that state no matter how high it is heated, or how large an external pressure is applied. Since the phenomena described for water are exhibited by all liquids, it must be concluded that *no liquid can exist as such at temperatures above the critical under any applied pressure.*

The critical phenomena are reversible. When the gas in the sealed tube is cooled below the critical temperature, if the pressure is sufficiently high the meniscus reappears, and again we have the two phases, liquid and vapor.

THE P–V–T RELATIONS OF GASES AND LIQUIDS

The first complete data on the P–V–T relations of a substance in both gaseous and liquid states were obtained by Andrews[6] on carbon dioxide.

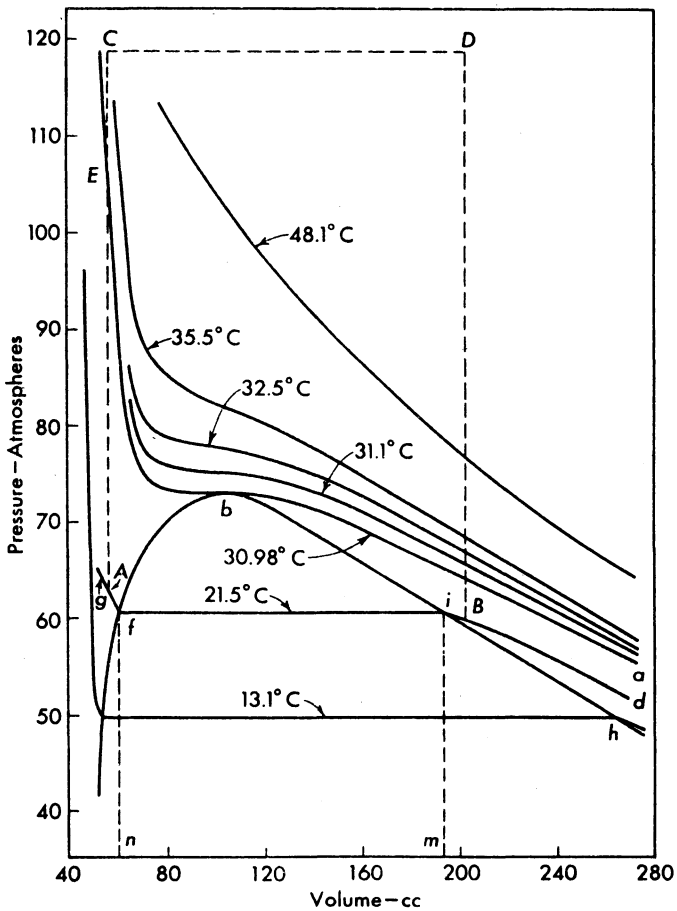

Figure 1–10. Isothermals of CO_2.

Andrews measured the variation of the volume of carbon dioxide with pressure at various constant temperatures, and he was able to show that the critical temperature of carbon dioxide is 31°C at a critical pressure of 73 atm.

Figure 1–10 shows the plot of pressure vs. volume for carbon dioxide at various constant temperatures. Each P–V plot is called an *isothermal*.

[6] Andrews, *Trans. Roy. Soc.*, **159**, 583 (1869).

The data on which the plot is based are not due to Andrews but are the composite results of several subsequent investigators. The 48.1°C isothermal is very similar to the hyperbolic plot demanded by Boyle's law and shows no presence of liquid carbon dioxide even at the highest pressures attained. The same conditions obtain at 35.5°C, 32.5°C, and 31.10°C, except that now the data indicate that Boyle's law when applied to carbon dioxide is considerably in error, since the gas does not behave ideally. At 30.98°C, however, the carbon dioxide remains gaseous only up to a pressure of 73 atm (line *ab*). At 73 atm (point *b*) liquid first appears, and since this is the highest temperature at which liquid is observed, 30.98°C must be the critical temperature of carbon dioxide. Further increase in pressure at this temperature (line *bE*) shows only the presence of liquid, and consequently this line must represent the compressibility of liquid carbon dioxide at this temperature. Below 30.98°C, the behavior of the gas on compression is quite different, as may be judged from the 21.5°C and 13.1°C isotherms. At 21.5°C, for instance, only gas exists on compression along line *di*. At *i* liquid, of specific volume *n*, first appears, and the pressure of the system remains constant thereafter as long as both gas and liquid are present. At this stage further application of pressure results merely in further condensation of gas until point *f* is reached. At *f* all the gas has been condensed, and further application of pressure results merely in compression of the liquid, as is shown by the steep line *fg*. At lower temperatures the behavior is similar to that at 21.5°C, except that the horizontal portions, corresponding to the range of coexistence of liquid and vapor, become longer the lower the temperature.

It may be concluded from this explanation that, in the area to the left of the dome-shaped area and below the line *bE*, only liquid carbon dioxide will exist; to the right of the line *bE* and to the right of the dome-shaped area, only gaseous carbon dioxide will exist; while within the dome-shaped area is the range of coexistence of liquid and vapor carbon dioxide.

All gases upon isothermal compression behave similarly to carbon dioxide. For each, of course, the curves will be displaced in line with the characteristics and critical temperature of the gas in question. Thus, for example, the critical temperature of helium is −268°C and the dome-shaped area is moved downward, while for chlorine the critical temperature is 144°C and the dome-shaped area is moved above that for carbon dioxide.

THE PRINCIPLE OF CONTINUITY OF STATES

For further theoretical considerations it is essential to show that the liquid state does not represent a sharp and discontinuous transition from the gaseous state, but is rather a continuation of the gaseous phase into

the region of very strong intermolecular attractions and small volumes. This can be shown from the following considerations. Suppose we wish to convert liquid carbon dioxide at 21.5°C and the pressure given by point A in Figure 1–10 to gaseous carbon dioxide at the same temperature and the pressure given by point B. The most obvious way to accomplish this transformation is to follow the 21.5°C isotherm and reduce the pressure along $AfiB$. In doing this gas appears suddenly and discontinuously, and coexists with liquid along fi until finally all liquid disappears at i. The same transformation may, however, be accomplished in another way. If the liquid at A is heated at constant volume, increase of temperature will lead to increased pressure, and the mass will move along the line AEC. As long as the carbon dioxide is below the critical isotherm, point E, the carbon dioxide is liquid; as soon as the carbon dioxide passes the critical isotherm, however, it becomes gaseous. At the critical temperature, as we have seen, the liquid passes to gas imperceptibly and continuously, and hence in heating the liquid from A to C we convert it without discontinuity to gas. The gas at C may now be expanded to D at constant pressure by heating, and then cooled at constant volume from D to B. By this series of operations we can convert liquid to gaseous carbon dioxide at 21.5°C without introducing any discontinuity between the phases.

The implication involved in this principle of the continuity of the gaseous and liquid states is highly important. It suggests that if we have an equation of state which is satisfactory in the region of high pressures and low temperatures, that equation should be applicable also to the conditions prevailing at the critical point and to the liquid itself. We shall see now how the van der Waals equation meets these requirements.

APPLICATION OF VAN DER WAALS' EQUATION TO THE ISOTHERMALS OF CARBON DIOXIDE

By substituting $n = 1$ and the values of the constants a and b for carbon dioxide in van der Waals' equation, namely,

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

we can calculate for any given temperature the P–V relationships above, at, and below the critical temperature. The results of such a calculation are summarized in Figure 1–11. The plot is, in general, similar to the one obtained experimentally. At t_1, for instance, which is above the critical temperature, the P–V relationship corresponds closely to that of the 48.1°C isotherm in Figure 1–10. At t_c, which is the critical temperature, a

slight break is observed at *a*, the critical point, which is again in accord with observation. However, below the critical temperature, the range determining the coexistence of liquid and gas is indicated by a continuous S-shaped portion as *bcd* at t_3, rather than by the horizontal constant pressure range actually observed. In this respect, therefore, and in point of strict quantitative agreement with observed data, the van der Waals

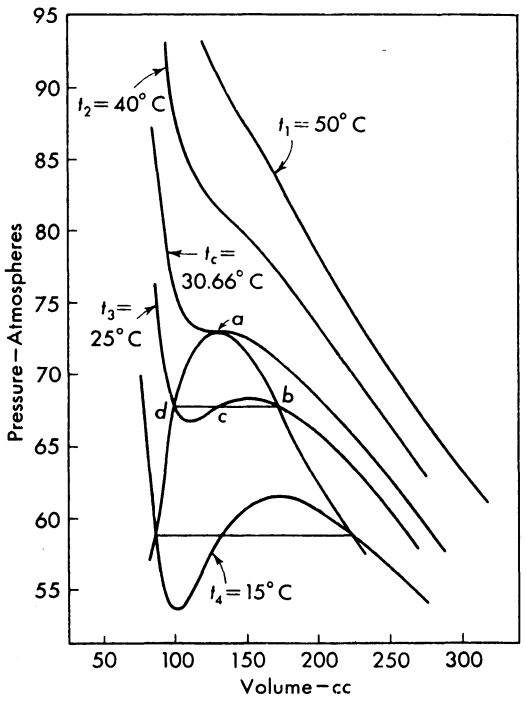

Figure 1–11. Isothermals of CO_2 according to van der Waals' equation.

equation leaves something to be desired. Nevertheless, some investigators have found that by compressing the gas very carefully part of the curve *bc* may be realized, though only in an unstable condition. Similarly, if the pressure on a liquid be released slowly, part of curve *cd* can be obtained, but again the condition is unstable.

DETERMINATION OF VAN DER WAALS CONSTANTS

If it be assumed that van der Waals' equation is applicable at the critical point, then the van der Waals constants for any gas can be calculated from the critical constants of the gas in the following manner. On

expanding and rearranging the equation we have

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

$$PV^3 - V^2(RT + Pb) + aV - ab = 0$$

and

$$V^3 - \left(\frac{RT + Pb}{P}\right)V^2 + \left(\frac{a}{P}\right)V - \left(\frac{ab}{P}\right) = 0 \tag{73}$$

This is a cubic equation in V and for any given value of P and T will yield three separate solutions for V. The three roots of this equation may all be real, or one may be real and positive and the other two imaginary. Thus in Figure 1–11 the equation yields the three roots d, c, and b at t_3, while at t_1 it yields only one real root. However, at the critical point the three roots are not only real and positive but also identical and equal to V_c. Hence the difference $(V - V_c) = 0$, and consequently,

$$(V - V_c)^3 = 0 \tag{74}$$

On expansion by the binomial theorem Eq. (74) becomes

$$V^3 - (3\,V_c)V^2 + (3\,V_c^2)V - V_c^3 = 0 \tag{75}$$

At the critical point Eqs. (75) and (73) must be identical. On comparing and equating coefficients we get

$$3\,V_c = \frac{RT_c + bP_c}{P_c} \tag{76}$$

$$3\,V_c^2 = \frac{a}{P_c} \tag{77}$$

$$V_c^3 = \frac{ab}{P_c} \tag{78}$$

From Eq. (77) a follows as

$$a = 3\,V_c^2 P_c \tag{79}$$

while from Eqs. (77) and (78) b is given by

$$b = \frac{V_c}{3} \tag{80}$$

Thus a and b may be calculated from known values of P_c and V_c, or vice versa.

Usually V_c is the critical constant known least accurately, and it is therefore preferable to calculate a and b from T_c and P_c only. This can readily be done. On eliminating V_c between Eqs. (76) and (80) we get

$$b = \frac{RT_c}{8\,P_c} \tag{81}$$

Again, on combining Eqs. (76), (80), and (77), a follows as

$$a = \frac{27}{64}\frac{R^2T_c^2}{P_c} \tag{82}$$

Combination of Eqs. (76) and (80) leads also to the value of R in terms of the critical constants, namely,

$$R = \frac{8}{3}\frac{P_cV_c}{T_c} = 2.67\frac{P_cV_c}{T_c} \tag{83}$$

Although the van der Waals equation predicts the coefficient in Eq. (83) to be 2.67, the values for it calculated from experimental data are generally higher and differ for various gases. Thus for helium this constant comes out to be 3.18, while for water it is 4.97. These differences are due to inaccuracies inherent in the van der Waals equation.

THE CRITICAL CONSTANTS OF GASES

Table 1–8 gives the critical constants of a number of gases. Instead of the critical volume, the critical density is given; this is the weight of substance at the critical point per cubic centimeter. The critical volume is obtained by dividing the molecular weight of the substance by the critical density.

Cailletet and Mathias found that when the mean values of the sum of the densities of liquid and saturated vapor of a substance are plotted

TABLE 1–8. CRITICAL CONSTANTS OF GASES

Gas	t_c (°C)	P_c (atm)	d_c (g/cc)
Ammonia	132.4	111.5	0.235
Argon	−122	48	0.531
Carbon dioxide	30.98	73.0	0.460
Carbon monoxide	−139	35	0.311
Chlorine	144.0	76.1	0.573
Ethane	32.1	48.8	0.21
Ethyl alcohol	243.1	63.1	0.2755
Ethylene	9.7	50.9	0.22
Helium	−267.9	2.26	0.0693
Hydrogen	−239.9	12.8	0.0310
Neon	−228.7	25.9	0.484
Nitric oxide	−94	65	0.52
Nitrogen	−147.1	33.5	0.3110
Oxygen	−118.8	49.7	0.430
Propane	96.81	42.01	0.226
Toluene	320.6	41.6	0.292
Water	374.4	219.5	0.307

against the temperature, the plot is a straight line. This is shown in Figure 1–12. The equation of the line is

$$t = A + B\left(\frac{d_l + d_v}{2}\right) \tag{84}$$

where d_l is the density of the liquid at any temperature t, d_v the density of the saturated vapor at the same temperature, and A and B constants

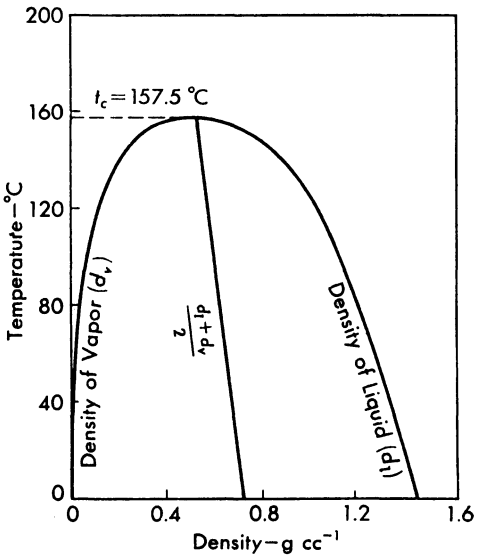

Figure 1–12. Linear variation of mean density of SO_2 with temperature.

evaluated from the plot. Once the equation is determined, the critical density may be calculated with ease, for at the critical temperature $d_v = d_l = d_c$, and the equation reduces to

$$t_c = A + B\left(\frac{2\,d_c}{2}\right) = A + Bd_c \tag{85}$$

Substitution of t_c then yields the critical density. Critical densities can usually be obtained more accurately in this manner than by direct measurement at the critical point.

THE PRINCIPLE OF CORRESPONDING STATES

If we substitute in the van der Waals equation the values of a, b, and R as given by Eqs. (81), (82), and (83), we obtain

$$\left(P + \frac{3\,V_c^2 P_c}{V^2}\right)\left(V - \frac{V_c}{3}\right) = \frac{8}{3}\frac{P_c V_c T}{T_c} \tag{86}$$

Dividing both sides of Eq. (86) by P_cV_c, we get

$$\left(\frac{P}{P_c} + \frac{3\,V_c^2}{V^2}\right)\left(\frac{V}{V_c} - \frac{1}{3}\right) = \frac{8}{3}\frac{T}{T_c}$$

or

$$\left(P_r + \frac{3}{V_r^2}\right)(3\,V_r - 1) = 8\,T_r \qquad (87)$$

where $P_r = P/P_c$, $V_r = V/V_c$, and $T_r = T/T_c$. P_r is termed the *reduced pressure*, V_r the *reduced volume*, and T_r the *reduced temperature*. Expressed in terms of P_r, V_r, and T_r, Eq. (87) involves no constants characterizing the individuality of various substances and should therefore be generally applicable to all liquids and gases. It is known as a *reduced equation of state*. Its physical meaning is that at any given value of T_r and P_r, all liquids and gases should have the same corresponding volumes, V_r.

The principle of corresponding states is only approximately correct, but it does suggest that frequently better correlation of experimental data may be obtained when the various substances are in corresponding states, i.e., at equal values of T_r, V_r, or P_r. The principle finds frequent and useful application in thermodynamic and chemical engineering calculations, especially at elevated pressures. For examples see Maron and Turnbull,[7] Dodge,[8] and Gouq-Jen Su.[9]

LIQUEFACTION OF GASES

The particular method employed in the liquefaction of a gas depends on the nature of the gas. Vapors of substances which are liquid at or near room temperature and atmospheric pressure are condensed simply by cooling. Other substances which are liquid at lower temperatures may be condensed either by pressure or by a combination of cooling and compression. Cooling reduces considerably the pressure required for liquefaction, as may be seen from Figure 1–10. With the "permanent" gases, however, such as oxygen, nitrogen, hydrogen, and helium, application of pressure alone will not produce liquefaction, and more involved methods of cooling, compression, and even expansion, are required before the gases will liquefy.

Before liquefaction is possible, a gas must be cooled below its critical temperature. Since their critical temperatures are very low, as may be seen from Table 1–8, liquefaction of the "permanent" gases requires intense cooling as well as considerable compression. To attain these low temperatures, two general principles, or a combination of the two, are

[7] Maron and Turnbull, *Ind. Eng. Chem.*, **34**, 544 (1942).

[8] Dodge, *Chemical Engineering Thermodynamics*, McGraw-Hill Book Company Inc., New York, 1944.

[9] Gouq-Jen Su, *Ind. Eng. Chem.*, **38**, 803 (1946).

employed, namely, (a) adiabatic expansion, in which advantage is taken of the Joule-Thomson effect[10] to attain cooling; and (b) allowing the gas to cool itself by performing work in an adiabatic expansion against a piston. These two methods are exemplified in the Linde and Claude processes for the liquefaction of air.

The basic principle of the Linde process is the adiabatic Joule-Thomson expansion and consequent cooling of the air. The steps in the process are in outline as shown in Figure 1–13. Air is first compressed to approxi-

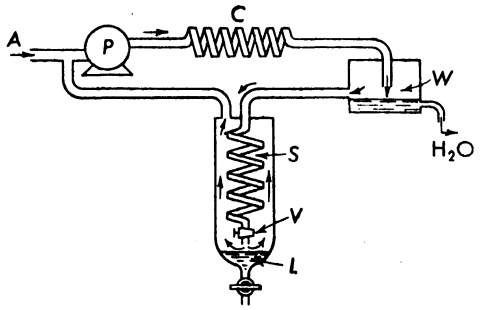

Figure 1–13. Linde process for liquefaction of air.

mately 100 atm. During the compression most of the water in the air condenses and is removed. The heat generated in compression is removed by passing the gas through coils *C*, refrigerated by water or ammonia. The dry gas is passed, then, through a copper spiral coil *S*, from which it is expanded to almost atmospheric pressure through a controlled valve *V*. The issuing gas, cooled now due to the Joule-Thomson effect, passes over the copper coil and cools further the incoming compressed gas. On repeating the cycle several times, the temperature of the expanding gas finally drops far enough to condense part of the air to liquid, which collects in the bottom of the chamber *L* and can be drawn off. Any uncondensed air is recirculated.

In the Claude process the gas, instead of being permitted to expand freely, is forced to do work against a confining piston. Since the gas is adiabatically insulated, work is achieved at the expense of the internal energy of the gas, and a cooling results. The work thus gained may be utilized to operate the compressors.

Easily liquefiable gases, such as sulfur dioxide, ammonia, methyl chloride, and dichloro-difluoromethane (freon), are used in refrigeration and air conditioning. In the laboratory other refrigerants frequently employed are ice, liquid air, liquid hydrogen and mixtures of "dry ice" (solid carbon dioxide) and alcohol, ether, or acetone. With one of the

[10] See Chapter 3.

last-named mixtures temperatures of −80 to −90°C can be obtained. Liquid air will give a temperature of −180°C, while, if needed, liquid hydrogen can give a temperature of −250°C.

VISCOSITY

Gases and liquids possess a property known as *viscosity*, which may be defined as the resistance that one part of a fluid offers to the flow of another part of the fluid. Viscosity is produced by the shearing effect of moving one layer of the fluid past another, and is quite distinct from intermolecular attraction. It may be thought of as caused by the internal friction of the molecules themselves and it is present in ideal gases as well as in real gases and liquids.

To define viscosity, let us visualize a fluid as being stratified into layers or planes of molecules. Let the area of each plane be A, and the distance between planes be dy. Further, consider each of the planes to be moving to the right with velocities v_1, v_2, etc., where each succeeding velocity is greater than the preceding by an amount dv. Flow occurring in this manner is called laminar flow, as distinct from turbulent flow where parallelism of the planes is not preserved. In laminar flow the force f required to maintain a steady velocity difference dv between any two parallel planes is directly proportional to A and dv, and is inversely proportional to dy. Consequently,

$$f = \eta A \left(\frac{dv}{dy}\right) \tag{88}$$

where η is a proportionality constant called the *viscosity coefficient* of the fluid. The quantity dv/dy in Eq. (88) is referred to as the rate of shear G, while f/A, the force per unit area, is called the shear stress F. In terms of F and G Eq. (88) becomes

$$\eta = \frac{F}{G} \tag{89}$$

Either Eq. (88) or Eq. (89) may be taken as the defining expression for η.

The viscosity coefficient may be thought of as the force per unit area required to move a layer of fluid with a velocity difference of 1 cm per second past another parallel layer 1 cm away. Although the force f may vary with experimental conditions, the viscosity coefficient η is a physical quantity characteristic of each fluid. In the cgs system of units the viscosity coefficient of a fluid is expressed in *poises*, a poise being the viscosity coefficient requiring a force of 1 dyne when A, dv, and dy are all unity in Eq. (88). Since this unit is rather large, the viscosities of gases are usually

given in *micropoises*, or 10^{-6} poise, while those of liquids in poises or *centipoises*, i.e., 10^{-2} poise.

THE VISCOSITY OF GASES

The viscosity of gases can be measured by various methods, some of which will be described in the next section. Results show that the viscosity coefficients of gases *increase* with increase in temperature. Thus chlorine at 1 atm pressure has an η of 132.7 micropoises at 20°C, 167.9 at 100°C, and 208.5 at 200°C. Again, although η is almost independent of pressure at low pressures, such is not the case at higher pressures. For instance, for carbon dioxide at 35°C and 1 atm pressure $\eta = 156$ micropoises, but at 80 atm and the same temperature $\eta = 361$ micropoises.

The kinetic theory of gases ascribes viscosity to a transfer of momentum from one moving plane to another. Considerations of this momentum transfer between flow planes show that for ideal gases η is related to the density of the gas ρ, the mean free path l, and the average velocity of the gas molecules v by the equation

$$\eta = \frac{1}{3} vl\rho \tag{90}$$

Since the mean free path varies inversely as the density of the gas, it may be concluded that the viscosity of an ideal gas should be independent of density, and hence also the pressure. This deduction has been confirmed at relatively low pressures.

Equation (90) may be employed to calculate the mean free path directly from the viscosity coefficients. To do this we need only substitute the value of v from Eq. (43), in which case l becomes

$$\begin{aligned} l &= \frac{3\eta}{v\rho} = \frac{3\eta}{0.921\,\rho\sqrt{3\,RT/M}} \\ &= \frac{1.88\,\eta}{\rho\sqrt{RT/M}} \end{aligned} \tag{91}$$

Once l is thus found, it may be inserted into Eq. (48) to obtain the molecular diameter σ of the gas molecules involved.

THE VISCOSITY OF LIQUIDS

Liquids exhibit much greater resistance to flow than gases, and consequently they have much higher viscosity coefficients. The viscosity coefficients of gases increase with temperature, while those of most liquids decrease. Again, we have seen that the viscosity coefficients for gases at

moderate pressures are essentially independent of pressure, whereas with liquids increase of pressure leads to an increase in viscosity.

Most methods employed for the measurement of the viscosity of liquids are based on either the Poiseuille or Stokes equations. The Poiseuille equation for the coefficient of viscosity of a fluid is

$$\eta = \frac{\pi P r^4 t}{8 L V} \tag{92}$$

where V is the volume of liquid of viscosity η which flows in time t through a capillary tube of radius r and length L under a pressure head of P dynes per square centimeter. This equation has been verified repeatedly. To determine the viscosity of a liquid by this equation it is not always necessary to measure all the quantities indicated when once the viscosity of some reference liquid, usually water, is known with accuracy. If we measure the time of flow of the same volume of two different liquids through the same capillary, then according to the Poiseuille equation the ratio of the viscosity coefficients of the two liquids is given by

$$\frac{\eta_1}{\eta_2} = \frac{\pi P_1 r^4 t_1}{8 L V} \cdot \frac{8 L V}{\pi P_2 r^4 t_2} = \frac{P_1 t_1}{P_2 t_2}$$

Since the pressures P_1 and P_2 are proportional to the densities of the two liquids ρ_1 and ρ_2, we may write also

$$\frac{\eta_1}{\eta_2} = \frac{P_1 t_1}{P_2 t_2} = \frac{\rho_1 t_1}{\rho_2 t_2} \tag{93}$$

Consequently, once ρ_1, ρ_2, and η_2 are known, determination of t_1 and t_2 permits the calculation of η_1, the viscosity coefficient of the liquid under consideration.

The quantities t_1 and t_2 are most conveniently measured with an Ostwald viscometer, Figure 1–14. A definite quantity of liquid is introduced into the viscometer immersed in a thermostat and is then drawn up

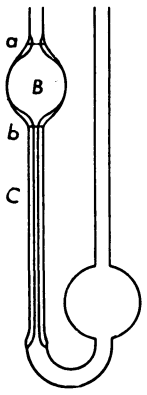

Figure 1–14. Ostwald viscometer.

by suction into bulb B until the liquid level is above the mark a. The liquid is then allowed to drain, and the time necessary for the liquid level to fall from a to b is measured with a stopwatch. The viscometer is now cleaned, the reference liquid added, and the whole operation repeated. In this simple manner t_1 and t_2 are obtained, and the viscosity of the liquid is calculated by Eq. (93).

Stokes's law is concerned with the fall of bodies through fluid media. A *spherical* body of radius r and density ρ, falling under gravity through a fluid of density ρ_m, is acted on by the gravitational force f_1,

$$f_1 = \frac{4}{3}\pi r^3(\rho - \rho_m)g \tag{94}$$

where g is the acceleration of gravity. This force, which tends to accelerate the body falling through the fluid medium, is opposed by frictional forces within the medium which increase with increase in velocity of the falling body. Eventually a uniform rate of fall is reached at which the frictional forces become equal to the gravitational force, and thereafter the body will continue to fall with a *constant velocity* v. Sir George G. Stokes showed that, for a spherical body falling under the conditions of constant uniform velocity, the force of friction, f_2, is given by

$$f_2 = 6\,\pi r \eta v \tag{95}$$

Equating the gravitational and frictional forces, we see that

$$\frac{4}{3}\pi r^3(\rho - \rho_m)g = 6\,\pi r \eta v$$

$$\eta = \frac{2\,r^2(\rho - \rho_m)g}{9\,v} \tag{96}$$

This equation, known as *Stokes's law*, is applicable to the fall of spherical bodies in all types of fluid media provided the radius of the falling body r is large compared with the distance between the molecules of the fluid. When r is smaller than the distance between molecules there is a tendency for the falling body to "drop" or "channel," and the equation is no longer applicable.

Stokes's law is the basis of the falling sphere viscometer. The viscometer consists of a vertical cylindrical tube filled with the liquid under test and immersed in a thermostat at the desired temperature. A steel ball, of density ρ and a diameter suitable to give a slow rate of fall, is now dropped through the neck of the tube, and the time of fall between two marks is determined with a stopwatch. If the process is repeated with a liquid of known density and viscosity, then Eq. (96) yields for the ratio

of the two viscosities

$$\frac{\eta_1}{\eta_2} = \frac{(\rho - \rho_{m_1})t_1}{(\rho - \rho_{m_2})t_2} \tag{97}$$

Therefore, knowing one of the viscosities, the density of the ball, and the densities of the two liquids, the viscosity of the liquid under study can be calculated by means of Eq. (97) from the observed values of t_1 and t_2.

A term frequently employed in connection with viscosity is *fluidity*. The fluidity, ϕ, of a substance is merely the reciprocal of the viscosity coefficient, namely, $\phi = 1/\eta$.

Table 1–9 gives the viscosity coefficients in centipoises of several liquids at various temperatures. With very rare exceptions (liquid carbon dioxide at low temperatures), the viscosity of a liquid decreases with increase in temperature. Various equations have been proposed to represent η as a function of T, of which the simplest is

TABLE 1–9. VISCOSITY COEFFICIENTS OF LIQUIDS
(Centipoises)

Liquid	0°C	20°C	40°C	60°C	80°C
Benzene	0.912	0.652	0.503	0.392	0.329
Carbon tetrachloride	1.329	0.969	0.739	0.585	0.468
Ethyl alcohol	1.773	1.200	0.834	0.592	—
Ethyl ether	0.284	0.233	0.197	0.140	0.118
Mercury	1.685	1.554	1.450	1.367	1.298
Water	1.792	1.002	0.656	0.469	0.357

$$\log \eta = \frac{A}{T} + B \tag{98}$$

A and B are constants, and T is the absolute temperature. This equation holds quite well for a large number of pure liquids.

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PROBLEMS

Note: Unless otherwise indicated, assume all gases in the following problems to be ideal.

1. Four grams of CH_4 at 27.0°C and a pressure of 2.50 atm occupy a volume of 2.46 liters. Calculate the value of the gas constant R in cc-atm degree^{-1} mole^{-1}.

2. Two grams of O_2 are confined in a 2-liter vessel by a pressure of 1.21 atm. What is the temperature of the gas in °C? *Ans.* 200°C.

3. A certain gas occupies a volume of 6 liters under a pressure of 720 mm Hg at 25°C. What volume will this gas occupy under standard conditions of temperature and pressure?

4. At 0°C and under a pressure of 1000 mm Hg, a given weight of N_2 occupies a volume of 1 liter. At −100°C the same weight of gas under the same pressure occupies a volume of 0.6313 liter. Calculate the absolute zero in degrees centigrade, and give reasons for the observed difference from the accepted value.
Ans. −271.2°C.

5. Find the density of ammonia gas at 100°C when confined by a pressure of 1600 mm Hg.

6. Assuming that dry air contains 79% N_2 and 21% O_2 by volume, calculate the density of moist air at 25°C and 1 atm pressure when the relative humidity is 60%. The vapor pressure of water at 25°C is 23.76 mm Hg.
Ans. 1.171 g/liter.

7. The composition of a mixture of gases in percentage by volume is 30% N_2, 50% CO, 15% H_2, and 5% O_2. Calculate the percentage by weight of each gas in the mixture.

8. (a) Find the weight of helium gas necessary to fill a balloon whose capacity is 1,000,000 liters at 1 atm pressure and 25°C. (b) What will be the lifting power of this balloon in grams per liter in the air described in problem 6? (c) What will be its total lifting power in kilograms?

9. At 27°C, 500 cc of H_2, measured under a pressure 400 mm Hg, and 1000 cc of N_2, measured under a pressure of 600 mm Hg, are introduced into an evacuated 2-liter flask. Calculate the resulting pressure. *Ans.* 400 mm Hg.

10. Find the total pressure exerted by 2 g of ethane and 3 g of CO_2 contained in a 5-liter vessel at 50°C.

11. The time required for a given volume of N_2 to diffuse through an orifice is 35 sec. Calculate the molecular weight of a gas which requires 50 sec to diffuse through the same orifice under identical conditions. *Ans.* 57.15 g/mole.

12. Compare the times of diffusion through a given orifice, and under the same conditions of temperature and pressure, of the gases H_2, NH_3, and CO_2 relative to that of N_2.

13. By means of a mercury vapor pump a vacuum of 10^{-7} mm Hg is obtained within a certain apparatus. Calculate the number of molecules which still remain in 1 cc of the apparatus at 27°C. *Ans.* 3.24×10^9.

14. What is the total kinetic energy of translation in ergs of 2 moles of a perfect gas at 27°C? In calories?

15. Calculate the root-mean-square velocity in centimeters per second of N_2 molecules at 27°C. Repeat the calculation at 127°C.

16. Calculate the root-mean-square, average, and most probable velocities in centimeters per second of H_2 molecules at 0°C.

17. The molecular diameter of CO is 3.19×10^{-8} cm. At 300°K and a pressure of 100 mm Hg what will be (a) the number of molecules colliding per cubic centimeter per second; (b) the number of bimolecular collisions; and (c) the mean free path of the gas? *Ans.* (a) 2.23×10^{27}; (b) 1.12×10^{27}; (c) 6.87×10^5 cm.

18. Repeat the calculations called for in problem 17 for the same temperature but a pressure of 200 mm Hg. How pronounced is the effect of pressure on the quantities sought?

19. Repeat the calculations called for in problem 17 for a pressure of 100 mm Hg and a temperature of 600°K. How pronounced is the effect of temperature on the quantities calculated?

20. By use of the van der Waals equation, find the temperature at which 3 moles of SO_2 will occupy a volume of 10 liters at a pressure of 15 atm. *Ans.* 350°C.

21. (a) Using the van der Waals equation, calculate the pressure developed by 100 g of CO_2 contained in a volume of 5 liters at 40°C. (b) Compare this value with that calculated using the ideal gas law.

22. At 0°C and under a pressure of 100 atm the compressibility factor of O_2 is 0.927. Calculate the weight of O_2 necessary to fill a gas cylinder of 100-liter capacity under the given conditions.

23. Using the Beattie-Bridgeman equation explicit in volume, calculate the density in grams per cubic centimeter of N_2 at 0°C and 100 atm pressure. *Ans.* 0.127 g/cc.

24. Utilizing the virial coefficients listed in Table 1–4, determine analytically the pressure at which the PV vs. P plot for N_2 at −50°C exhibits a minimum.

25. Employing the Kamerlingh Onnes equation of state, find the compressibility factors of CO at −50°C and pressures of (a) 10, (b) 100, and (c) 1000 atm pressure. *Ans.* (a) $z = 0.981$.

26. The following data were taken in measuring the molecular weight of a certain gas by the Regnault method:

Wt. of evacuated bulb	= 42.5050 g
Wt. of bulb + gas	= 43.3412 g
Wt. of bulb + H_2O	= 365.31 g
Temperature	= 25°C
Pressure (corrected)	= 745 mm

Find the molecular weight of the gas.

27. In a Victor Meyer experiment involving the determination of the molecular weight of ethyl alcohol the data obtained were

Wt. of liquid taken	= 0.1211 g
Volume of air measured over water	= 67.30 cc
Temperature	= 28.0°C
Atmospheric pressure	= 755.2 mm Hg (corrected)
Vapor pressure of water at 28°C (from tables)	= 28.3 mm Hg

From these data (a) calculate the molecular weight of the alcohol, and (b) compare the result with that calculated from the atomic weights.

Ans. (a) 46.5 g/mole.

28. The elementary analysis of a compound yielded the following results: C, 39.98%; H, 6.72%; and O, 53.30%. In a Victor Meyer determination 0.1510 g of the vaporized compound displaced 33.8 cc of air measured at 25°C over H_2O and at a barometric pressure of 745 mm. Calculate (a) the empirical formula, (b) the approximate molecular weight, and (c) the molecular formula of the compound.

29. A sample of vapor weighing 0.180 g occupies a volume of 53.1 cc at 27°C and 760 mm pressure (corrected). The critical pressure of the vapor is 47.7 atm, while the critical temperature is 288.5°C. By use of the Berthelot equation calculate the molecular weight of the vapor, and compare the result with that calculated by the ideal gas law.

30. The densities of CH_4 at 0°C were measured at several pressures with the following results:

Pressure (atm)	Density (g/liter)
¼	0.17893
½	0.35808
¾	0.53745
1	0.71707

Find the exact molecular weight of CH_4. *Ans.* 16.03 g/mole.

31. How much heat will be required to raise the temperature of 3 moles of helium from 0°C to 100°C at (a) constant volume and (b) constant pressure?

32. Utilizing the data given in Table 1–4, find the Boyle temperature of carbon monoxide.

33. (a) Calculate the van der Waals constants for C_2H_6 from the critical temperatures and pressures listed in Table 1–8. (b) Using the constants thus calculated find the pressure exerted by 10 g of C_2H_6 when contained in a liter flask at 13°C. *Ans.* (b) 7.39 atm.

34. The van der Waals constants for HCl are $a = 3.67$ atm-liter^2 mole^{-2}, and $b = 40.8$ cc mole^{-1}. Find the critical constants of this substance.

35. A modified form of the van der Waals equation (Berthelot) is

$$\left(P + \frac{n^2\alpha}{TV^2}\right)(V - n\beta) = nRT$$

where all the terms have their usual significance, and α and β are constants. Deduce the expressions for α, β, and R in terms of the critical constants.

36. Calculate the critical density of methyl alcohol from the following data:

t°C	P (atm)	$d_{\text{liq.}}$ (g/cc)	$d_{\text{vap.}}$ (g/cc)
150	13.57	0.6495	0.01562
225	61.25	0.4675	0.1003

The critical temperature is 240.0°C.

37. Compare the reduced pressures of N_2 and NH_3 when each exerts a pressure of 100 atm. *Ans.* N_2: 2.99; NH_3: 0.90.

38. Compare the reduced temperatures of ethylene and H_2 at 27°C.

39. Set up the reduced equation of state for the modified van der Waals equation given in problem 35.

40. The equation of state of a liquid gives the volume as a function of the temperature and pressure. Further, the thermal coefficient of expansion, α, is defined as

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

while the compressibility coefficient, β, is defined as

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

Assuming α to be independent of temperature and β to be independent of pressure, deduce the expression for V as a function of T and P.

41. (a) For liquid benzene $\alpha = 1.24 \times 10^{-3}$ degree^{-1} at 20°C and 1 atm pressure. Utilizing the equation derived in problem 40 and assuming α to be independent of temperature, find the percentage change in volume of a sample of benzene on being heated at 1 atm pressure from 20 to 50°C. (b) What would be the percentage change in volume of an ideal gas heated over the same temperature interval at constant pressure? *Ans.* (a) 3.8%; (b) 10.2%.

42. (a) For liquid benzene $\beta = 9.30 \times 10^{-5}$ atm^{-1} at 20°C and 1 atm pressure. Utilizing the equation derived in problem 40 and assuming β to be independent of pressure, find the percentage change in volume of a sample of benzene on being compressed at constant temperature from a pressure of 1 atm to a pressure of

11 atm. (b) What would be the percentage change in volume of an ideal gas compressed over the same pressure interval at constant temperature?

43. (a) Suppose that a sample of benzene, initially at 20°C and 1 atm pressure, is subjected to a pressure of 11 atm at 50°C. Assuming α and β to be constant, find the percentage change in volume of the benzene. (b) What would be the percentage change in volume exhibited by an ideal gas on being subjected to the same change in pressure and temperature?

44. The viscosity coefficient of gaseous Cl_2 at 1 atm pressure and 20°C is 147.0 micropoises. Find the molecular diameter of the chlorine molecule.

Ans. 4.30×10^{-8} cm.

45. Consider two parallel layers of NH_3 gas, one of large area and stationary, and the other 10 cm^2 in area and moving at a fixed distance of 1×10^{-6} cm above the first. What force in dynes will be required to keep the upper layer moving with a velocity of 5 cm per second when the pressure of the gas is 10 mm Hg and the temperature is 300°K? The molecular diameter of the NH_3 molecule is 3.0×10^{-8} cm.

46. A gas whose viscosity is 200 micropoises flows through a capillary tube 2 mm in diameter and 2 meters long. If 5 liters of gas pass through the tube every 10 seconds, what must be the pressure head under which the gas is flowing?

Ans. 5.09×10^5 dynes/cm^2.

47. The time of efflux of H_2O through an Ostwald viscometer is 1.52 minutes. For the same volume of an organic liquid of density 0.800 g/cc the time is 2.25 minutes. Find the viscosity of the liquid relative to that of water and its absolute value in millipoises. The temperature is 20°C.

48. A steel ball of density 7.90 g/cc and 4 mm diameter requires 55 seconds to fall a distance of 1 meter through a liquid of density 1.10 g/cc. Calculate the viscosity of the liquid in poises.

49. A sphere of radius 5×10^{-2} cm and density of 1.10 g/cc falls at constant velocity through a liquid of density 1.00 g/cc and viscosity of 1.00 poise. What is the velocity of the falling sphere? *Ans.* 5.45×10^{-2} cm/sec.

50. Suppose that all the conditions given in problem 49 are the same except that the density of the sphere is 0.90 g/cc. What is the velocity of the sphere in this case? Explain the significance of the result.

51. Using the data for the viscosity coefficients of C_2H_5OH as a function of temperature given in Table 1–9, find for this substance the constants A and B in Eq. (98).