Equation of state
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States of Matter

•Gases, liquid and crystalline solid are the three primary state of matter or phase.

Solids with high vapor pressures, such as iodine and camphor, can pass directly from the solid to the gaseous state without melting at room temperature. This process is known as *sublimation*

The Gaseous State

a *pressure*—a force per unit area—expressed in dynes/cm^2.

Pressure is also recorded in atmospheres or in millimeters of mercury

Another important characteristic of a gas, its *volume*, is usually expressed in liters or cubic centimeters (1 cm^3 = 1 mL)

The temperature involved in the gas equations is given according the absolute or Kelvin scale.

Zero degrees on the centigrade scale is equal to 273.15 Kelvin (K).

The Ideal Gas Law

the gas laws formulated by Boyle, Charles, and Gay-Lussac

an ideal situation where no intermolecular interactions exist and collisions are perfectly elastic, and thus no energy is exchanged upon collision.

Boyle's law relates the volume and pressure of a given mass of gas at constant temperature,

$$P \propto \frac{1}{V}$$

or

$$PV = k \qquad\qquad (2\text{–}2)$$

The law of Gay-Lussac and Charles states that the volume and absolute temperature of a given mass of gas at constant pressure are directly proportional,

$$V \propto T$$
$$V = kT \qquad\qquad (2\text{–}3)$$

These equations can be combined to obtain the familiar relationship

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

In equation (2-4), P_1, V_1, and T_1 are the values under one set of conditions and P_2, V_2, and T_2 the values under another set.

Example 2-1

The Effect of Pressure Changes on the Volume of an Ideal Gas

In the assay of ethyl nitrite spirit, the nitric oxide gas that is liberated from a definite quantity of spirit and collected in a gas burette occupies a volume of 30.0 mL at a temperature of 20°C and a pressure of 740 mm Hg. Assuming the gas is ideal, what is the volume at 0°C and 760 mm Hg? Write

$$\frac{740 \times 30.0}{273 + 20} = \frac{760 \times V_2}{273}$$

$$V_2 = 27.2 \text{ mL}$$

From equation (2-4) it is seen that PV/T under one set of conditions is equal to PV/T under another set, and so on. Thus, one reasons that although P, V, and T change, the ratio PV/T is constant and can be expressed mathematically as

$$\frac{PV}{T} = R$$

or

$$PV = RT \tag{2-5}$$

in which R is the constant value for the PV/T ratio of an ideal gas. This equation is correct only for 1 mole (i.e., 1 g molecular weight) of gas; for n moles it becomes

$$PV = \bar{n}RT \tag{2-6}$$

Equation (2-6) is known as the *general ideal gas law*, and because it relates the specific conditions or state, that is, the pressure, volume, and temperature of a given mass of gas, it is called the *equation of state* of an ideal gas.

Real gases do not interact without energy exchange, and therefore do not follow the laws of Boyle and of Gay-Lussac and Charles as ideal gases are assumed to do.

To obtain a numerical value for R.

If 1 mole of an ideal gas is chosen, its volume under standard conditions of temperature and pressure (i.e., at 0°C and 760 mm Hg) has been found by experiment to be 22.414 liters. Substituting this value in equation (2-6), we obtain

$$1 \text{ atm} \times 22.414 \text{ liters} = 1 \text{ mole} \times R \times 273.16 \text{ K}$$
$$R = 0.08205 \text{ liter atm/mole K}$$

The molar gas constant can also be given in energy units by expressing the pressure in dynes/cm² (1 atm = 1.0133×10^6 dynes/cm²) and the volume in the corresponding units of cm³ (22.414 liters = 22,414 cm³). Then

$$R = \frac{PV}{T} = \frac{(1.0133 \times 10^6) \times 22.414}{273.16}$$

$$= 8.314 \times 10^6 \text{ erg/mole K}$$

or, because 1 joule = 10^7 ergs,

$$R = 8.314 \text{ joules/mole K}$$

The constant can also be expressed in cal/mole deg, employing the equivalent 1 cal = 4.184 joules:

$$R = \frac{8.314 \text{ joules/mole deg}}{4.184 \text{ joules/cal}} = 1.987 \text{ cal/mole deg}$$

Example 2-2

Calculation of Volume Using the Ideal Gas Law

What is the volume of 2 moles of an ideal gas at 25°C and 780 mm Hg?

$$(780 \text{ mm}/760 \text{ mm atm}^{-1}) \times V$$

$$= 2 \text{ moles} \times (0.08205 \text{ liter atm/mole deg}) \times 298 \text{ K}$$

$$V = 47.65 \text{ liters}$$

Molecular Weight

The approximate molecular weight of a gas can be determined by use of the ideal gas law. The number of moles of gas n is

replaced by its equivalent g/M, in which g is the number of grams of gas and M is the molecular weight:

$$PV = \frac{g}{M}RT \qquad\qquad (2\text{–}7)$$

or

$$M = \frac{gRT}{PV} \qquad\qquad (2\text{–}8)$$

Example 2-3

Molecular Weight Determination by the Ideal Gas Law

If 0.30 g of ethyl alcohol in the vapor state occupies 200 mL at a pressure of 1 atm and a temperature of 100°C, what is the molecular weight of ethyl alcohol? Assume that the vapor behaves as an ideal gas. Write

$$M = \frac{0.30 \times 0.082 \times 373}{1 \times 0.2}$$

$$M = 46.0 \text{ g/mole}$$

Kinetic Molecular Theory

some of the more important statements of the theory:

1.   Gases are composed of particles called atoms or *molecules*, the total volume of which is so small as to be negligible This condition is approximated in actual gases only at low pressures and high temperatures

2.   The particles of the gas do not attract one another, this statement applies only at low pressures.

3.   The particles exhibit continuous random motion owing to their kinetic energy. The average kinetic energy, E, is directly proportional to the absolute temperature of the gas, or $E = (3/2)RT$.

4.   The molecules exhibit perfect elasticity; that is, there is no net loss of speed or transfer of energy after they collide with one another and with the molecules in the walls of the confining vessel, which latter effect accounts for the gas pressure.

From these and other postulates, the following *fundamental kinetic equation* is derived:

$$PV = \frac{1}{3}nm\overline{c^2} \qquad\qquad (2\text{–}9)$$

where P is the pressure and V the volume occupied by any number n of molecules of mass m having an average velocity [C with bar above].

$$\mu = \sqrt{\frac{3RV}{nm}} \qquad (2\text{–}10)$$

Restricting this case to 1 mole of gas, we find that PV becomes equal to RT from the equation of state (2-5), n becomes Avogadro's number N_A, and N_A multiplied by the mass of one molecule becomes the molecular weight M. The root mean square velocity is therefore given by

$$\mu = \sqrt{\frac{3RT}{M}} \qquad (2\text{–}11)$$

Example 2-4
Calculation of Root Mean Square Velocity

What is the root mean square velocity of oxygen (molecular weight, 32.0) at 25°C (298 K)?

$$\mu = \sqrt{\frac{3 \times 8.314 \times 10^7 \times 298}{32}} = 4.82 \times 10^4 \text{cm/sec}$$

Because the term nm/V is equal to density, we can write equation (2-10) as

$$\mu = \sqrt{\frac{3P}{d}} \qquad (2\text{--}12)$$

Remembering that density is defined as a mass per unit volume, we see that the rate of diffusion of a gas is inversely proportional to the square root of its density.

The van der Waals Equation for Real Gases

The fundamental kinetic equation (2-9) is found to compare with the ideal gas equation because the kinetic theory is based on the assumptions of the ideal state.
real gases are not composed of infinitely small and perfectly elastic nonattracting spheres.
they are composed of molecules of a finite volume that tend to attract one another.
A number of such expressions have been suggested, the *van der Waals equation* being the best known of these.
For 1 mole of gas, the van der Waals equation is written as

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \qquad (2\text{--}13)$$

For the more general case of n moles of gas in a container of volume V, equation (2-13) becomes

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \qquad (2\text{--}14)$$

The term a/V^2 accounts for the *internal pressure* per mole resulting from the intermolecular forces of
   attraction between the molecules

b accounts for the incompressibility of the molecules,

When the volume of a gas is large, the molecules are well dispersed. Under these

conditions, a/V^2 and b become insignificant with respect to P and V, respectively. Under these

conditions, the van der Waals equation for 1 mole of gas reduces to the ideal gas equation, $PV = RT$,

Example 2-5

Application of the van der Waals Equation

A 0.193-mole sample of ether was confined in a 7.35-liter vessel at 295 K. Calculate the pressure produced using (a) the ideal gas equation and (b) the van der Waals equation. The van der Waals a value for ether is 17.38 liter^2 atm/mole^2; the b value is 0.1344 liter/mole. To solve for pressure, the van der Waals equation can be rearranged as follows:

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

(a)

$$P = \frac{0.193 \text{ mole} \times 0.0821 \text{ liter atm/deg mole} \times 295 \text{ deg}}{7.35 \text{ liter}}$$

$$= 0.636 \text{ atm}$$

(b)

$$P = \frac{0.193 \text{ mole} \times 0.0821 \text{ liter atm/deg mole} \times 295 \text{ deg}}{7.35 \text{ liter} - (0.193 \text{ mole}) \times (0.1344 \text{ liter/mole})}$$

$$- \frac{17.38 \text{ liter}^2 \text{ atm/mole}^2 \, (0.193 \text{ mole})^2}{(7.35 \text{ liter})^2}$$

$$= 0.626 \text{ atm}$$

Example 2-6

Calculation of the van der Waals Constants

Calculate the pressure of 0.5 mole of CO_2 gas in a fire extinguisher of 1-liter capacity at 27°C using the ideal gas equation and the van der Waals equation. The van der Waals constants can be calculated from the critical temperature T_c and the critical pressure P_c (see the section Liquefaction of Gases for definitions):

$$a = \frac{27 R^2 T_c^2}{64 P_c} \quad \text{and} \quad b = \frac{R T_c}{8 P_c}$$

The critical temperature and critical pressure of CO_2 are 31.0°C and 72.9 atm, respectively. Using the ideal gas equation, we obtain

$$P = \frac{nRT}{V} = \frac{0.5 \text{ mole} \times 0.0821 \text{ liter atm/deg mole} \times 300.15 \text{ deg}}{1 \text{ liter}}$$

$$= 12.32 \text{ atm}$$

Using the van der Waals equation, we obtain

$$a = \frac{27 \times (0.0821 \text{ liter atm/deg mole})^2 \times (304.15 \text{ deg})^2}{64 \times 72.9 \text{ atm}}$$

$$= 3.608 \text{ liter}^2 \text{ atm/mole}^2$$

$$b = \frac{(0.0821 \text{ liter atm/deg mole}) \times 304.15 \text{ deg}}{8 \times 72.9 \text{ atm}}$$

$$= 0.0428 \text{ liter/mole}$$

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

$$= \frac{(0.5 \text{ mole} \times 0.821 \text{ liter atm/deg mole}) \times 300.15 \text{ deg}}{1 \text{ liter} - (0.5 \text{ mole} \times 0.0428821 \text{ liter/mole})}$$

$$- \frac{(3.608 \text{ liter}^2 \text{ atm/mole}^2) \times 0.5 \text{ mole}^2}{(1 \text{ liter})^2}$$

$$= 11.69 \text{ atm}$$