

1

Gaseous State

1.1 THE THREE STATES OF MATTER

Introduction

In order to determine experimentally the properties of substances, we deal with the aggregates of molecules as they occur in nature. It is the aggregations of molecules which come within the scope of human experience that constitute what is known as matter. The various kinds of substances that make up matter can be divided roughly into three categories, namely, gases, liquids and solids. These are called the three states of matter. These states can be considered to arise as a result of competition between two opposing molecular forces, namely, the forces of attraction which tend to hold the molecules together, and the disruptive forces due to the thermal energy of molecules.

Gaseous State

If the thermal energy is much greater than the forces of attraction, then we have matter in its gaseous state. Molecules in the gaseous state move with very large speeds and the forces of attraction amongst them are not sufficient to bind the molecules at one place, with the result that the molecules move practically independent of one another. Because of this feature, gases are characterized by marked sensitivity of volume change with change in temperature and pressure. There exists no boundary surface and, therefore, gases tend to fill completely any available space, resulting in no fixed volume to the gaseous state.

Liquid State

If the forces of attraction are greater than the thermal energy, we have matter in the liquid state. Molecules in the liquid state too have kinetic energy but they cannot go very far away because of the larger forces of attraction amongst them. Due to this feature, liquids have definite volume, but no definite shape. They take the shape of the vessel in which they are placed. In general, liquids are more dense and less compressible than gases.

Solid State

If the forces of attraction between molecules are much greater than the thermal energy, the positions of the molecules remain fixed and we have matter in the solid state. The molecules in the solid state, therefore, do not possess any translational energy, but have only vibrational energy since they can vibrate about their mean positions. Extremely large forces of attraction exist amongst them. That is why solids differ markedly from liquids and gases in respect of size, shape and volume. Solids, in general, have definite size, shape and volume.

Comments on the Gaseous System

Of all the three states of molecular aggregation, only the gaseous state allows a comparatively simple quantitative description. We are generally concerned with the relations among four properties, namely, mass, pressure, volume and



temperature. A system is in a definite state (or condition) when all the properties of the system have definite values. It is not necessary to specify each and every property of the matter as these are interrelated. The relationship which connects the above four variables is known as the *equation of state* of the system. For gases, only three of these must be specified to describe the state, the fourth automatically has a fixed value and can be calculated from the equation of state established from the experimental behaviour of the system.

1.2 EXPERIMENTALLY DERIVED GASEOUS LAWS

Boyle's Law

At constant temperature, the volume of a definite mass of a gas is inversely proportional to its pressure, that is,

$$V \propto \frac{1}{p} \quad \text{i.e.,} \quad V = \frac{K}{p} \quad \text{or} \quad pV = K \quad (1.2.1)$$

where K is a constant whose value depends upon (i) nature of the gas, (ii) temperature of the gas, and (iii) mass of the gas. For a given mass of a gas at constant temperature, Boyle's law gives

$$p_1 V_1 = p_2 V_2 \quad (1.2.2)$$

where V_1 and V_2 are volumes at pressures p_1 and p_2 , respectively.

Graphical Representation

Equation (1.2.1) can be represented graphically by plotting pressures as ordinates and the corresponding volumes as abscissae (Fig. 1.2.1). The nature of the curve is a rectangular hyperbola. The general term *isothermal* or *isotherm* (meaning at constant temperature) is used to describe these plots.

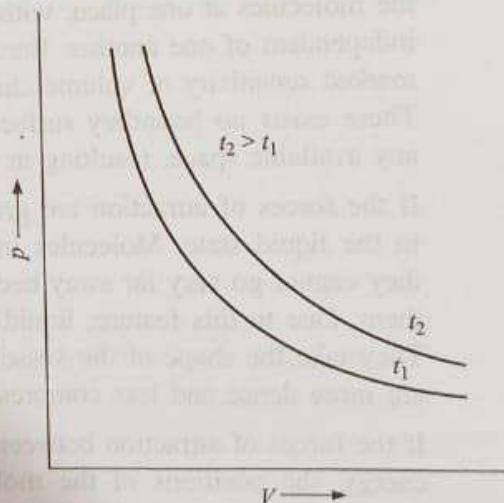


Fig. 1.2.1 A Typical variation of pressure of a gas with volume

Charles Law

Charles made measurements of the volume of a fixed mass of a gas at various temperatures under the condition of constant pressure and found that the volume of a fixed mass of a gas at constant pressure is a linear function of its Celsius temperature. This can be expressed as

$$V_t = a + bt \quad (1.2.3)$$

where t is Celsius temperature and a and b are constants.

Graphical Representation

Equation (1.2.3) has been plotted in Fig. 1.2.2. The intercept on the vertical axis is a and it is equal to V_0 , the volume at 0°C . The slope of the plot is the derivative

$$b = \left(\frac{\partial V_t}{\partial t} \right)_p$$

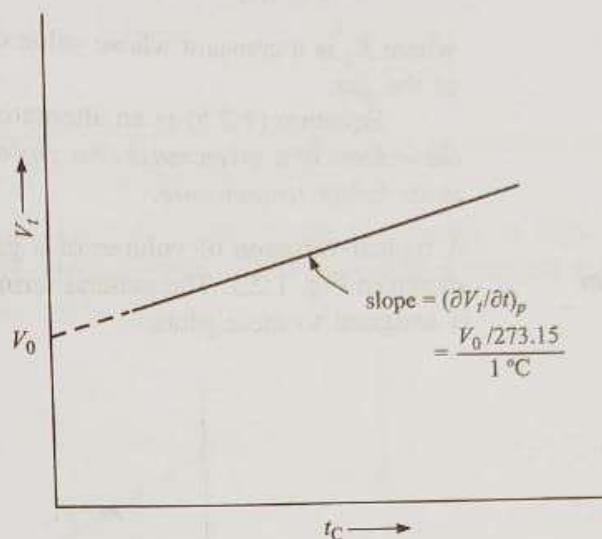


Fig. 1.2.2 A typical variation of volume of a gas with temperature expressed in $^\circ\text{C}$

Alternative Form of Charles Law

Experimental data shows that for each Celsius degree rise in temperature, the volume of a gas expands $1/273.15$ of its volume at 0°C . If V_0 is the volume of a gas at 0°C , then b is given by

$$b = \left(\frac{V_0 / 273.15}{1^\circ\text{C}} \right)$$

With this, Eq. (1.2.3) becomes

$$V_t = V_0 + \left(\frac{V_0 / 273.15}{1^\circ\text{C}} \right) t$$

$$\text{or } V_t = V_0 \left(1 + \frac{t/^\circ\text{C}}{273.15} \right) = V_0 \left(\frac{273.15 + t/^\circ\text{C}}{273.15} \right) \quad (1.2.4)$$

$$\text{or } V_T = V_0 \frac{(T/\text{K})}{273.15} \quad (T \text{ is kelvin temperature})^\dagger$$

[†]It is convenient to use the absolute temperature scale on which temperatures are measured in kelvin (K). A reading on this scale is obtained by adding 273.15 to the Celsius value. Temperature on the kelvin scale is denoted by T . Thus

$$T/\text{K} = 273.15 + t/^\circ\text{C}$$

$$\text{i.e. } V_T = \left(\frac{V_0}{273.15 \text{ K}} \right) T$$

Since V_0 , the volume of the gas at 0°C , has a constant value at a given pressure, the above relation can be expressed as

$$V = K_2 T \quad (1.2.5)$$

where K_2 is a constant whose value depends upon the nature, mass and pressure of the gas.

Equation (1.2.5) is an alternative form of Charles law according to which the volume of a given mass of a gas at constant pressure is directly proportional to its kelvin temperature.

A typical variation of volume of a gas with change in its kelvin temperature is shown in Fig. 1.2.3. The general term *isobar*, which means at constant pressure, is assigned to these plots.

Graphical Representation

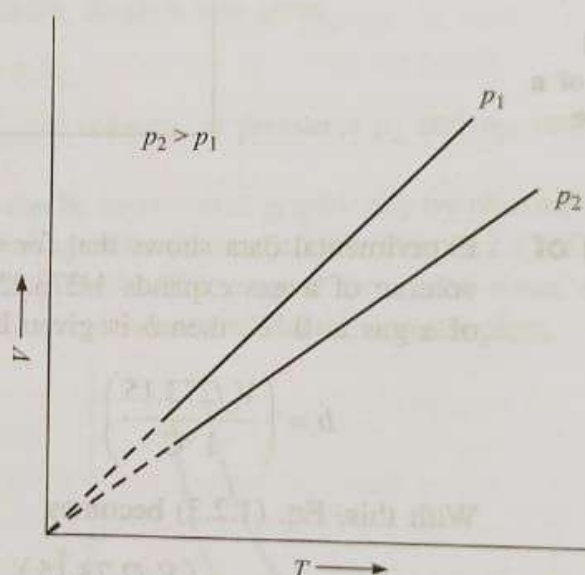


Fig. 1.2.3 Variation of volume of a gas with kelvin temperature

Comment on Zero Kelvin

Since volume is directly proportional to kelvin temperature, the volume of a gas should theoretically be zero at kelvin zero. However, gases liquefy and then solidify before this low temperature is reached. In fact, no substance exists as a gas at a temperature near kelvin zero, though the straight-line plots can be extrapolated to zero volume. The temperature that corresponds to zero volume is -273.15°C .

Gay-Lussac's Law: Dependence of Pressure on Temperature

An expression similar to volume dependence of gas on temperature has been derived for the pressure dependence also. The pressure of a given mass of a gas at constant volume varies linearly with Celsius temperature.

$$p_t = a + bt \quad (1.2.6)$$

where $a = p_0$ and $b = (\partial p_t / \partial t)_V$. The value of the latter can be determined



experimentally and is found to be $(p_0/273.15^\circ\text{C})$. Thus, Eq. (1.2.6) modifies to

$$p_t = p_0 + \left(\frac{p_0}{273.15} \right) (t/^\circ\text{C})$$

$$\text{Therefore } p_t = p_0 \left(\frac{273.15 + (t/^\circ\text{C})}{273.15} \right) = \left(\frac{p_0}{273.15 \text{ K}} \right) T$$

$$\text{or } p_t \propto T$$

(1.2.7)

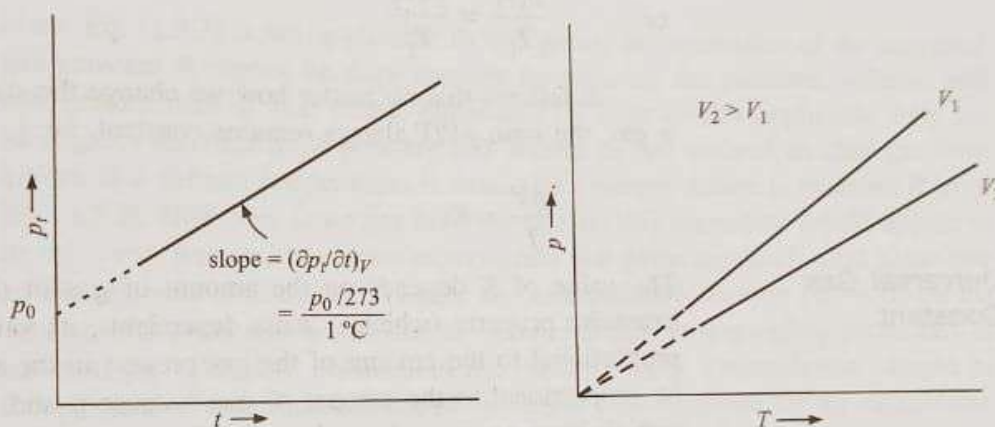
that is, the pressure of a given mass of a gas at constant volume is directly proportional to its kelvin temperature.

Equations (1.2.6) and (1.2.7) are shown graphically in Figs. 1.2.4 and 1.2.5, respectively. The general term *isochor* (meaning at constant volume) is given to the plots of Fig. 1.2.5.

Graphical Representations

Fig. 1.2.4 A typical variation of pressure of a gas with temperature expressed in $^\circ\text{C}$

Fig. 1.2.5 A typical variation of pressure of a gas with kelvin temperature



Graham's Law of Diffusion

The phenomenon of diffusion may be described as the tendency for any substance to spread uniformly throughout the space available to it. Diffusion through fine pores is called effusion.

According to Graham's law of diffusion, the rate of diffusion (or effusion) of a gas is inversely proportional to the square root of its density or molar mass. If r_1 and r_2 are the rates of diffusion of two gases under identical conditions, whose densities under the given conditions are ρ_1 and ρ_2 , respectively, then from Graham's law,

$$\frac{r_1}{r_2} = \sqrt{\frac{\rho_2}{\rho_1}} \quad \text{or} \quad \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} \quad (1.2.8)$$

where M_1 and M_2 are the respective molar masses of the two gases.

1.3 EQUATION OF STATE

Derivation of Equation of State

The results of the laws of Boyle and Charles can be combined into an expression which represents the relationship between pressure, volume and temperature of a given mass of a gas; such an expression is described as an equation of state.

Suppose the gas is in the initial state with volume V_1 , pressure p_1 and temperature T_1 . We then change the state of the gas to a volume V_2 , pressure p_2 and temperature T_2 . Let us carry out this change in two steps.

(i) First we change the pressure from p_1 to p_2 keeping the temperature T_1 constant. The resultant volume V_r as given by Boyle's law is

$$V_r = \frac{p_1 V_1}{p_2}$$

(ii) Next, temperature is changed from T_1 to T_2 , keeping the pressure p_2 constant. The final volume V_2 as given by Charles law is

$$\frac{V_2}{T_2} = \frac{V_r}{T_1} \quad \text{i.e.} \quad V_2 = \frac{V_r T_2}{T_1} = \frac{(p_1 V_1 / p_2) T_2}{T_1}$$

$$\text{or} \quad \frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2} \quad (1.3.1)$$

It follows that no matter how we change the state of the given amount of a gas, the ratio pV/T always remains constant, i.e.

$$\frac{pV}{T} = K$$

Universal Gas Constant

The value of K depends on the amount of gas in the system. Since V is an extensive property (which is mass dependent), its value at constant p and T is proportional to the amount of the gas present in the system. Then K must also be proportional to the amount of gas because p and T are intensive properties (which have no mass dependence). We can express this by writing $K = nR$, in which n is the amount of gas in a given volume of gas and R is independent of all variables and is, therefore, a universal constant. We thus have the general gas law

$$pV = nRT \quad (1.3.2)$$

Physical Significance of Gas Constant R

The universal gas constant as given by Eq. (1.3.2) is $R = pV/nT$. Thus, it has the units of (pressure \times volume) divided by (amount of gas \times temperature). Now the dimensions of pressure and volume are,

$$\text{Pressure} = (\text{force/area}) = (\text{force/length}^2) = \text{force} \times \text{length}^{-2}$$

$$\text{Volume} = \text{length}^3$$

$$\begin{aligned} \text{Thus } R &= \frac{(\text{force} \times \text{length}^{-2}) (\text{length}^3)}{(\text{amount of gas}) (\text{kelvin})} = \frac{(\text{force} \times \text{length})}{(\text{amount of gas}) (\text{kelvin})} \\ &= \frac{\text{work (or energy)}}{(\text{amount of gas}) (\text{kelvin})} \end{aligned}$$

Thus, the dimensions of R are energy per mole per kelvin and hence it represents the amount of work (or energy) that can be obtained from one mole of a gas when its temperature is raised by one kelvin.



1.4 APPLICATION OF EQUATION OF STATE

Gaseous State 7

Concept of an Ideal Gas

So far, we have assumed that all gases obey the gas laws under all conditions of temperature and pressure; however, for real gases this is not true. Real gases obey these laws only under limited conditions of low pressures and high temperatures. They exhibit deviations from the gaseous laws and these deviations are greater when the temperature and pressure are close to the conditions at which the gas can be condensed into a liquid. Thus Boyle's law, Charles law, and the equation of state derived from these two laws may be regarded as approximations for real gases and are expected to be applicable only at relatively low pressures and moderately high temperatures. It is, nevertheless, very useful to postulate a hypothetical ideal gas, defined as a gas to which the laws of Boyle and Charles are strictly applicable under all conditions of temperatures and pressures. It is for this reason that Eq. (1.3.2) is commonly referred to as the *ideal gas equation*. Real gases attain ideal behaviour only at very low pressures and very high temperatures.

Characteristics of an Ideal Gas

Since Eq. (1.3.2) is not applicable to real gases, the evaluation of the universal gas constant R cannot be done directly by utilizing the pressure, volume, and temperature data of real gases. Equation (1.3.2) is strictly applicable only for ideal gases and thus if the pressure and volume of one mole of an ideal gas were known at a definite temperature, it would be a simple matter to evaluate R from Eq. (1.3.2). However, as no gas behaves ideally, this procedure would appear to be ruled out. But we know from experiments that gases approach ideal behaviour as the pressure is decreased. Hence, the extrapolation method ($p \rightarrow 0$) on the data of real gases can be utilized to determine the corresponding properties of an ideal gas. The data obtained in this manner, after extrapolation, should be independent of the characteristics of the actual gas employed for the experiment.

By measuring the volumes of one mole of a real gas at different pressures and constant temperature, a graph between pV and p can be drawn. On extrapolating this graph to zero pressure to correct for departure from ideal behaviour it is possible to determine the value of pV which is expected to be applicable to one mole of an ideal gas. Since this value of pV is expected to be independent of the nature of the gas, the same value of $(pV)_{p \rightarrow 0}$ would be obtained irrespective of the gas employed for this purpose. In other words, the graphs of pV versus p of different gases must yield the same value of $(pV)_{p \rightarrow 0}$. In fact, it is found to be so, as is evident from Fig. 1.4.1. The value of $(pV)_{p \rightarrow 0}$ at 273.15 K is found to be 22.711 dm³ bar. Thus if $p = 1$ bar, then $V = 22.711$ dm³, that is, the volume occupied by one mole of an ideal gas at standard temperature (273.15 K) and pressure (1 bar) is 22.711 dm³.

Value of Gas Constant in SI Units

The value of R in SI units can be worked out as follows.

$$R = \frac{pV}{nT} = \frac{(1 \text{ bar})(22.711 \text{ dm}^3)}{(1 \text{ mol})(273.15 \text{ K})} = 0.08314 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$$

Since $10^2 \text{ kPa} = 1 \text{ bar}$, the value of R expressed in $\text{kPa dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$ will be

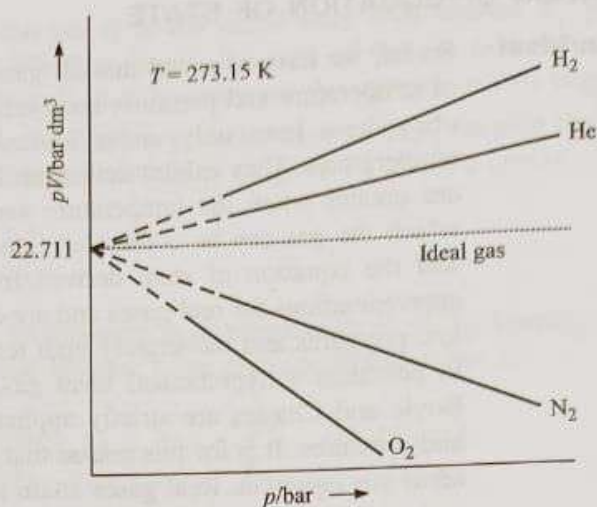


Fig. 1.4.1 Plots of pV versus p of a few gases

$$\begin{aligned}
 R &= 0.08314 (10^2 \text{ kPa}) \text{ dm}^3 \text{ K}^{-1} \text{ mol}^{-1} \\
 &= 8.314 \text{ kPa dm}^3 \text{ K}^{-1} \text{ mol}^{-1} \equiv 8.314 \text{ MPa cm}^3 \text{ K}^{-1} \text{ mol}^{-1} \\
 &\equiv 8.314 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1} \equiv 8.314 \text{ J K}^{-1} \text{ mol}^{-1}
 \end{aligned}$$

Example 1.4.1

Determine the value of gas constant R when pressure is expressed in Torr and volume in dm^3 .

Solution

By definition, $1.01325 \text{ bar} = 760 \text{ Torr}$. Hence

$$\begin{aligned}
 R = \frac{pV}{nT} &= \frac{\left\{ (1 \text{ bar}) \left(\frac{760 \text{ Torr}}{1.01325 \text{ bar}} \right) \right\} (22.711 \text{ dm}^3)}{(1 \text{ mol}) (273.15 \text{ K})} \\
 &= 62.36 \text{ Torr dm}^3 \text{ K}^{-1} \text{ mol}^{-1}
 \end{aligned}$$

Example 1.4.2

Derive the value of R when (a) pressure is expressed in atmospheres, volume in cm^3 and (b) p in dyn m^{-2} and V in mm^3 .

Solution

Since $pV = 22.711 \text{ dm}^3 \text{ bar}$, the volume of an ideal gas at $1 \text{ atm} (= 1.01325 \text{ bar})$ will be

$$V = \frac{22.711 \text{ dm}^3 \text{ bar}}{1.01325 \text{ bar}} = 22.414 \text{ dm}^3$$

(a) p in atm and V in cm^3

$$R = \frac{pV}{nT} = \frac{(1 \text{ atm}) (22414 \text{ cm}^3)}{(1 \text{ mol}) (273.15 \text{ K})} = 82.06 \text{ atm cm}^3 \text{ K}^{-1} \text{ mol}^{-1}$$

(b) p in dyn m^{-2} and V in mm^3

$$p = 1 \text{ atm} \equiv 1.0132 \times 10^6 \text{ dyn cm}^{-2} \equiv 1.0132 \times 10^{10} \text{ dyn m}^{-2}$$

$$V = 22414 \text{ cm}^3 \equiv 22414 \times 10^3 \text{ mm}^3$$

$$\begin{aligned}
 R = \frac{pV}{nT} &= \frac{(1.0132 \times 10^{10} \text{ dyn m}^{-2}) (22414 \times 10^3 \text{ mm}^3)}{(1 \text{ mol}) (273.15 \text{ K})} \\
 &= 8.314 \times 10^{14} (\text{dyn m}^{-2}) (\text{mm}^3) \text{ K}^{-1} \text{ mol}^{-1}
 \end{aligned}$$

According to Avogadro's law, equal number of molecules of different gases under identical conditions of temperature and pressure occupy the same volume.

When this law is applied to real gases, it is found that the law does not hold good at ordinary temperatures and pressures. However, when the measurements are made at low pressures, deviations from the law become less and thus, like other gaseous laws, Avogadro's law may be regarded as an approximation which is expected to be applicable only under conditions of low pressures and high temperatures. Strictly speaking, this law would be applicable only for ideal gases.

The fact that Avogadro's law is applicable to real gases at very low pressures and high temperatures indicates that the volume occupied by different gases having the same number of molecules under identical conditions of temperature and pressure is independent of the nature of the gaseous molecules. Thus, whether the molecules are heavy (e.g. Br_2) or light (e.g. H_2), gases with equal number of molecules would occupy the same volume. This leads to one of the most important features of gases that the distance between molecules is much larger than the actual dimensions of molecules, since otherwise, Avogadro's law would not have been true.

Avogadro Constant

The facts that the behaviour of a real gas approaches that of an ideal gas as $p \rightarrow 0$ and the volume occupied by one mole of an ideal gas at the specified temperature (273.15 K) and pressure (101.325 kPa) has a fixed value (22.414 dm^3) indicate that the number of molecules contained in one mole of any real gas should be a constant quantity. This physical quantity has a value of $6.022 \times 10^{23} \text{ mol}^{-1}$ and is known as *Avogadro constant*.

Equation of State in Terms of Numbers of Molecules

The amount of gas containing N number of molecules is given by

$$n = \frac{N}{N_A}$$

With this, Eq. (1.3.2) becomes

$$pV = nRT = \frac{N}{N_A} RT \quad (1.4.1)$$

Avogadro's law follows directly from the Eq. (1.4.1). We have

$$V = \left(\frac{RT}{pN_A} \right) N$$

For a fixed condition of pressure and temperature, a gas will have fixed volume for a fixed number of gaseous molecules.

Example 1.4.3

Estimate the number of gaseous molecules left in a volume of 1 mm^3 if it is pumped out to give a vacuum of 10^{-6} mmHg at 298 K.

Solution

We are given that

$$V = 1 \text{ mm}^3 = 10^{-6} \text{ dm}^3$$

$$p = 10^{-6} \text{ mmHg} = (10^{-6} \text{ mmHg}) \left(\frac{101.325 \text{ kPa}}{760 \text{ mmHg}} \right) = 1.333 \times 10^{-7} \text{ kPa}$$

Handwritten notes:
 $760 \text{ mmHg} = 101 \text{ kPa}$
 $10^{-6} \text{ mmHg} = \frac{101}{760} \times 10^{-6}$

Handwritten notes:
 $1 \text{ mm} = 10^{-3} \text{ dm}$
 $1 \text{ mm}^3 = (10^{-3})^3 \text{ dm}^3$
 $= 10^{-9} \text{ dm}^3$

$$\text{Amount of the gas, } n = \frac{pV}{RT} = \frac{(1.333 \times 10^{-7} \text{ kPa})(10^{-6} \text{ dm}^3)}{(8.314 \text{ kPa dm}^3 \text{ K}^{-1} \text{ mol}^{-1})(298 \text{ K})}$$

$$= 5.38 \times 10^{-17} \text{ mol}$$

Hence, number of molecules

$$N = n N_A = (5.38 \times 10^{-17} \text{ mol})(6.022 \times 10^{23} \text{ mol}^{-1}) = 3.240 \times 10^7$$

Equation of State in Terms of Mass of a Gas

For a gas of mass m , the amount of gas is given by

$$n = \frac{m}{M}$$

where M is the molar mass of the gas. With this, Eq. (1.3.2) becomes

$$pV = nRT = \left(\frac{m}{M}\right)RT \quad (1.4.2)$$

Example 1.4.4

When 2 g of gaseous substance A is introduced into an initially evacuated flask kept at 25 °C, the pressure is found to be 101.325 kPa. The flask is evacuated and 3 g of B is introduced. The pressure is found to be 50.662 5 kPa at 25 °C. Calculate the ratio M_A/M_B .

Solution

From the ideal gas equation, we have

$$pV = nRT = \left(\frac{m}{M}\right)RT \quad \text{or} \quad M = m \frac{RT}{pV}$$

$$\text{Hence } M_A = (2 \text{ g}) \frac{RT}{(101.325 \text{ kPa})V} \quad \text{and} \quad M_B = (3 \text{ g}) \frac{RT}{(50.662 5 \text{ kPa})V}$$

$$\text{Thus, } \frac{M_A}{M_B} = \frac{2 \times 0.5}{3} = \frac{1}{3}$$

Example 1.4.5

A certain mixture of helium and argon weighing 5.0 g occupies a volume of 10 dm³ at 25 °C and 101.325 kPa. What is the composition of the mixture in mass percentage?

Solution

Given that $m_{\text{mix}} = 5.0 \text{ g}$; $V = 10 \text{ dm}^3$; $T = 25 \text{ °C} \equiv 298.15 \text{ K}$; $p = 101.325 \text{ kPa}$

Let the mass of He be x . Therefore

$$\text{Amount of He} = \frac{m}{M} = \frac{x}{(4.0 \text{ g mol}^{-1})}$$

$$\text{Amount of Ar} = \frac{m}{M} = \frac{5.0 \text{ g} - x}{(39.95 \text{ g mol}^{-1})}$$

$$\text{Total amount of gases} = \frac{pV}{RT} = \frac{(101.325 \text{ kPa})(10 \text{ dm}^3)}{(8.314 \text{ kPa dm}^3 \text{ K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}$$

$$= 0.409 \text{ mol}$$

$$\text{Hence } \left(\frac{x}{4.0 \text{ g mol}^{-1}}\right) + \left(\frac{5.0 \text{ g} - x}{39.95 \text{ g mol}^{-1}}\right) = 0.409 \text{ mol}$$

Solving for x , we get

$$x = 1.262 \text{ g}$$



$$\text{Mass per cent of He} = \frac{1.262 \text{ g}}{5.0 \text{ g}} \times 100 = 25.24$$

$$\text{Mass per cent of Ar} = 100 - 25.24 = 74.76$$

Example 1.4.6

A flask of 2 dm^3 capacity contains O_2 at 101.325 kPa and 300 K . The gas pressure is reduced to 0.10 Pa by attaching the flask to a pump. Assuming ideal behaviour, answer the following:

- What will be the volume of the gas which is left behind?
- What amount of O_2 and the corresponding number of molecules are left behind in the flask?
- If now 2 g of N_2 is introduced, what will be the pressure of the flask?

Solution

Given that $V_1 = 2 \text{ dm}^3$, $p_1 = 101.325 \text{ kPa}$, $p_2 = 0.10 \text{ Pa}$, $T = 300 \text{ K}$
We have the following results.

- The volume of O_2 left behind will be the same, i.e. 2 dm^3 .
- The amount of O_2 left behind is given by

$$n = \frac{p_2 V_1}{RT} = \frac{(10^{-4} \text{ kPa})(2 \text{ dm}^3)}{(8.314 \text{ kPa dm}^3 \text{ K}^{-1} \text{ mol}^{-1})(300 \text{ K})} = 8.019 \times 10^{-8} \text{ mol}$$

$$N = nN_A = (8.109 \times 10^{-8} \text{ mol})(6.022 \times 10^{23} \text{ mol}^{-1}) = 4.88 \times 10^{16}$$

$$\text{(iii) } 2 \text{ g of } \text{N}_2 = \frac{1}{14} \text{ mol}$$

$$\text{Total amount of gases in flask} = \frac{1}{14} \text{ mol} + 8.019 \times 10^{-8} \text{ mol} = \frac{1}{14} \text{ mol}$$

Thus, the pressure of the flask is given by

$$p = \frac{nRT}{V} = \frac{(1 \text{ mol}/14)(8.314 \text{ kPa dm}^3 \text{ K}^{-1} \text{ mol}^{-1})(300 \text{ K})}{(2 \text{ dm}^3)} = 89.08 \text{ kPa}$$

Example 1.4.7

Two flasks of equal volume connected by a narrow tube (of negligible volume) are at 300 K and contain 0.70 mol of H_2 gas at 50.6625 kPa pressure. One of the flasks is then immersed into a bath kept at 400 K , while the other remains at 300 K . Calculate the final pressure and the amount of H_2 in each flask.

Solution

The final pressure in both the flasks will be the same, since both of them are connected with each other. Let n_1 be the amount of the gas in flask 1 ($T_1 = 300 \text{ K}$) and n_2 in the flask 2 ($T_2 = 400 \text{ K}$);

$$\text{For flask 1, } pV = n_1 RT_1$$

$$\text{For flask 2, } pV = n_2 RT_2$$

$$\text{Therefore, } n_1 T_1 = n_2 T_2 \quad \text{i.e.}$$

$$\frac{n_1}{n_2} = \frac{T_2}{T_1} = \frac{400 \text{ K}}{300 \text{ K}} = \frac{4}{3}$$

$$\text{But } n_1 + n_2 = 0.7 \text{ mol}$$

$$\text{Hence } n_1 = 0.4 \text{ mol at } 300 \text{ K}$$

$$n_2 = 0.3 \text{ mol at } 400 \text{ K}$$

Volume of each flask is

$$V = \frac{nRT}{p} = \frac{(0.35 \text{ mol})(8.314 \text{ kPa dm}^3 \text{ K}^{-1} \text{ mol}^{-1})(300 \text{ K})}{(50.6625 \text{ kPa})} = 17.23 \text{ dm}^3$$



Final pressure is

$$p_f = \frac{n_1 RT_1}{V} = \frac{(0.4 \text{ mol}) (8.314 \text{ kPa dm}^3 \text{ K}^{-1} \text{ mol}^{-1}) (300 \text{ K})}{(17.23 \text{ dm}^3)} = 57.90 \text{ kPa}$$

1.5 CONCEPTS OF PARTIAL PRESSURE AND PARTIAL VOLUME

Definition of Partial Pressure

The relation between the total pressure of a mixture of gases and the pressures of the individual gases was expressed by Dalton in the form of law of partial pressures. The partial pressure of a gas in a mixture is defined as the pressure which the gas would exert if it is allowed to occupy the whole volume of the mixture at the same temperature.

Definition of Dalton's Law

According to Dalton's law of partial pressures, *the total pressure of a mixture of gases is equal to the sum of the partial pressures of the constituent gases.*

Partial Pressures in a Gaseous Mixture

Let a mixture of gases have the amount n_1 of the first gas, n_2 of the second gas, and so on. Let the corresponding partial pressures be p_1, p_2, \dots . The total pressure is given by

$$p_{\text{total}} = p_1 + p_2 + \dots$$

If the gases present in the mixture behave ideally, then, it is possible to write separately for each gas,

$$p_1 V = n_1 RT \quad (1.5.1a)$$

$$p_2 V = n_2 RT \quad (1.5.1b)$$

.....

$$\text{Hence } (p_1 + p_2 + \dots) V = (n_1 + n_2 + \dots) RT$$

$$\text{i.e. } p_{\text{total}} V = n_{\text{total}} RT \quad (1.5.2)$$

where n_{total} is the total amount of gases in the mixture. Dividing Eqs (1.5.1a) and (1.5.1b) by Eq. (1.5.2), we get

$$p_1 = \frac{n_1}{n_{\text{total}}} p_{\text{total}} = x_1 p_{\text{total}} \quad (1.5.3a)$$

$$p_2 = \frac{n_2}{n_{\text{total}}} p_{\text{total}} = x_2 p_{\text{total}} \quad (1.5.3b)$$

Definition of Amount (Mole) Fraction

The fractions n_1/n_{total} , n_2/n_{total} , are called the *amount (mole) fractions* of the respective gases. The amount fraction of a constituent in any mixture (gaseous, liquid or solid) is defined as the amount (or number of molecules) of that constituent divided by the total amount (or number of molecules) of constituents in the mixture. If x_s are given, it is possible to calculate partial pressures by using Eqs (1.5.3).

Partial Volumes: Amagat's Law

The partial volume of a gas in a mixture is defined as the volume which the gas would occupy if it were present alone in a container at temperature T and pressure p of the mixture. According to the ideal gas equation, this is given by

$$V_1 = n_1 \left(\frac{RT}{p} \right) \quad (1.5.6a)$$

$$V_2 = n_2 \left(\frac{RT}{p} \right) \quad (1.5.6b)$$

...

Adding, we get

$$V_1 + V_2 + \dots = (n_1 + n_2 + \dots) \frac{RT}{p} = n_{\text{total}} \left(\frac{RT}{p} \right)$$

From the ideal gas equation

$$n_{\text{total}} \left(\frac{RT}{p} \right) = V_{\text{total}} \quad (1.5.7)$$

we have $V_1 + V_2 + \dots = V_{\text{total}}$

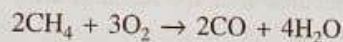
which is Amagat's law of partial volumes according to which the total volume of a mixture of gases is equal to the sum of the partial volumes of the constituent gases.

Dividing Eqs (1.5.6) by Eq. (1.5.7), we get

$$V_i = x_i V_{\text{total}} \quad i = 1, 2, \dots \quad (1.5.8)$$

Example 1.5.1

The following reaction is carried out at 101.325 kPa and 383 K,



with the initial amounts of CH_4 and O_2 as 0.01 mol and 0.03 mol, respectively. All reactants and products are gaseous at 383 K. A short while after completion of the reaction, the flask is cooled to 283 K at which temperature H_2O is completely condensed. Calculate:

- The volume of the flask.
- Total pressure and partial pressures of various species after the reaction at 383 K and 283 K.
- The number of molecules of the various substances before and after the reaction.

Solution

The reaction is $2\text{CH}_4 + 3\text{O}_2 \rightarrow 2\text{CO} + 4\text{H}_2\text{O}$

Amount/mol					Temp.
In the beginning	0.01	0.03	0	0	383 K
At the end	0.0	0.015	0.01	0.02	383 K
	0.0	0.015	0.01	condensed	283 K

- Volume of the flask

$$V = \frac{nRT}{p} = \frac{(0.04 \text{ mol}) (8.314 \text{ kPa dm}^3 \text{ K}^{-1} \text{ mol}^{-1}) (383 \text{ K})}{(101.325 \text{ kPa})} = 1.257 \text{ dm}^3$$



$$(ii) \quad p(\text{total}, 383 \text{ K}) = \left(\frac{0.045 \text{ mol}}{0.040 \text{ mol}} \right) (101.325 \text{ kPa}) = 113.99 \text{ kPa}$$

$$p(\text{total}, 283 \text{ K}) = \left(\frac{0.025 \text{ mol}}{0.040 \text{ mol}} \right) \left(\frac{283 \text{ K}}{383 \text{ K}} \right) (101.325 \text{ kPa}) = 46.81 \text{ kPa}$$

$$p(\text{CH}_4, 383 \text{ K}) = 0$$

$$p(\text{O}_2, 383 \text{ K}) = \left(\frac{0.015 \text{ mol}}{0.045 \text{ mol}} \right) (113.99 \text{ kPa}) = 38.00 \text{ kPa}$$

$$p(\text{CO}, 383 \text{ K}) = \left(\frac{0.01 \text{ mol}}{0.045 \text{ mol}} \right) (113.99 \text{ kPa}) = 25.33 \text{ kPa}$$

$$p(\text{H}_2\text{O}, 383 \text{ K}) = \left(\frac{0.02 \text{ mol}}{0.045 \text{ mol}} \right) (113.99 \text{ kPa}) = 50.66 \text{ kPa}$$

$$p(\text{CH}_4, 283 \text{ K}) = 0$$

$$p(\text{O}_2, 283 \text{ K}) = \left(\frac{0.015 \text{ mol}}{0.025 \text{ mol}} \right) (46.81 \text{ kPa}) = 28.09 \text{ kPa}$$

$$p(\text{CO}, 283 \text{ K}) = \left(\frac{0.01 \text{ mol}}{0.025 \text{ mol}} \right) (46.81 \text{ kPa}) = 18.72 \text{ kPa}$$

(iii) Number of molecules before the reaction are

$$N(\text{CH}_4) = (0.01 \text{ mol}) (6.022 \times 10^{23} \text{ mol}^{-1}) = 6.022 \times 10^{21}$$

$$N(\text{O}_2) = (0.03 \text{ mol}) (6.022 \times 10^{23} \text{ mol}^{-1}) = 1.807 \times 10^{22}$$

Number of molecules after the reaction are

$$N(\text{CH}_4) = 0$$

$$N(\text{O}_2) = (0.015 \text{ mol}) (6.022 \times 10^{23} \text{ mol}^{-1}) = 9.033 \times 10^{21}$$

$$N(\text{CO}) = (0.01 \text{ mol}) (6.022 \times 10^{23} \text{ mol}^{-1}) = 6.022 \times 10^{21}$$

$$N(\text{H}_2\text{O}) = (0.02 \text{ mol}) (6.022 \times 10^{23} \text{ mol}^{-1}) = 1.204 \times 10^{22}$$

1.6 THE KINETIC GAS EQUATION

Postulates of an Ideal Gas

After knowing the experimental gas laws, it is of interest to develop a theoretical model based on the structure of gases, which can correlate the experimental facts. Fortunately, such a theory has been developed (known as the kinetic theory of gases) and based upon certain essential postulates (which are supposed to be applicable to an ideal gas) it is possible to derive an expression (known as the kinetic gas equation) from where all these gas laws can be derived. The essential postulates are:

- A gas consists of a large number of very small spherical tiny particles, which may be identified with the molecules. The molecules of a given gas are completely identical in size, shape and mass.



- The volume occupied by the molecules is negligible in comparison to the total volume of the gas.
- The molecules are in rapid motion which is completely random. During their motion, they collide with one another and with the sides of the vessel. The pressure of the gas is due to the collisions of molecules with the sides of the vessel.
- The molecules are perfectly elastic, i.e. there occurs no loss of energy when they collide with one another and with the sides of the vessel.
- The laws of classical mechanics, in particular Newton's second law of motion, are applicable to the molecules in motion.
- There is no force of attraction or repulsion amongst the molecules, i.e. they are moving independent of one another.
- At any instant, a given molecule can have energy ranging from a small value to a very large value, but the average kinetic energy remains constant for a given temperature, i.e. the average kinetic energy is proportional to the absolute temperature of the gas.

Derivation of the Kinetic Gas Equation

Imagine a cube of edge-length l , containing N molecules, each having a mass of m . Molecules are moving at random in all directions, with speed covering a considerable range of values.

The velocity u of any molecule may be resolved into three-component velocities designated as u_x , u_y and u_z . These are in the three directions at right angles to each other and parallel to the sides of the cube as shown in Fig. 1.6.1. The component velocities are related by the expression

$$u^2 = u_x^2 + u_y^2 + u_z^2 \quad (1.6.1)$$

Considering the x -component motion of a molecule, we will have

Momentum of the molecule before collision with the side ABCD = mu_x

Momentum of the molecule after collision with the side ABCD = $-mu_x$

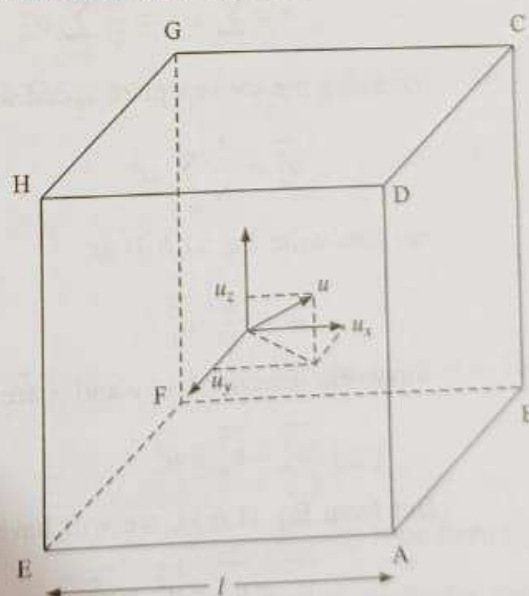


Fig. 1.6.1 Molecular velocity and its components

Change of momentum of the molecule in a single collision with the side ABCD
 $= 12mu_x l$

Since l is the edge length of the cube, the molecule has to travel a distance $2l$ to arrive back at the wall ABCD. The number of collisions per unit time with the wall ABCD will be equal to $u_x/2l$.

The total change of momentum per unit time due to such impacts is

$$2mu_x \left(\frac{u_x}{2l} \right) = \frac{mu_x^2}{l}$$

According to Newton's second law of motion

Force = mass \times acceleration

$$\begin{aligned} &= \text{mass} \times \frac{d(\text{velocity})}{dt} = \frac{d}{dt} (\text{mass} \times \text{velocity}) \\ &= \frac{d}{dt} (\text{momentum}) = \text{rate of change of momentum} \end{aligned}$$

Hence, total force due to impacts of a single molecule with the wall ABCD of the vessel is mu_x^2/l .

The area of the wall is l^2 . Hence, the pressure exerted due to the collision of x -component velocity of a single molecule with the side ABCD is

$$p_x = \frac{mu_x^2/l}{l^2} = \frac{mu_x^2}{V} \quad (1.6.2)$$

where V is the volume of the vessel.

Since each molecule will exert similar pressure, the total pressure exerted on the wall ABCD will be

$$p = \sum_{i=1}^N p_{ix} = \frac{m}{V} \sum_{i=1}^N u_{ix}^2 \quad (1.6.3)$$

Defining the mean square speed as

$$\overline{u_x^2} = \frac{1}{N} \sum_{i=1}^N u_{ix}^2 \quad (1.6.4)$$

we can write Eq. (1.6.3) as

$$p = \frac{mN}{V} \overline{u_x^2} \quad (1.6.5)$$

Since the directions x , y and z are equivalent, we will also have

$$\overline{u_x^2} = \overline{u_y^2} = \overline{u_z^2} \quad (1.6.6)$$

But from Eq. (1.6.1), we will have

$$\overline{u^2} = \overline{u_x^2} + \overline{u_y^2} + \overline{u_z^2} \quad (1.6.7)$$

From Eqs (1.6.6) and (1.6.7), we can write

$$\overline{u_x^2} = \overline{u_y^2} = \overline{u_z^2} = \frac{1}{3} \overline{u^2} \quad (1.6.8)$$

Substituting this in Eq. (1.6.5), we get

$$p = \frac{mN}{V} \left(\frac{1}{3} \overline{u^2} \right) \quad \text{or} \quad pV = \frac{1}{3} mN \overline{u^2} \quad (1.6.9)$$

Example 1.6.1

Solution

Calculate the pressure exerted by 10^{23} gas particles each of mass 10^{-22} g in a container of volume 1 dm^3 . The root mean square speed is 10^5 cm s^{-1} .

From the given data, we have

$$N = 10^{23}; \quad m = 10^{-22} \text{ g} = 10^{-25} \text{ kg}; \quad V = 1 \text{ dm}^3 = 10^{-3} \text{ m}^3$$

$$\sqrt{\overline{u^2}} = 10^5 \text{ cm s}^{-1} = 10^3 \text{ m s}^{-1}$$

Therefore, from the kinetic gas equation

$$p = \frac{1}{3} \frac{mN \overline{u^2}}{V}$$

$$\begin{aligned} \text{we have } p &= \frac{1}{3} \frac{(10^{-25} \text{ kg})(10^{23})(10^3 \text{ m s}^{-1})^2}{(10^{-3} \text{ m}^3)} \\ &= \frac{1}{3} (10^7) \text{ kg m}^{-1} \text{ s}^{-2} = \frac{1}{3} \times 10^7 \text{ Pa} \end{aligned}$$

1.7 SOME DERIVATIONS FROM THE KINETIC GAS EQUATION

Kinetic Gas Equation Involving Kelvin Temperature

The kinetic gas equation (1.6.9) can be used to derive the various gaseous laws and to define expressions for some useful quantities such as the root mean square speed and the average kinetic energy. Before deriving these, it is helpful to write this equation in the following form:

One of the postulates of the kinetic theory of gases is

$$\text{Average kinetic energy} \propto T$$

$$\text{i.e.} \quad \frac{1}{2} m \overline{u^2} \propto T \quad \text{or} \quad \frac{1}{2} m \overline{u^2} = KT$$

where K is the proportionality constant. Introducing this in Eq. (1.6.9) we have

$$pV = \frac{1}{3} mN \overline{u^2} = \frac{2}{3} N \left(\frac{1}{2} m \overline{u^2} \right) = \frac{2}{3} NKT \quad (1.7.1)$$

Now, we proceed to derive the various gaseous laws from Eq. (1.7.1).

The essential conditions for Boyle's law to be applicable are:

Boyle's Law

- (i) Temperature (T) should remain constant.
- (ii) Mass of the gas should remain constant. In other words, the total number of molecules (N) remains unchanged.

Under these conditions, Eq. (1.7.1) yields

$$pV = \text{constant} \quad \text{or} \quad p \propto \frac{1}{V}$$

which is the expression for Boyle's law.

Charles Law

In this case:

- (i) Pressure (p) remains fixed.
- (ii) Mass of the gas remains unchanged, i.e. N is constant.

With these conditions, Eq. (1.7.1) yields

$$V = \left(\frac{2}{3} \frac{NK}{p} \right) T \quad \text{i.e.} \quad V = (\text{constant}) T \quad \text{or} \quad V \propto T$$

as required by Charles law.

Avogadro's Law

It states that *under similar conditions of pressure and temperature, equal volume of all gases contain equal number of molecules*. Considering two gases, we have

$$p_1 V_1 = \frac{2}{3} N_1 K T_1 \quad \text{and} \quad p_2 V_2 = \frac{2}{3} N_2 K T_2$$

Since $p_1 = p_2$ and $T_1 = T_2$, therefore

$$\frac{p_1 V_1}{p_2 V_2} = \frac{(2/3) N_1 K T_1}{(2/3) N_2 K T_2} \Rightarrow \frac{V_1}{V_2} = \frac{N_1}{N_2}$$

If volumes are identical, obviously $N_1 = N_2$.

Graham's Law of Effusion

The rate of diffusion or effusion can be assumed to be directly proportional to the root mean square speed (or any other average speed). Thus

$$\frac{r_1}{r_2} = \sqrt{\frac{u_1^2}{u_2^2}}$$

From Eq. (1.6.9), we have

$$\overline{u^2} = \frac{3pV}{mN}$$

For 1 mol of an ideal gas

$$pV = RT$$

$$\text{and} \quad N = N_A$$

(N_A is Avogadro constant)

With these, the above equation becomes

$$\overline{u^2} = \frac{3RT}{mN_A} = \frac{3RT}{M} \quad (1.7.2)$$

where M is the molar mass of the gas.

$$\text{Thus, } \frac{r_1}{r_2} = \sqrt{\frac{u_1^2}{u_2^2}} = \sqrt{\frac{3RT/M_1}{3RT/M_2}} = \sqrt{\frac{M_2}{M_1}}$$

which is Graham's law of effusion.

Root mean square (rms) speed is defined as the square root of the average of the squares of speeds, i.e.

$$\sqrt{u^2} = \sqrt{\frac{u_1^2 + u_2^2 + \dots + u_N^2}{N}}$$

According to Eq. (1.7.2), this is given as

$$\sqrt{u^2} = \sqrt{\frac{3RT}{M}} \quad (1.7.3)$$

$$\text{or } \sqrt{u^2} = \sqrt{\frac{3pV_m}{M}} \quad (1.7.4)$$

Thus, rms speed is directly proportional to the square root of temperature and inversely proportional to the square root of molar mass. Hence, at a given temperature lighter molecules (say H_2 , He) move faster than the heavier molecules (say O_2 , N_2). There is no effect of change of pressure or volume on the rms speed since, at a given temperature, $pV_m = \text{constant}$.

Example 1.7.1

A bulb of capacity 1 dm^3 contains 1.03×10^{23} gaseous hydrogen molecules and the pressure exerted by these molecules is 101.325 kPa . Calculate the average square molecular speed and the temperature.

Solution

We have $V = 1 \text{ dm}^3$, $N = 1.03 \times 10^{23}$, $p = 101.325 \text{ kPa}$

$$n = \frac{N}{N_A} = \frac{1.03 \times 10^{23}}{(6.022 \times 10^{23} \text{ mol}^{-1})} = 0.171 \text{ mol}$$

$$T = \frac{pV}{nR} = \frac{(101.325 \text{ kPa})(1 \text{ dm}^3)}{(0.171 \text{ mol})(8.314 \text{ kPa dm}^3 \text{ K}^{-1} \text{ mol}^{-1})} = 71.27 \text{ K}$$

$$\begin{aligned} \overline{u^2} &= \frac{3RT}{M} = \frac{3(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(71.27 \text{ K})}{(2.0 \times 10^{-3} \text{ kg mol}^{-1})} \\ &= 8.888 \times 10^5 \text{ J kg}^{-1} = 8.888 \times 10^5 (\text{m s}^{-1})^2 \end{aligned}$$

Average Kinetic Energy

The average kinetic energy ($\overline{\text{KE}}$) is defined as

$$\overline{\text{KE}} = \frac{1}{2} m \overline{u^2}$$

According to Eq. (1.7.1), this is given as

$$\overline{\text{KE}} = \frac{3}{2} \frac{pV}{N}$$

For 1 mole of an ideal gas

$$pV = RT \quad \text{and} \quad N = N_A$$

With these, the above equation becomes

$$\overline{\text{KE}} = \frac{3}{2} \frac{RT}{N_A} = \frac{3}{2} kT \quad (1.7.5)$$

where $k = R/N_A$ and is known as the Boltzmann constant. Its value is given by

$$k = \frac{R}{N_A} = \frac{8.314 \text{ J K}^{-1} \text{ mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 1.3806 \times 10^{-23} \text{ J K}^{-1}$$

The total kinetic energy for 1 mole of the gas is

$$E_{\text{total}} = N_A (\overline{\text{KE}}) = \frac{3}{2} RT \quad (1.7.6)$$

Example 1.7.2

For a gas containing 10^{23} molecules (each having mass 10^{-22} g) in a volume of 1 dm^3 , calculate the total kinetic energy of molecules if their root mean square speed is 10^5 cm s^{-1} . What will be its temperature?

Solution

Total kinetic energy

$$\begin{aligned} &= N \left(\frac{1}{2} m \overline{u^2} \right) = (10^{23}) \left\{ \frac{1}{2} (10^{-25} \text{ kg}) (10^3 \text{ m s}^{-1})^2 \right\} \\ &= 0.5 \times 10^4 \text{ kg m}^2 \text{ s}^{-2} = 0.5 \times 10^4 \text{ J} \end{aligned}$$

Total kinetic energy is also equal to $N(3/2)kT$. Thus

$$N \left(\frac{3}{2} \right) kT = 0.5 \times 10^4 \text{ J}$$

$$\begin{aligned} \text{Hence} \quad T &= \frac{2}{3} \frac{(0.5 \times 10^4 \text{ J})}{Nk} = \frac{2}{3} \frac{(0.5 \times 10^4 \text{ J})}{(10^{23}) (1.3806 \times 10^{-23} \text{ J K}^{-1})} \\ &= 2414 \text{ K} \end{aligned}$$

Example 1.7.3

Calculate the total kinetic energy of 0.5 mol of an ideal gas at 273 K.

Solution

Total Kinetic energy

$$= n \left(\frac{3}{2} RT \right) = (0.5 \text{ mol}) \left\{ \frac{3}{2} (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (273 \text{ K}) \right\} = 1702 \text{ J}$$

1.8 REAL GASES

Deviation from Ideal Behaviour

Real gases do not obey the ideal gas laws exactly under all conditions of temperature and pressure. Experiments show that at low pressure and moderately