

Bahir Dar University
College of Science
Chemistry Department

Kinetics and Electrochemistry (Chem. 3051)

Unit four

Kinetic Theory of Gases

Kinetic Theory of Gases

- **Kinetic theory of gases or** kinetic molecular theory (KMT) is a scientific model that explain the physical **behavior** of a gas as the motion of the molecular particles of the gas.
- *Maxwell and boltzmann (1859)* developed a mathematical theory to explain the *behavior of gases and the gas laws*.

Kinetic molecular theory is based on the fundamental concept that;

- ✓ A gas is made of a large number of molecules in continuous motion *and*
- ✓ *The gases molecule collides not only with each other but also with the sides of a container that the gas is within.*

Assumptions of the kinetic molecular theory of gases

- 1) A gas consists of extremely small discrete particles called gases molecules and they are identical and have the same mass (m). The actual volume of the molecules is negligible compared to the total volume of the container.
- 2) **Gas molecules are in constant random motion with high velocities.** They move in straight lines with uniform velocity and change direction on collision with other molecules or the walls of the container.
- 3) **The distance between the molecules are very large or they have low intermolecular interaction.** Thus the gas molecules can move freely, independent of each other.
- 4) **All collisions are perfectly elastic.** Hence, there is no loss or gain of the kinetic energy of a molecule during a collision.

Ideal Gas Laws

- The volume of a given sample of gas depends on the temperature and pressure applied to it. “Any change in temperature or pressure will affect the volume of the gas”.
- As results of experimental studies from *17th to 19th century*, scientists derived the relationships among the pressure, temperature and volume of a given mass of gas.
- These relationships, which describe the general behavior of gases, are called the **gas laws**.

i. Boyle's Law(1660)

Robert Boyle “**Father of Modern Chemistry**”

- Boyle found out experimentally the change in volume of a given sample of gas with pressure at room temperature. From his observations he formulated a generalization known as **Boyle's Law**. It states that: at constant temperature, the volume of a fixed mass of gas is inversely proportional to its pressure.

❖ Pressure and volume are inversely related at constant temperature.

Mathematically;

$$V \propto 1/P \quad (T, n \text{ are constant})$$

$$V = k \times 1/P$$

$\text{❖ } PV = K$

Gas Laws ...

If P_1 , V_1 are the initial pressure and volume of a given sample of gas and P_2 , V_2 the changed

we can write the pressure and volume relation as;

$$P_1 V_1 = K = P_2 V_2 \text{ or}$$

$$P_1 V_1 = P_2 V_2$$

- ✓ This relationship is useful for the determination of the volume of a gas at any pressure, if its volume at any other pressure is known.
- Gas pressure and volume are inversely related; one increases when the other decreases.

Gas Laws ...

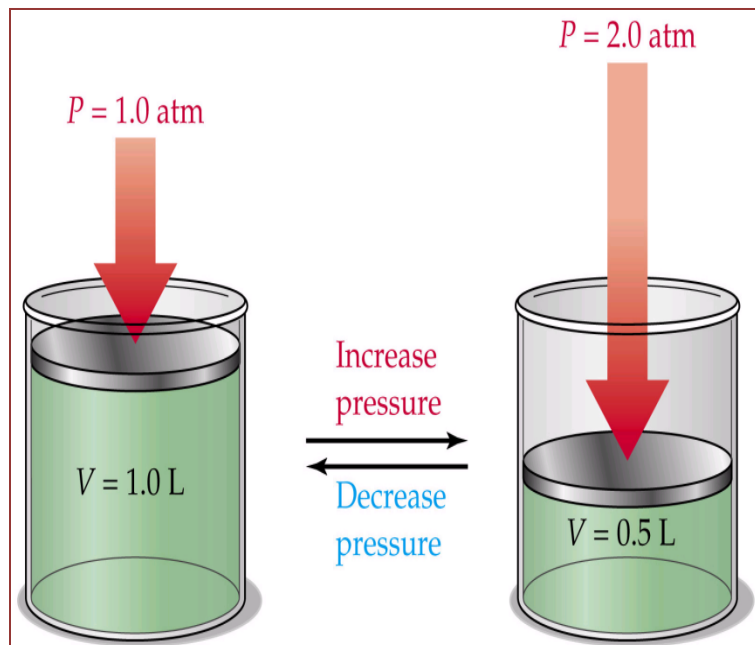


Figure 4.1 : Boyle's law relation between the volume of gas and its pressure.

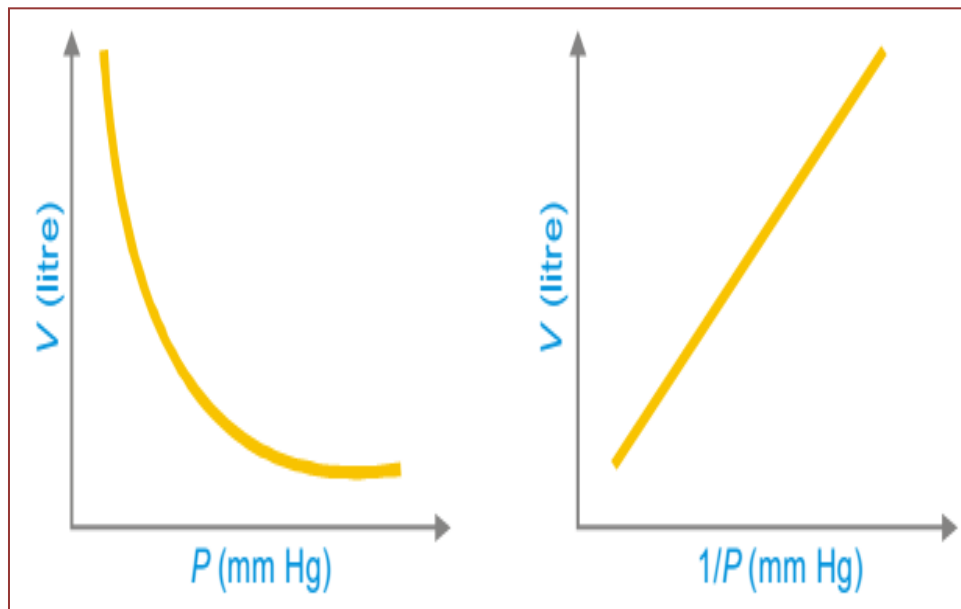


Figure 4. 2: Graphical representation of Boyle's law. (a) a plot of V vs. P for a gas sample is hyperbola; (b) a plot of V vs. $1/P$ is a straight line.

ii. Charles' Law (1787)

- Jacques Charles investigated the effect of change of temperature on the volume of a fixed amount of gas at constant pressure.
- It states that: at **constant pressure**, the **volume** of a fixed mass of gas is directly proportional to the **Kelvin temperature** or absolute temperature.

Charles' Law may be expressed mathematically as

$$V \propto T \quad (P, n \text{ are constant})$$

or $V = k T$

where k is a constant.

or

$$\frac{V}{T} = k$$

If V_1 and T_1 are the initial volume and temperature of a given mass of gas at constant pressure and V_2 and T_2 be the final values,

Gas Laws ...

we can write

$$\frac{V_1}{T_1} = k = \frac{V_2}{T_2}$$

or

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

Using this expression, the new volume V_2 , can be found from the experimental values of V_1 , T_1 and T_2 .

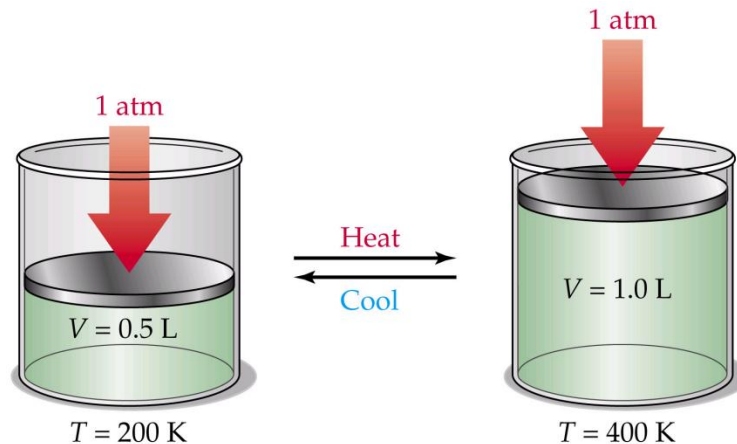


Figure 4.3: Charles law relation between the volume gas and its absolute temperature

iii. The Combined Gas Law

- ❖ Boyle's Law and Charles' Law can be combined into a single relationship called the combined gas law.

$$\text{Boyle's Law} \quad V \propto \frac{1}{P} \quad (T, n \text{ constant})$$

$$\text{Charles' Law} \quad V \propto T \quad (P, n \text{ constant})$$

$$\text{Therefore,} \quad V \propto \frac{T}{P} \quad (n \text{ constant})$$

- ❖ The combined law can be stated as: for a fixed mass of gas, the volume is directly proportional to kelvin temperature and inversely proportional to its pressure.

If k be the proportionality constant,

$$V = \frac{kT}{P} \quad (n \text{ constant})$$

$$\text{or} \quad \frac{PV}{T} = k \quad (n \text{ constant})$$

Gas Laws ...

If the pressure, volume and temperature of a gas be changed from P_1, V_1 and T_1 to P_2, T_2 and V_2 , then

$$\frac{P_1 V_1}{T_1} = k$$

$$\frac{P_2 V_2}{T_2} = k$$

or

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

This is the form of combined law for two sets of conditions. It can be used to solve problems involving a change in the three variables P, V and T for a fixed mass of gas.

iv. Gay Lussac's Law (1802)

- ❖ Joseph Gay Lussac as a result of his experiments established a general relation between the pressure and temperature of a gas. This is known as Gay Lussac's law or pressure-temperature law.
- ❖ It states that: at constant volume, the pressure of a fixed mass of gas is directly proportional to the kelvin temperature or absolute temperature.

The law may be expressed mathematically as

$$P \propto T \quad (\text{Volume, } n \text{ are constant})$$

or

$$P = kT$$

or

$$\frac{P}{T} = k$$

For different conditions of pressure and temperature

$$\frac{P_1}{T_1} = k = \frac{P_2}{T_2}$$

or

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

Knowing P_1 , T_1 , and T_2 , P_2 can be calculated.

v. Avogadro's Law

- Let us take a cylinder containing a certain mass of gas. If we add to it more mass of gas, holding the temperature (T) and pressure (P) constant, the volume of gas (V) will increase.
- It was found experimentally that the amount of gas in moles is proportional to its volume. This can be expressed as;

$$V \propto n \quad (T \text{ and } P \text{ constant})$$

or

$$V = A n$$

where A is constant of proportionality.

or

$$\frac{V}{n} = A$$

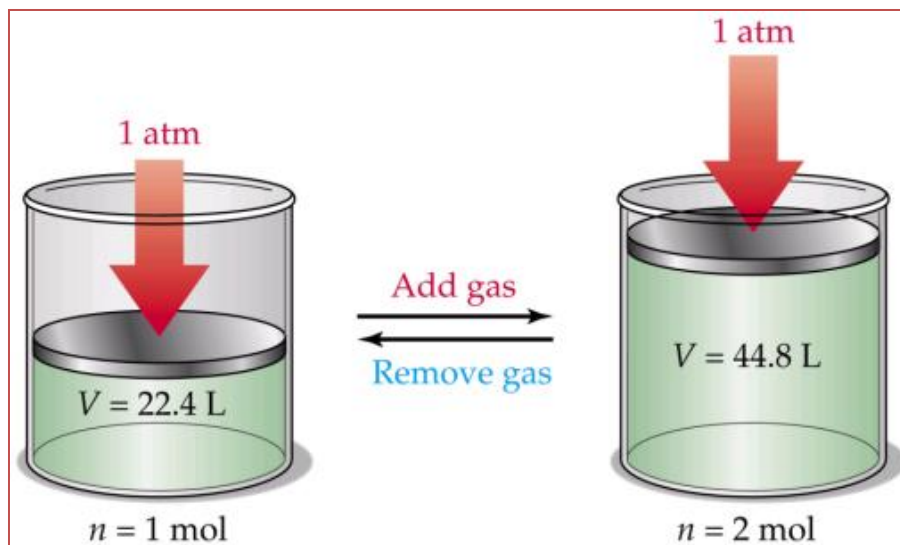
For any two gases with volumes V_1 , V_2 and moles n_1 , n_2 at constant T and P ,

$$\frac{V_1}{n_1} = A = \frac{V_2}{n_2}$$

- ❖ Thus for equal volumes of the two gases at fixed T and P , number of moles is also equal. This is the basis of Avogadro's Law which may be stated as: equal volumes of gases at the same temperature and pressure contain equal number of moles or molecules.

$$\text{If } V_1 = V_2, \quad n_1 = n_2$$

- ✓ *If the molar amount is doubled, the volume is also doubled.*



Example; 25.8 litre of a gas has a pressure of 690 torr and a temperature of 17°C. What will be the volume if the pressure is changed to 1.85 atm and the temperature to 345 K.

Use the relation 1 atm = 760 torr

SOLUTION

Initial conditions :

$$V_1 = 25.8 \text{ litres}$$

$$P_1 = \frac{690}{760} = 0.908 \text{ atm}$$

$$T_1 = 17 + 273 = 290 \text{ K}$$

Final Conditions :

$$V_2 = ?$$

$$P_2 = 1.85 \text{ atm}$$

$$T_2 = 345 \text{ K}$$

Substituting values in the equation

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

$$\frac{0.908 \text{ atm} \times 25.8 \text{ litre}}{290 \text{ K}} = \frac{1.85 \text{ atm} \times V_2}{345 \text{ K}}$$

Hence,

$$V_2 = \frac{0.908 \times 25.8 \times 345}{290 \times 1.85} = \mathbf{15.1 \text{ litres}}$$

Ideal Gas Equation

We have studied three simple gas laws :

$$\text{Boyle's Law} \quad V \propto \frac{1}{P} \quad (T, n \text{ constant})$$

$$\text{Charles' Law} \quad V \propto T \quad (n, P \text{ constant})$$

$$\text{Avogadro's Law} \quad V \propto n \quad (P, T \text{ constant})$$

These three laws can be combined into a single more general gas law :

$$V \propto \frac{nT}{P} \quad \dots(1)$$

This is called the **Universal Gas Law**. It is also called **Ideal Gas Law** as it applies to all gases which exhibit ideal behaviour *i.e.*, obey the gas laws perfectly. The ideal gas law may be stated as : **the volume of a given amount of gas is directly proportional to the number of moles of gas, directly proportional to the temperature, and inversely proportional to the pressure.**

Introducing the proportionality constant R in the expression (1) we can write

$$V = R \frac{nT}{P}$$

or $PV = nRT$... (2)

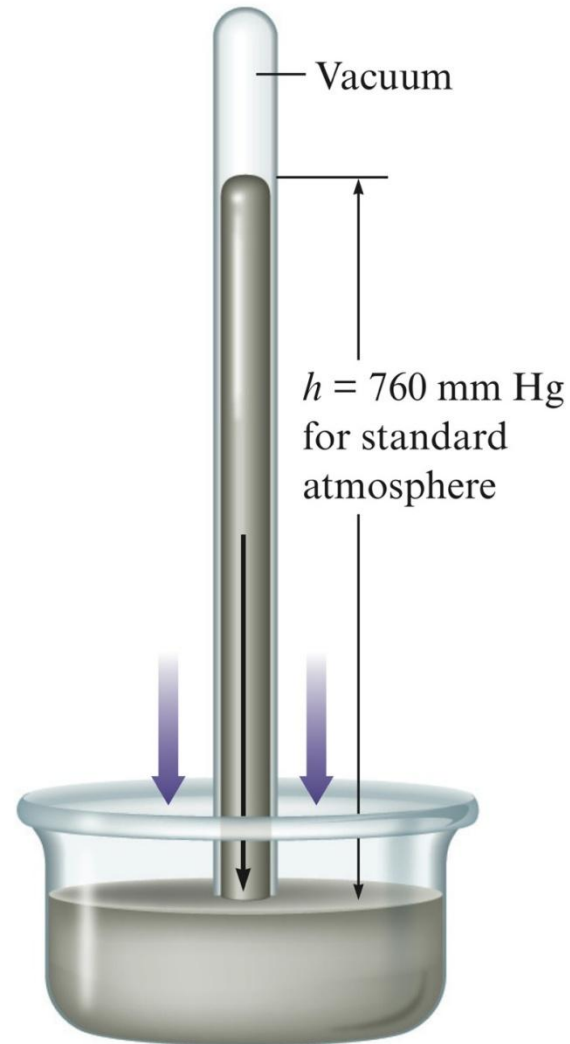
The equation (2) is called the **Ideal-gas Equation** or simply the general **Gas Equation**. The constant R is called the **Gas constant**. The ideal gas equation holds fairly accurately for all gases at low pressures. For one mole ($n = 1$) of a gas, the ideal-gas equation is reduced to

$$PV = RT$$
 ... (3)

Therefore an ideal gases are gases which obeys these equation.

4.3. Barometric formula

- **Barometer** is a device used to measure atmospheric pressure.



4.3. Barometric formula ...

- In this section we derive **how the gas pressure P depends** on the height over **sea level h** in the gravitational field of the earth. If we take an arbitrary gas column with intersection area A and height h , then the weight of this column is given by;

$$F = mg = \rho gV = \rho ghA$$

where ρ is the gas density, F is force, m is mass, g is gravitational force, V volume, h is height and A is area.

- Then the gas pressure is expressed by the following formula:

$$P = \frac{F}{A} = \frac{\rho ghA}{A} = \rho gh$$

Now imagine such a column in the atmosphere and separate a thin layer of air with the height dh (Figure 4.3). It's clear that such a layer causes the pressure change by the value of

$$dP = -\rho gdh$$

- The minus sign is included, because the pressure must decrease as the altitude increases.

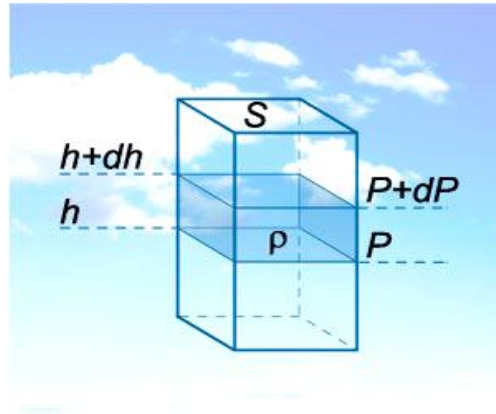


Figure.4.3 Schematic representation of the atmospheric thin layer with the height dh .

- Considering atmospheric air as an ideal gas, we can use the ideal gas law to express the density ρ through pressure P :

$$PV = \frac{m}{M}RT, \quad \Rightarrow \quad P = \frac{m}{VM}RT = \frac{\rho}{M}RT$$

Here T is the absolute temperature, R is the universal gas constant equal to 8.314 J/K.mol , M is the molar mass which is for air equal to $0.029 \frac{\text{kg}}{\text{mol}}$

- It follows from here that the density is given by the formula

$$\rho = \frac{MP}{RT}$$

- Putting this into the differential relation for dP gives:

$$dP = -\rho g dh = -\frac{MP}{RT} g dh, \quad \text{or} \quad \frac{dP}{P} = -\frac{Mg}{RT} dh$$

- We obtain a differential equation describing the gas pressure P as a function of the altitude h and integrating gives the relation:

$$\int \frac{dP}{P} = -\int \frac{Mg}{RT} dh, \quad \Rightarrow \ln P = -\frac{Mg}{RT} h + \ln C$$

- Getting rid of the logarithms, we obtain the *so-called barometric formula*

$$P = C \exp\left(-\frac{Mg}{RT} h\right)$$

- The constant of integration C can be determined from the initial condition $P(h = 0) = P_0$, where P_0 is the average sea level atmospheric pressure. Thus, dependency of the barometric pressure on the altitude is given by the formula;

$$P = P_o \exp\left(-\frac{Mg}{RT} h\right)$$

Exercise; Find the air pressure in a mine at a depth of 1 km at the temperature of 40 degrees celsius.

Solution.

The air pressure in the mine can be estimated using the general *barometric formula*:

$$P = P_0 \exp\left(-\frac{Mg}{RT}h\right).$$

We substitute the following values into the formula: $h = -1000$ m (the sign is minus because the mine is under sea level); $T = 40 + 273.15 = 313.15$ K. The remaining parameters are standard: $M = 0.02896 \frac{\text{kg}}{\text{mol}}$, $R = 8.3143 \frac{\text{N}\cdot\text{m}}{\text{mol}\cdot\text{K}}$, $g = 9.807 \frac{\text{m}}{\text{s}^2}$.

After simple calculations we find:

$$P = P_0 \exp\left(-\frac{Mg}{RT}h\right) = P_0 \exp\left[-\frac{0.02896 \cdot 9.807}{8.3143 \cdot 313.15}(-1000)\right] \approx P_0 \exp(0.109) \approx 1.115P_0$$

Since the atmospheric sea level pressure is $P_0 = 760$ mmHg, the air pressure in the mine will be 848 mmHg, that is about 12 percent greater than on the sea level.

Distribution of molecular velocities

- While **deriving kinetic gas equation**, it was assumed that all molecules in a **gas have the same velocity**. But it is not so.
- When any two molecules collide, one molecule **transfers kinetic energy to the other molecule**. That means velocity of the molecule which **gains energy** increases and that of the other decreases.
- Therefore, the velocities of molecules are *changing constantly*. Since the number of molecules is very large, **a fraction of molecules** will have the same particular velocity.
- In this way there is a broad distribution of velocities over different fractions of molecules.

- In 1860 James Clark **Maxwell** calculated the distribution of velocities from **the laws of probability.**
- He derived the following equation for the distribution of molecular velocities.

$$\frac{dN_c}{N} = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} e^{\frac{-MC^2}{2RT}} C^2 dc$$

where

dN_c = number of molecules having velocities between C and $(C + dc)$

N = total number of molecules

M = molecular mass

T = temperature on absolute scale (K)

- ✓ This relation is called **Maxwell's law of distribution of velocities.**

Different kinds of velocities

In our study of kinetic theory we come across three different kinds of molecular velocities :

- a) The average velocity (\bar{V})
- b) The root mean square velocity (μ)
- c) The most probable velocity (v_{mn})

a) Average Velocity

- ❑ Let there be n molecules of a gas having individual velocities $v_1, v_2, v_3 \dots v_n$.
- ❑ The ordinary average velocity is the mean of the various velocities of the molecules.

$$\bar{v} = \frac{v_1 + v_2 + v_3 + \dots + v_n}{n}$$

b) Root Mean Square Velocity

If $V_1, V_2, V_3 \dots V_n$ are the velocities of n molecules in a gas, and μ^2 , is the mean of the squares of all the velocities; then,

$$\mu^2 = \frac{v_1^2 + v_2^2 + v_3^2 \dots + v_n^2}{n}$$

Taking the root

$$\mu = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 \dots + v_n^2}{n}}$$

μ is thus the **Root Mean Square velocity or RMS velocity**. It is denoted by u .

The value of the RMS of velocity u , at a given temperature can be calculated from the Kinetic Gas Equation.

$$PV = \frac{1}{3}mNu^2 \quad \dots \text{Kinetic Equation}$$

$$u^2 = \frac{3PV}{mN}$$

For one mole of gas

$$PV = RT$$

Therefore,

$$u^2 = \frac{3RT}{M} \quad \dots M \text{ is molar mass}$$

$$u = \sqrt{\frac{3RT}{M}}$$

By substituting the values of R , T and M , the value of u (RMS velocity) can be determined.

c) Most Probable Velocity

As already stated the most probable velocity is possessed by the largest number of molecules in a gas. According to the calculations made by Maxwell, the most probable velocity, v_{mp} , is given by the expression.

$$v_{mps} = \sqrt{\frac{2RT}{M}}$$

Substituting the values of R , T and M in this expression, the most probable velocity can be calculated.

Relation between Average Velocity, RMS Velocity and Most Probable Velocity

We know that the average velocity, \bar{v} , is given by the expression

$$\bar{v} = \sqrt{\frac{8RT}{\pi M}}$$

and

$$\mu = \sqrt{\frac{3RT}{M}}$$

\therefore

$$\begin{aligned}\frac{\bar{v}}{\mu} &= \sqrt{\frac{8RT}{\pi M}} \times \sqrt{\frac{M}{3RT}} = \sqrt{\frac{8}{3\pi}} \\ &= 0.9213\end{aligned}$$

or

$$\bar{v} = \mu \times 0.9213$$

That is,

$$\text{Average Velocity} = 0.9213 \times \text{RMS Velocity}$$

Kinetic Theory of Gases ...

The expression for the most probable velocity, v_{mp} , is

$$v_{mp} = \sqrt{\frac{2RT}{M}}$$

and

$$\mu = \sqrt{\frac{3RT}{M}}$$

\therefore

$$\frac{v_{mp}}{\mu} = \sqrt{\frac{2RT}{M}} \times \sqrt{\frac{M}{3RT}} = \sqrt{\frac{2}{3}} = 0.8165$$

or

$$v_{mp} = \mu \times 0.8165$$

That is,

$$\text{Most Probable Velocity} = 0.8165 \times \text{RMS Velocity}$$

Kinetic Theory of Gases ...

Calculation of Molecular Velocity when pressure and density are given

In this case we have

$$u = \sqrt{\frac{3PV}{M}} \quad \text{or} \quad u = \sqrt{\frac{3P}{D}} \quad \left[\frac{M}{V} = D \right]$$

where P is expressed in dynes cm^{-2} and D in gm ml^{-1} .

SOLVED PROBLEM. Oxygen at 1 atmosphere pressure and 0°C has a density of 1.4290 grams per litre. Find the RMS velocity of oxygen molecules.

SOLUTION

We have

$$P = 1 \text{ atm} = 76 \times 13.6 \times 981 \text{ dynes cm}^{-2}$$

$$\begin{aligned} D &= 1.4290 \text{ g l}^{-1} = \frac{1.4290}{1000} \text{ g ml}^{-1} \\ &= 0.001429 \text{ g ml}^{-1} \end{aligned}$$

Applying

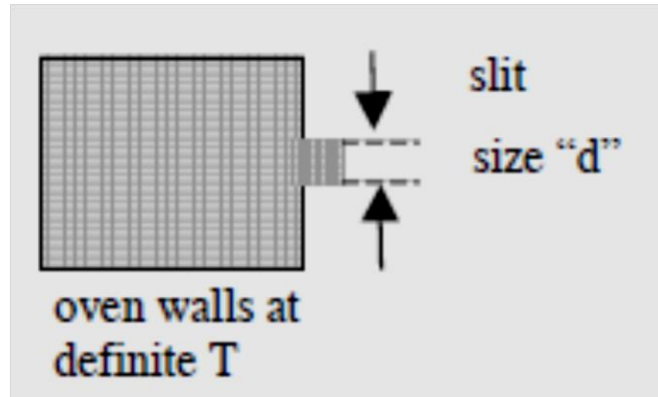
$$u = \sqrt{\frac{3P}{D}}$$

we get

$$u = \sqrt{\frac{3 \times 76 \times 13.6 \times 981}{0.001429}} = 46138 \text{ cm sec}^{-1}$$

Molecular Collisions

- Consider the process by which molecules escape through a hole in a vessel and into a vacuum which is called effusion. We assume that:
 - The size d is so small that the pressure in the vessel is unchanged;
 - The effusion does not perturb the velocity of the gas in the vessel; and
 - There are no collisions when the molecules pass through the slit.



- The effusion rate, v , has been found to be inversely proportional to the square root of its molar mass:

$$v \propto \sqrt{\frac{1}{M}}$$

- By Graham's law of effusion the **lighter molecules** are the first to exit because they **have a faster speed**.
- It tells us the rate at which the molecules of a certain gas exit from the container, or effuse.
- To see how Graham's law of effusion is derived **from kinetic theory**, consider the equation for the kinetic energy of a gas.

$$KE = \frac{1}{2}mv^2$$

- Because temperature **is a measure of the average kinetic energy of a gas**, two gases at the same temperature will also have the same kinetic energy.

Thus,

$$\frac{1}{2}m_1v_1^2 = \frac{1}{2}m_2v_2^2$$

- By rearranging terms, we get

$$\frac{v_1}{v_2} = \sqrt{\frac{M_2}{M_1}} \quad \text{How?}$$

- The **effusion time** (the time it takes for a certain amount of gas to escape a vessel) is inversely proportional **to the effusion rate** (the amount of gas effusing from the hole per unit time).
- Gas may effuse, but for this to happen a molecule must pass through a pore or pinhole and escape to the outside. In effect, a molecule must 'collide' with an escape hole.
- The number of such collisions will be linearly proportional to the **average speed** of the molecules in the gas and thus the effusion **rate**.

- The effusion **time** should be inversely proportional to the average *speed* of the molecules or proportional to the square root of the ratio of the molecular masses.
- The ratio of effusion rates, r_i , for two gases labelled by i , is proportional to the ratio of the RMS speeds of the gases, u_i

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} = \frac{u_1}{u_2}$$

Transport phenomena in Gases

- If a gas **is not uniform** with respect to composition, temperature, and velocity, transport processes occur until the **gas does become uniform**.
- The **transport of matter** in the absence of bulk flow is referred to as **diffusion**.
- The **transport of heat** from regions of high temperature to regions of lower temperature without convection is referred to as **thermal conduction** and
- The transfer of **momentum** from a region of higher velocity to a region of lower velocity gives rise to the phenomenon of **viscous flow**.
- In each case the rate of flow is proportional to the rate of change of some property with distance, a **so-called gradient**.

a. Diffusion

- ✓ The flux of component i in the **z-direction** due to diffusion is proportional to the concentration gradient dc_i/dz , according to **Fick's law**:

$$J_{iz} = -D \frac{dc_i}{dz}$$

- ✓ The proportionality constant is the **diffusion coefficient “D”**.
- ✓ The flux J_{iz} is expressed in terms of quantity per unit area per unit time.
- ✓ If the SI units are used, J_{iz} has the units $\text{mol m}^{-2} \text{s}^{-1}$ dc_i/dz has the units of mol m^{-4} and D has the units of $\text{m}^2 \text{s}^{-1}$.
- ✓ The **negative sign comes** from the fact that if c_i increases in the positive z direction, dc_i/dz is positive, but the flux is in the negative z direction because the flow is in the direction of **lower concentration**.

b. Thermal conductivity

- The transport of heat is due to a **gradient in temperature**. Thus the flux of energy q_z in the z direction due to the temperature gradient in that direction is given by:

$$q_z = -k \frac{dT}{dz}$$

Where the proportionality constant k is the **thermal conductivity**.

- ✓ When q_z has the units of $\text{J m}^{-2} \text{s}^{-1}$ and dT/dz has the units of K m^{-1} , k has the units of $\text{J m}^{-1} \text{s}^{-1} \text{K}^{-1}$.
- ✓ The negative sign in the equation indicates that if dT/dz is positive, the flow of the heat is in the negative z direction, which is direction toward lower temperature.
- ✓ **Thermal diffusion** is the flux of material due to a temperature gradient of dT/dz .

c. Viscosity

- **Viscosity** is a measure of the resistance that a fluid offers to an applied shearing force.
- The **velocity gradient** is represented by dv_y/dz . The viscosity η is defined by the equation,

$$F = -\eta \frac{dv_y}{dz}$$

- Here F is the force per unit area required to move one plane relative to the other.
- The negative sign comes from the fact that if F is in the +y direction, the velocity v_y decreases in successive layers away from the moving plane and dv_y/dz is negative.
- If F has the units of $\text{kg m}^{-1}\text{s}^{-2}$ and dv_y/dz has the units of ms^{-1}/m , then the viscosity has the units of $\text{kg m}^{-1}\text{s}^{-1}$.
- The SI unit of viscosity is **the Pascal second**.