

## Graham's Law of Diffusion

1. Molecules of gas are in continuous motion. When two or more gases are placed in contact, their molecules mix spontaneously until a homogeneous mixture is formed. Mixing of gases occur even against the gravitational force. The process of mixing of gases is not reversible. The process of mixing is accelerated by wind.
2. The phenomenon of spontaneous intermixing of two or more gases in all directions irrespective of gravitational force is called Diffusion.
3. Diffusion is the characteristic property of gases. Due to this phenomenon we can readily detect the fragrance of a flower or bad rotten egg smell of hydrogen sulphide.
4. 'Effusion' is the passage of gas molecules through a small aperture, from high pressure region to a region of low pressure.

\*Both diffusion and effusion processes are essentially same. However, in the case of diffusion the gas spontaneously streams, but in the case of effusion the gas is forced out by applying pressure.

5. **Rate of Diffusion:** The amount of gas diffused in one sec is called rate of diffusion. Rate of diffusion is equal to the distance travelled by a gas through a tube of uniform cross-section in one sec. rate of effusion ( $r$ ) is given by

$$r = \frac{V}{t} \quad \text{or} \quad l/t$$

Where 'V' is the volume of gas diffused and 'l' is distance travelled by a gas, 't' is the time taken for diffusion. The units of rate of diffusion are  $\text{cc s}^{-1}$  (or)  $\text{L s}^{-1}$  (or)  $\text{mol s}^{-1}$  (or)  $\text{g s}^{-1}$  (or)  $\text{cm/sec}$ .

6. Rate of diffusion of a gas increases with an increase in the temperature, pressure and also with velocity of gas. Generally lighter gases diffuses faster than heavier gases.

### Graham's Law

7. **Graham's law** is stated as, at constant temperature and pressure, the rate of diffusion of a gas is inversely proportional to square root of its density.

The rate of diffusion (r) is related to the density (d) of gas by the equation

$$r \propto \frac{1}{\sqrt{d}}$$

Density is directly proportional to the molecular weight (M) or vapour density (VD) of gas. Graham's law is also stated as the rate of diffusion of gas is inversely proportional to the square root of its molecular weight or vapour density.

$$r \propto \frac{1}{\sqrt{M}} \text{ (or) } \frac{1}{\sqrt{VD}}$$

8. **The ratio of rates of diffusion of two gases under identical conditions of temperature and pressure is given as**

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{VD_2}{VD_1}}$$

9. **The ratio of rates of diffusion of two gases is also related as**

$$\frac{r_1}{r_2} = \frac{V_1 t_2}{V_2 t_1}$$

- i. If volumes of two gases diffused are same, the ratio of times (t) taken for

diffusion is given as 
$$\frac{t_2}{t_1} = \sqrt{\frac{M_2}{M_1}}$$

- ii. If the time taken for the diffusion of two gases is same the ratio of volumes

(V) is given as 
$$\frac{V_1}{V_2} = \sqrt{\frac{M_2}{M_1}}$$

iii. Combining Graham's law and Avogadro's law, the ratio of number of

moles (n) of two gases is given as  $\frac{n_1 \cdot t_2}{n_2 \cdot t_1} = \sqrt{\frac{M_2}{M_1}}$  (Or)  $\frac{w_1}{t_1} \times \frac{t_2}{w_2} = \sqrt{\frac{M_1}{M_2}}$

10. The ratio of rate of diffusion of two gases is also related to pressure (P) and

molecular weight (M) at a given temperature is  $\frac{r_1}{r_2} = \frac{P_1}{P_2} \sqrt{\frac{M_2}{M_1}}$

11. The rate of diffusion of two gases are related to their molecular weights and

absolute temperatures at a given pressure is  $\frac{r_1}{r_2} = \sqrt{\frac{T_1}{T_2} \times \frac{M_2}{M_1}}$

12. Some important applications of the phenomenon of mixing of gases, diffusion and effusion are

- Spreading of poisonous gases in atmosphere.
- Ansil alarm in coal mines for the detection of marsh gas is based on diffusion.
- At molysis, a process of separation of uranium isotopes is also based on diffusion, where the isotopes are converted to volatile uranium hexafluorides
- Leakage of domestic cooking gas can be detected based on effusion (smelling agent used is methyl thioalcohol).
- For the separation of components of gaseous mixture.
- Useful in the calculation of molecular weights and density of gases and vapours.

**Dalton's Law Of Partial Pressures:-** At a given temperature, the total pressure exerted by two or more non reacting gases occupying a definite volume is equal to the sum of the partial pressures of the component gases.

Mathematically  $P = p_1 + p_2 + p_3 + \dots$  (T, V constant)

Where  $P_1$ ,  $P_2$  and  $P_3$  are the partial pressures of the component gases respectively.

i. In a mixture the pressure exerted by the individual gas is known as its partial pressure

ii. **Partial pressure in terms of mole fraction** :- Let  $n_1, n_2$  be the no. of moles of two non-reacting gases A and B filled in a vessel of volume V at temperature T,

Total pressure in the vessel P may be calculated as  $PV = (n_1 + n_2)RT$  ..... (1)

Partial pressures may be calculated as  $P_A V = n_1 RT$  .....(2)

$$P_B V = n_2 RT$$
 .....(3)

Adding eq 2 & 3, we get  $(P_A + P_B)V = (n_1 + n_2)RT$  .....(4)

Comparing equation (1) and (4), we get.  $P = P_A + P_B$

Dividing equation (2) and (1), we get  $\frac{P_A}{P} = \frac{n_1}{n_1 + n_2} = X_A \Rightarrow P_A = P_{total} \cdot X_A$

Similarly dividing equation (3) and (1), we get  $\Rightarrow P_B = P_{total} \cdot X_B$

Hence partial pressure of a component = mole fraction x total pressure.

### Applications of Dalton's Partial pressure law

i. Water insoluble gases like  $N_2, O_2, He, H_2$  etc are collected over water. When a gas is collected over water the observed pressure of the gas is equal to the sum of the pressures dry gas and pressure of water vapour.  $P_{moist\ gas} = P_{dry\ gas} + P_{water\ Vapour}$

ii. The partial pressure of the water in the gas mixture collected is called aqueous tension and is equal to vapour pressure of water at that temperature

$$\Rightarrow P_{dry\ gas} = P_{moist\ gas} - \text{Aqueous tension}$$

3. Dalton's law is applicable only to those gaseous mixtures with chemically non-interacting components.

**E.g.,** Helium and hydrogen,

Hydrogen and nitrogen,

Nitrogen and oxygen,

Oxygen and carbondioxide,

Hydrogen and oxygen etc

The law is not applicable to those mixtures with interacting components,

**E.g.,** Ammonia and hydrogen chloride

Hydrogen sulphide and ammonia,

Oxygen and nitric oxide

Chlorine and carbon monoxide

Carbon monoxide and oxygen

Ammonia and hydrogen fluoride

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