PHYSICAL GAS LAWS

Matter in the gaseous state has different characteristics from that in the solid and liquid states. Thus, the behaviour of gases is expected to differ from that of solids and liquids. This was investigated by many of the early scientists like Boyle, Charles, Graham and Dalton. They studied the physical behaviour of gases. Their important findings are now named after them. The chemical behaviour of gases was studied by Gay-Lussac.

Assumptions of the Kinetic Theory of Gases

The gas laws which explain the physical behaviour of gases can be expained by the Kinetic Theory of Gases. This theory describes the behaviour of an Ideal or Perfect Gas. It states the following:

- The gas molecules move randomly in straight lines, colliding with one another and with the walls of the container.

- The collisions of the gas molecules are perfectly elastic, i.e. no kinetic energy is converted to heat.
- The actual volume occupied by the gas molecules themselves is negligible relative to the volume of the container.
- The cohesive forces between the gas molecules are negligible.
- The temperature of the gas is a measure of the average kinetic energy of the gas particles.

The particles of a gas contained in a vessel move randomly at high speeds, often colliding with one another and with the walls of the vessels. Each time a gaseous particle hits or collides with the wall of the vessel, it exerts a very small force on it. Since the gas particles are numerous and evenly distributed, their collisions exert a constant force on the walls of the vessel. This force that the gaseious particles exert per unit area of the wall is known as the gas pressure. It will be constant in

every unit area of the walls of the vessel in which the gas is enclosed.

Gas pressure is commonly measured in atmospheres (atm) or millimeter mercury (mmHg). The SI unit for measuring pressure is the Pascal (Pa), i.e. newtons per square metre (Nm^{-2}).

Boyle's Law

Consider a given mass of gas enclosed in a vess with a movable piston, which is kept stationary by placing a suitable weight on it. At constant temperature, the avarage velocity of the gas molecules is constant, so the number of collisions they make per unit area of the wall of the vessel is also constant, i.e. the gas exerts a certain constant pressure P, on the walls of the vessel.

If the weight on the piston is replaced with a light one such that the piston moves up and the original volume, V, of the gas is doubled, then the gas molecules will be spread out. As a result, the number of collisions the gas molecules make per

unit area of wall is halved, i.e. the gas only half its original pressure, P. Hence, at constant temperature, volume of gas increases as pressure reduces.

The above illustrates the law of gas by Robert Boyle in 1662. The law states that the volume of a given mass of gas is inversely proportional to its pressure, provided that the temperature remains constant. Mathematically:

$$V \propto \frac{1}{P} \rightarrow V = kP \; or \; PV = k$$

where V is the volume, P is the pressure, k is constant.

Charles' Law

Consider a given mass of gas confined in a vessel with a movable piston. If the gas is heated, the molecules acquire more kinetic energy, move faster and collide more often with the walls of the vessel, thereby increasing the pressure they exert. To maintain the same number of collisions on the

walls of the vessel (i.e. to remain at constant pressure), the piston moves up so that the volume of the gas is increased. Hence, at a constant pressure, the volume of a given mass of gas is directly proportional to the temperature.

The above illustration describes the effect of temperature changes on the volume of a given mass of gass at a constant pressure describe by Jacques Charles, a French scientist.

Charles' Law states that the volume of a given mass of gas is directly proportional to its temperature in Kelvin, provided that pressure remains constant. Mathematically, the law can be expressed as:

$$V \propto T \rightarrow V = kT \; or \frac{V}{T} = k$$

where V=volume, T=kelvin temperature, k=constant.

Kelvin Temperature: Temperature affects the volume of matter. The effect is most pronounced on gases. Charles discovered that the volume of a given mass of gas will increase or decrease by $\frac{1}{273}$ of its volume at 0°C for every 1°C rise or fall in the temperature, provided that the pressure remains constant. Thus, if a gas has a volume of 273cm^3 at 0°C, its volume would be 272cm^3 at -1°C, 271cm^3 at -2°C and 0cm^3 at -273°C. In actual practice this is not possible because all gases liquefy above this temperature and hence Charles' Law would no longer apply. But this temperature, at which the volume of gas would be theoretically reduced to zero, is significant because it is the lowest possible temperature that can be reached. Earlier scientist describes this temperature of -273°C as the absolute zero. The Kelvin temperatures are also called the *absolute temperatures*.

The equivalent temperatures on the Celsius and Kelvin scales which should be remembered are 0°C=273K and -273°C=0K.

The formula of converstion among Kelvin and Celsius scales are:

$$K = {}^{o}C + 273; \quad {}^{o}C = K - 273$$

General Gas Equation

From the gas laws, we know that the volume of a gas depend on both its temperature and pressure. The relationship between the three variables, i.e. volume, temperature, and pressure, can be summed up as follows:

$$V \propto \frac{1}{P}; V \propto T; V \propto \frac{T}{P} \rightarrow V = \frac{kT}{P} \; or \; k = \frac{VP}{T}$$

The above equation $\frac{PV}{T} = k$ is often known as the General Gas Equation. It simply states that for a fixed mass of gas under any set of conditions of V, P, and T, the value of $\frac{PV}{T}$ must remain constant.

Standard Temperature and Pressure (stp). The physical behaviour of gases is very much affected by weather conditions. As such, scientists decided

that 0^oC or 273K and 760mmHg or $101325Nm^{-2}$ should be standard temperature and pressure (stp) at which gas volumes are given and sometimes analyzed.

John Dalton's Law of Partial Pressure

According to Dalton's law, the total pressure of a mixture of gases is the sum of the presssures which each individual gas would exert if it were confied alone in the volume occupied by the mixture. Mathematically, this can be expressed as:

$$P_{Total} = P_A + P_B + P_C + \cdots$$

where P_{total} = total pressure of the mixture, and P_A, P_B, P_C are the partial pressures exerted separately by the individual gases A, B, C, that make up the mixture.

The Dalton's law of partial pressure assumes that the gases do not react chemically together.

For example, if a certain mass of hydrogen gas is collected over water at 6°C and 765mmHg pressure has a volume of 35cm^3. Find the actual pressure of the hydrogen gas. (SVP of water at 6°C = 7mmHg).

Solving

$$P_{total} = P_{hydrogen} + P_{steam}$$

$$P_{total} = 765mmHg; \qquad P_{steam} = 758mmHg$$

$$P_{hydrogen} = P_{total} - P_{steam}$$

$$P_{hydrogen} = 765 - 758 = 7mmHg.$$

Ideal Gas Equation

This equation states that for an ideal gas $\frac{PV}{T}$ is a constant. It has also been proven experimentally that equal volumes of all gases at the same temperature and pressure contain the same number of molecules, and that one mole of any gas at stp occupies a volume of 22.4dm^3. This fact,

together with Boyle's and Charles' laws, leads to another equation:

$$PV = RT$$

where R is a constant termed as the *molar gas constant*. The equation is called the *Ideal Gas Equation* and holds true for all gases. For *n* moles of gas, the formular is

$$PV = nRT$$

where P is in atm, V in dm^3, T in K, n= no. of moles. At stp, for 1 mole of gas,

$$Molar\ Gas\ Constant\ (R) = \frac{PV}{nT} = \frac{1 \times 22.4}{1 \times 273}$$
$$= 0.082\ atm dm^3 K^{-1} mol^{-1}$$

Relative Vapour Density of Gases

The vapour density of a gas (or vapour) is expressed as the number of times a given volume of the gas (or vapour) is as heavy as the same

volume of hydrogen at a particular temperature and pressure.

The Vapour Density (V.D.) of a gas or vapour can be expressed as follows (the temperature and pressure must be constant):

$$V.D. = \frac{mass\ of\ a\ given\ volume\ of\ the\ gas}{mass\ of\ an\ equal\ volume\ of\ hydrogen\ gas}$$

Vapour Density and Relative Molecular Mass

$$V.D. = \frac{mass\ of\ x\ volumes\ of\ the\ gas/vapour}{mass\ of\ x\ volumes\ of\ hydrogen\ gas}$$

Apply Avogadro's law,

$$V.D. = \frac{mass\ of\ x\ molecules\ of\ the\ gas}{mass\ of\ x\ molecules\ of\ hydrogen\ gas}$$

$$= \frac{mass\ of\ 1\ molecule\ of gas/vapour}{mass\ of\ 1\ molecule\ of\ hydrogen}$$

$$V.D. = \frac{molar\ mass\ of\ the\ gas/vapour}{2}$$

On the hydrogen scale,

$$V.D. = \frac{1}{2} \times molar\ mass\ of\ gas/vapour$$

Graham's Law of Diffusion of Gases

Graham, an English Chemist, in 1833, discovered that a less dense gas can diffuse through a medium much faster than a denser gas. He carried out an experiment to examine the relationship between the rate of diffusion of a gas and its density.

Note the formular for the Rate of Diffusion, R and Density, ρ.

$$R = \frac{volume\ or\ number\ of\ molecules}{time}$$

$$Density, \rho = \frac{mass}{volume}$$

Graham's Law of Diffusion states that at a constant temperature and pressure, the rate of diffusion of a gas is inversely proportional to the square root of its density.

i.e $R \propto \frac{1}{\sqrt{\rho}} \rightarrow R = \frac{k}{\sqrt{\rho}}$

where k is the proportionality constant. If we compare two gases A and B with rate of diffusion R_A and R_B and densities ρ_A and ρ_B, we would have:

$$\frac{R_A}{R_B} = \sqrt{\frac{\rho_B}{\rho_A}}$$

Rate of diffusion is inversely proportional to time t, i.e.

$$R \propto \frac{1}{t} \rightarrow R = \frac{1}{t} (if\ k = 1)$$

By substituting, $R_A = \frac{1}{t_A}$ and $R_B = \frac{1}{t_B}$

$$\frac{R_A}{R_B} = \frac{t_B}{t_A} = \sqrt{\frac{\rho_B}{\rho_A}}$$

$$Vapour\ Density = \frac{1}{2} \times molar\ mass\ of\ gas\ or\ vapour$$

Thus, density is proportional to the relative molecular mass, m of a gas. Thus in place of density we can substitute relative molecular mass. Generally

$$\frac{R_A}{R_B} = \frac{t_B}{t_A} = \sqrt{\frac{\rho_B}{\rho_A}} = \sqrt{\frac{m_B}{m_A}}$$