Dalton's law of partial pressure

In 1801, john Dalton established the relationship between partial pressures of the component gases and total pressure of the mixture of gases. This is called Dalton's law of partial pressure.

Statement

> *The total pressure exerted by a gaseous mixture of two or more non-reacting gases equal to the sum of the partial pressures of the component gases at a constant temperature.*

If the partial pressure of the gases A, B and C are P_A, P_B and P_C and the total pressure of the mixture of gases is P.

According to Dalton's law,

$$P = P_A + P_B + P_C$$

Partial pressures of each component gas can be determined either by applying Boyle's law and ideal gas equation.

Partial pressure

The pressure exerted by a component gas in a gaseous mixture is called partial pressure.

Mathematical deduction of Dalton's law of partial pressure **by** *Boyle's law*

Let us consider three gases A, B and C at pressure P_1, P_2 and P_3 and volume V_1, V_2 and V_3 respectively, by mixed together to form a gaseous mixture at constant temperature.

If the partial pressure of gas A, B and C are P_A, P_B and P_C respectively. Boyle's law can be used their calculation.

Partial pressure of the gas A

$$P_A (V_1 + V_2 + V_3) = P_1 V_1$$

$$P_A = \frac{P_1 V_1}{(V_1 + V_2 + V_3)} \text{------------- (1)}$$

Partial pressure of the gas B

$$P_B (V_1 + V_2 + V_3) = P_2 V_2$$

$$P_B = \frac{P2\ V2}{(V1 + V2 + V3)} \text{------------- (2)}$$

Partial pressure of the gas C

$$P_C (V_1 + V_2 + V_3) = P_3 V_3$$

$$P_C = \frac{P3\ V3}{(V1 + V2 + V3)} \text{------------- (3)}$$

According to Dalton's law of partial pressure, total pressure of a gaseous mixture P will be the sum of the partial pressure of the component gases.

$$P = P_A + P_B + P_C$$

$$= \frac{P1\ V1}{(V1 + V2 + V3)} + \frac{P2\ V2}{(V1 + V2 + V3)} + \frac{P3\ V3}{(V1 + V2 + V3)}$$

$$= \frac{P1V1 + P2V2 + P3V3}{(V1 + V2 + V3)} \text{-------------- (4)}$$

The equation (4) is mathematical equation of Dalton's law of partial pressure.

Mathematical deduction of Dalton's law of partial pressure by ideal gas equation

Suppose, A gaseous mixture composed of n_A moles of gas A, n_B moles of gas B and n_C moles of gas C. Let the total volume of gaseous mixture be V and temperature be T. If n_t be the total no. of moles of the gaseous mixture then,

$$n_{total} = n_A + n_B + n_c$$

Multiplying both sides the above equation $\dfrac{RT}{V}$

$$n_{total}\frac{RT}{V} = n_A\frac{RT}{V} + n_B\frac{RT}{V} + n_C\frac{RT}{V}$$

According to ideal gas equation

$$PV = n\ RT$$
$$P_A = n_A RT/V$$
$$P_B = n_B RT/V$$
$$P_C = n_C RT/V \text{ and } P_{total} = n_{total} RT/V$$
$$P_{total} = P_A + P_B + P_c$$

This equation verifies Dalton's law of partial pressure.

Applications of Dalton's law

### 1) In determination of pressure of dry gas from moist gas.

A gas collected over water, it becomes saturated with water vapor. Thus, the total   pressure exerted by the moist gas will be the sum of the partial pressure of dry gas and that of water vapor. The pressure exerted by water vapor is also called aqueous tension.

$P_{total} = P_{gas} + P_{water\ vapour}$

$P_{gas} = P_{total} - P_{water\ vapour}$

Water Vapor is also called aq. Tension and is denoted by f.

$P_{gas} = P_{total} - f$
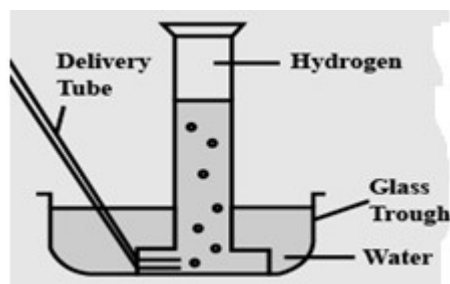
2) In the calculation of partial pressure

If A, B and C be the three different component gases with partial pressure P_A, P_B, and p_c then from the ideal gas equation

$PV = nRT$

$P = \dfrac{nRT}{V}$

$P_A = n_A RT / V$
$P_B = n_B RT / V$
$P_C = n_C RT / V$ and so on.

By Dalton's law of partial pressure,

$P_{total} = P_A + P_B + P_C$

$= \dfrac{RT}{V}[\ n_A + n_B + n_C]$

Then $P_A / P_{total} = n_A / [\ n_A + n_B + n_C]$
$P_B / P_{total} = n_B / [\ n_A + n_B + n_C]$
And, $P_C / P_{total} = n_C / [\ n_A + n_B + n_C]$
$P_A / P_{total} = X_A$ [Mole fraction of A]
$P_A = X_A \cdot P_{total}$

Partial pressure of a component = (Mole fraction of the component gas x Total Pressure)

According to kinetic molecular theory, the gases exert pressure on the wall of the vessel due to collision of the gas molecules on the vessel. The pressure exerted by gas depends on the number of collisions of molecules on the wall per unit time but not on their nature. Hence two or more gases are present in the container and they contain two or more type of molecules then the total pressure exerted by the mixture of gases must be equal to the sum of pressure of component gases. If it alone occupied the inter space of the vessel (constant volume) at constant temperature. This result is also the statement of Dalton's law of partial pressure

Graham's law of Diffusion

In 1829, Graham's state the law

Statement

Under similar condition of temperature and pressure the rate of diffusion of gases are inversely proportional to the square root of their densities.

Mathematically,

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

Where r = rate of diffusion of gas

d = density of gas

Let r_1 and r_2 be the rate of diffusion of two gases of their densities d_1 and d_2 respectively.

$$r_1 \propto \frac{1}{\sqrt{d_1}} \quad \& \quad r_2 \propto \frac{1}{\sqrt{d_2}}$$

$$\therefore r_1 = K\frac{1}{\sqrt{d_1}} \quad \& \quad r_2 = K\frac{1}{\sqrt{d_2}} \quad \text{where 'k' is proportionality constant}$$

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} \quad \text{(At same temperature and pressure)}\ldots\ldots\text{(iii)}$$

Since molecular weight (M) = 2 × vapour density,

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2/2}{M_1/2}} = \sqrt{\frac{M_2}{M_1}} \quad \ldots\ldots\ldots\ldots\text{(iv)}$$

Where M_1 and M_2 are the molecular weight of gases having density d_1 and d_2 respectively

This equation is another form of Graham's law of diffusion, on the basis of this equation, Graham's law may be stated that

Statement

Under similar condition of temperature and pressure the rate of diffusion of gases are inversely proportional to the square root of molecular weights.

Rate of diffusion is the volume of gas diffused per unit time

i.e*., rate of diffusion = volume of the gas diffused (V)/ diffusion time (t)*
Accordingly,

$$r_1 = \frac{V_1}{t_1} \quad \text{.....................(v)}$$

$$r_2 = \frac{V_2}{t_2} \quad \text{....................(vi)}$$

where V_1 and V_2 are the volume of two gases that diffuse in time t_1 and t_2 respectively

Substituting these values in equation (iv), we get

$$\frac{r_1}{r_2} = \frac{V_1/t_1}{V_2/t_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}} \quad \text{...................(vii)}$$

If $V_1 = V_2 = V$, we get

$$\frac{r_1}{r_2} = \frac{t_2}{t_1} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}} \quad \text{...................(viii)}$$

If $t_1 = t_2 = t$, then from equation (vii), we get

$$\frac{r_1}{r_2} = \frac{V_1}{V_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}} \quad \text{...................(ix)}$$

Diffusion: *Diffusion is a natural phenomenon by virtue of which two or more gases intermix with one another irrespective of gravitational force of attraction without any aid of external agency.*

Or, the tendency of mixing of non-reacting gases with each other spontaneously without external pressure is called diffusion.

Effusion *If a gas enclosed in a vessel under pressure is allowed to escape through a small hole, then the process is called effusion of gases*.

Applications of Graham's law of diffusion

➢ **It is used to measure the rate of diffusion of gas.**
➢ **It is used to determine the vapor density of gas.**

- ➢ **It is used to determine the molecular wt. of gas.**
- ➢ **It is used to separate the isotopes of gases.**
- ➢ **It is used to separate the mixture of gases.**

Rate of diffusion = $\dfrac{distance\ travelled\ by\ diffused\ gas\ (d)}{time\ taken\ (t)}$

Rate of diffusion (r) = $\dfrac{moles\ of\ diffused\ gas\ (n)}{time\ taken\ (t)}$

Effect of pressure: *Rate of diffusion of gas is directly proportional to pressure and inversely proportional to square root of their molecular mass.*

Rate of diffusion (r) α 1/ √M

Rate of diffusion (r) α P

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} \times \frac{P_1}{P_2}$$

Kinetic theory of gases

The kinetic theory of gases was put forward by Bernoulli and further developed and extended by Clausius, kroning, Maxwell, Boltzmann and others. The fundamental postulates of this theory are:

- ➢ All gases are made up of large number of tiny (Minute) particles called molecules.
- ➢ The molecules are separated from one another by large distance with a lot of empty space between them; hence the volume occupied by the molecules is negligible compared to the volume of the gas.
- ➢ The molecules are in the state of constant motion in all directions along straight line. During their motion they collide with one another and also with the wall of the container.
- ➢ Molecular collision is perfectly elastic so, that is no loss of kinetic energy occurs when the molecule collides with one another as well as with the wall of the vessel.
- ➢ There is no force of attraction between molecules that is intermolecular forces in gas are negligible.
- ➢ The pressure exerted by the gas is due to the bombardment of the molecule of gas on the walls of the vessel.
- ➢ The average kinetic energy of the gas molecules is directly proportional to the absolute or kelvin temperature. K.E. α T

IDEAL GAS AND REAL GAS

Ideal gas or perfect gas

Gases which obey the gas laws under all the conditions of temperature and pressure are called ideal gases. Actually, no gas is an ideal gas.

Real or gas or non-ideal gas

Gases which do not obey the gas laws under all the conditions of temperature and pressure are called non ideal gases.

Difference between ideal and non ideal gas

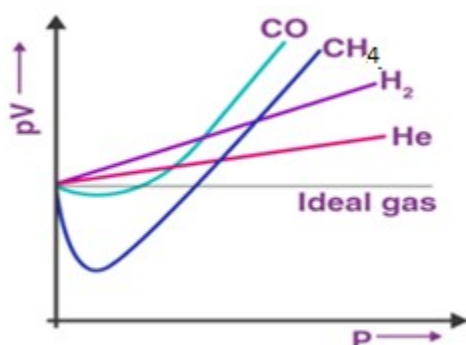| Ideal Gas	Real Gas
They have no designated volume.	They have a definite and designated volume of their own.
The molecules present in the ideal gas have elasticity in them.	The particles present in the real gas experience non-elastic collision.
They do not have a defined mass.	They have a defined mass of their own.
The intermolecular forces of attraction present in the ideal gas are negligible or non-existent.	The intermolecular forces of attraction present in the real gas are prominent and cannot be ignored or neglected.
When the total volume of the ideal gas is considered, the volume of the molecules is negligible.	When the total volume of the ideal gas is considered, the volume of the molecules cannot be ignored.
An ideal gas is hypothetical. It doesn't exist in free form in the environment.	Real gas is not hypothetical. It does exist in the environment.
An ideal gas always exists under high pressure.	Real gas exists at low pressure as compared to the ideal gas.
There is no presence of any attractive or repulsive forces between the particles.	A very small amount of attractive or repulsive forces can be present between the particles.
The ideal gas has only kinetic energy.	It has both potential as well as kinetic energy.
The volume of an ideal gas is Zero.	The volume of a real gas is non-zero.

| Examples of an ideal gas are no ideal gases.	Examples of real gas are carbon dioxide, nitrogen, water vapor, and so on.

Deviation of real gases from ideal behavior

Real gases nearly obey the ideal gas equation at high temperature and low pressure. On decreasing the temperature and increasing the pressure, there is deviation of real gas from ideal behavior. The deviation of real gas from ideal behavior can be explained on the basis of following carves.

If PV verses P plot of some gases like He, H_2, CH_4, CO etc. at 273K temperature all are deviate from ideal gas.

A plot of PV verses P for single nitrogen gas at different low temperature, the larger is the deviation from ideal behavior.
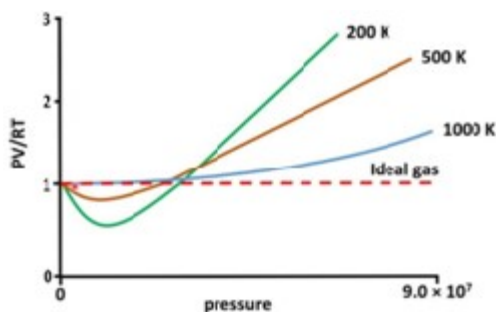
Causes of deviation of real gas

Vander Waal's was the first man who put forward a simple and logical explanation for the deviation of real gases from ideal behavior. According to him, the causes of deviation may be attributed to the two faulty assumptions made in kinetic theory of gases. They are:

➢ The actual volume of the molecules is negligible compared to the total volume occupied by the gas.
➢ There is no force of attraction between the gas molecules that is the intermolecular forces of attraction are negligible.

These two assumptions are justifiable at low pressure and high temperature. However, at high pressure and low temperature neither of these two assumptions are justifiable. It is because at high pressure and low temperature molecule come closer to each other hence the intermolecular forces of attraction operate. Therefore, intermolecular forces cannot be neglected. Again, as the molecules come closer, the empty space decreases and the finite actual volume of the gas molecules cannot be ignored compared to the total volume occupied by the gas.

Vander Waal's took into considerations the above factors, made necessary correction in the volume and pressure of the gas and finally modified the ideal gas law equation to the form.

For n mole of gas

$$\left(P + \frac{a\,n^2}{V^2}\right)(V - nb) = nRT$$

For 1 mole

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

Where a and b are constant and known as Vander Waal's constant and it is characteristic of gases.