Dalton's Law of Partial Pressure

- The relation between the pressures of the mixture of non-reacting gases enclosed in a vessel to their individual pressure is described in the law.

- The law was given by John Dalton in 1807.

- *At constant temperature, the pressure exerted by a mixture of two or more non-reacting gases enclosed in a definite volume, is equal to the sum of the individual pressures which each gas would exert if present alone in the same volume.*

- The individual pressures of gases are known as partial pressures.

- **Mathematically**
  If P is the total pressure of the mixture of non-reacting gases at temperature T and volume V, and P_1, P_2, P_3 …. represent the partial pressures of the gases, then

- **P = P₁ +   P₂ +   P₃+   ………   (T,   V   are   constant)**

- **Partial Pressure in terms of Mole Fraction**
  Mole fraction (X) defines the amount of a substance in a mixture as a fraction of total amount of all substances.

  If n =1 moles of any substance is present in n moles of the mixture, then mole fraction of the substance,

$$X_1 = n_1 / n$$
$$X_1 = P_1 / P$$
$$P_1 = X_1 \times P$$
$$P = P_1 + P_2 + P_3 + ………. + P_i$$
$$n = n_1 + n_2 + n_3 + ………. + n_i$$

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Question:
A 2.5 litre flask contains 0.25 mole each of sulphur dioxide and nitrogen gas at 27°C. Calculate the partial pressure exerted by each gas and also the total pressure.
Solution:
Partial pressure of SO_2
$P_{SO2} = nRT / V = 0.25 \times 8.314 \times 300 / 2.5 \times 10^{-3}$ $= 2.49 \times 10^5$ $Nm^{-2} = 2.49 \times 10^5$ P_a
Similarly $P_{N2} = 2.49 \times 10^5$ P_a
Following Dalton's Law
$P_{Total} = P_{N2} + P_{SO2}$ $= 2.49 \times 10^5$ $P_a + 2.49 \times 10^5$ P_a $= 4.98 \times 10^5$ P_a

H.W) A vessel of volume 22.4 dm^3 contains 1.5 mol H_2 and 2.5 mol N_2 at 273.1 K. Calculate (a) the mole fractions of each component, (b) their partial pressures, and (c) their total pressure.

Real gas

A gas which obeys the gas laws and the gas equation PV = nRT strictly at all temperatures and pressures is said to be an ideal gas. The molecules of ideal gases are assumed to be volume less points with no attractive forces between one another. But no real gas strictly obeys the gas equation at all temperatures and pressures. Deviations from ideal behaviour are observed particularly at high pressures or low temperatures.
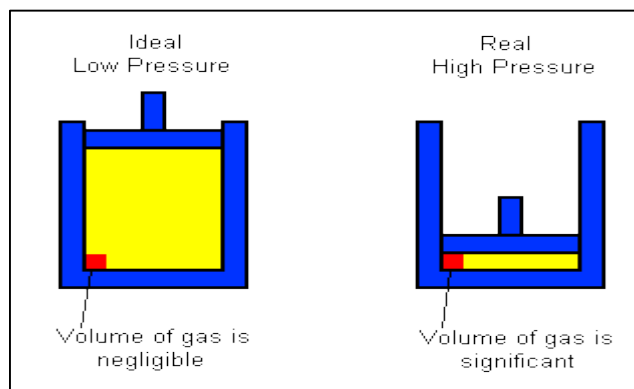
The deviation from ideal behaviour is expressed by introducing a factor Z known as **compressibility factor** in the ideal gas equation. Z may be expressed as $Z = PV / nRT$

- **In case of ideal gas, $PV = nRT \therefore Z = 1$**
- **In case of real gas, $PV \neq nRt \therefore Z \neq 1$**

Thus in case of real gases Z can be < 1 or > 1

- When $Z < 1$, it is a negative deviation. It shows that the gas is more compressible than expected from ideal behaviour.

- When $Z > 1$, it is a positive deviation. It shows that the gas is less compressible than expected from ideal behaviour.

Question

1 mole of SO_2 occupies a volume of 350 ml at 300K and 50 atm pressure. Calculate the compressibility factor of the gas.

Solution:

$P = 50$ atm

$V = 350$ ml $= 0.350$ litre

$n = 1$ mole

$T = 300L$ $Z = PV / nRT$

$\therefore Z = 50 \times 0.350 / 1 \times 0.082 \times 300 = 0.711$

Thus SO_2 is more compressible than expected from ideal behaviour.

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Van der Waals' Equation of State for a Real Gas

This equation can be derived by considering a real gas and 'converting ' it to an ideal gas.

Volume Correction

We know that for an ideal gas $P´V = nRT$. Now in a real gas the molecular volume cannot be ignored and therefore let us assume that 'b' is the volume excluded (out of the volume of container) for the moving gas molecules per mole of a gas. Therefore due to n moles of a gas the volume excluded would be nb. \ a real gas in a container of volume V has only available volume of (V - nb) and this can be thought of as an ideal gas in container of volume (V - nb).

Hence, Ideal volume

$V_i = V – nb$ …..........(i)

Pressure Correction

It can be seen that the pressure the real gas exerts would be less than the pressure an ideal gas would have exerted. The real gas experiences attractions by its molecules in the reverse direction. Therefore if a real gas exerts a pressure P, then an ideal gas would exert a pressure equal to $P + p$ (p is the pressure lost by the gas molecules due to attractions).

Therefore $p \propto n/v$ (concentration of molecules which are hitting the container's wall)

$P \propto n/v$ (concentration of molecules which are attracting these molecules) $\Rightarrow p \propto n^2/v^2$

$P = an^2/v^2$ where a is the constant of proportionality which depends on the nature of gas.

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$P_i = (P + an^2 / V^2)$ …............(ii)

Here,

a = A constant whose value depends upon the nature of the gas

Substituting the values of ideal volume and ideal pressure in ideal gas equation i.e. pV=nRT, the modified equation is obtained as

$$\boxed{(P + \frac{an^2}{V^2})(V - nb) = nRT}$$

$$\text{or } P = \frac{nRT}{V - nb} - \frac{n^2a}{V^2}$$

The constants a & b
Vander Waals constant for attraction (a) and volume (b) are characteristic for a given gas. Some salient feature of a & b are: • For a given gas Vander Waal's constant of attraction 'a' is always greater than Vander Waals constant of volume (b).   • The units of a = litre^2 atm mole^{-2} & that of b = litre mole $^{-1}$

Some Other Important Definitions

• **Critical Temperature (T_c)**

It (T_c) is the maximum temperature at which a gas can be liquefied i.e. the temperature above which a gas can't exist as liquid.

$$T_c = 8a / 27Rb$$

• **Critical Pressure (P_c)**

It is the minimum pressure required to cause liquefaction at T_c

$$P_c = a/27b^2$$

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- **Critical Volume**

It is the volume occupied by one mol of a gas at T_c and P_c

$$\underline{V_c = 3b}$$

Q) find the pressure of 2.00 moles of carbon dioxide gas at 298 K in a 5.00 L container. The van der Waals constants for carbon dioxide are: a = 3.592 $L^{2.}$ atm/mol^2 and b = 0.04267 L/mol.

$$P = \frac{nRT}{V - nb} - \frac{n^2a}{V^2}$$

$$P = \frac{(2.00\,\text{mol})(0.0821\,\text{L}\cdot\text{atm})(298\,\text{K})}{5.00\,\text{L} - (2.00\,\text{mol})\text{mol}\cdot\text{K}(0.04267\,\text{L})} - \frac{(2.00\,\text{mol})^2(3.592\,\text{L}^2\cdot\text{atm})}{(5.00\,\text{L})^2\text{mol}^2} = 9.38\,\text{atm}$$

Compare this to the pressure calculated using the ideal gas law:

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

$$P = \frac{(2.00\,\text{mol})(0.0821\,\text{L}\cdot\text{atm})(298\,\text{K})}{(5.00\,\text{L})\text{mol}\cdot\text{K}} = 9.77\,\text{atm}$$

Q) The critical constants of ethane are p_C = 48.20 atm, Vc= 148 cm and Tc = 305.4 K. Calculate the van der Waals parameters of the gas (a, b)

$$b = \tfrac{1}{3}V_c = \tfrac{1}{3}(148\,\text{cm}^3\,\text{mol}^{-1}) = 49.3\,\text{cm}^3\,\text{mol}^{-1} = \boxed{0.0493\,\text{dm}^3\,\text{mol}^{-1}}$$

$$a = 27\,p_c b^2 = 27(48.20\,\text{atm}) \times (0.0493\,\text{dm}^3\,\text{mol}^{-1})^2 = \boxed{3.16\,\text{dm}^6\,\text{atm}\,\text{mol}^{-2}}$$

H.w) The critical constants of methane are pc = 45.6 atm, Vc = 98.7 cm^3 , and Tc= 190.6 K. Calculate the van der Waals parameters of the gas.

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