

Abnormal vapour density:-

vapour density of a substance is defined as the ratio of the density of the gaseous state of the substance and density of hydrogen under same temp. and Pr. It is unitless quantity and expected vapour density $D_0 = \frac{M_0}{2}$, where M_0 is the molecular formula weight of the substances.

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$$V.P = \frac{\text{Density of the gaseous state of the substance}}{\text{Density of } H_2 \text{ under same temp and Pr.}}$$

But for many substances like NH_4Cl , PCl_5 , N_2O_4 , I_2 , etc. it is found that vapour density (D) is observed to be less than that of the expected theoretical value (D_0). Even at high temp., $D = \frac{D_0}{2}$. This phenomenon is called abnormal vapour density.

The cause of the abnormal vapour density is attributed to the thermal dissociation of the above substances.



Due to dissociation, number of moles of the system is increased. At constant temp. and Pr., the volume is proportionately increased. Since mass remaining same, density is decreased, resulting the decrease of vapour density.

The extent of dissociation (α), i.e., fraction of the total number of molecules dissociated can be related with the abnormal vapor density (D) of the substance at a given temp. and Pr.

Let us take a general representation of the thermal dissociation as



So, one molecule of A is dissociated into n molecules of B .

Let 1 mole of A is taken initially and α mole is dissociated at a given T and P. Thus $(1-\alpha)$ mole of A remains undissociated and $n\alpha$ mole of B is produced.

The total number of moles at equilibrium at constant T and P = $1 - \alpha + n\alpha = 1 + (n-1)\alpha$

If V_0 be the volume, which the system would have occupied had there been no dissociation, and V be the actual volume of the vapour due to dissociation, we should have according to Avogadro's Law at const. T and P;

$$\frac{V}{V_0} = \frac{1 + (n-1)\alpha}{1} ; \text{ but } \frac{V}{V_0} = \frac{D_0}{D} \quad \left| \begin{array}{l} d = \frac{m}{V} \\ m = \text{const.} \\ D_0 V_0 = V D \end{array} \right.$$

$$\text{So, } \frac{D_0}{D} = 1 + (n-1)\alpha$$

$$\Rightarrow \alpha = \frac{D_0 - D}{(n-1)D} = \frac{M_0 - M}{(n-1)M}$$

D_0 = Expected vapour density from the formula wt. M_0 of the substance

D = Actual vapour density at the given T and P.

M = Determined molecular wt. of the substance by expt.

At high T, $\alpha = 1$ (complete dissociation)

For NH_4Cl and PCl_5 , $n = 2$

So $D = \frac{D_0}{2}$. This is confirmed also by expt.

At least two cases can be cited where substances undergo dissociation but do not show abnormal vapour density



(2) measurement of density at constant volume also does not lead to abnormal vapour density.

Problem: At 60°C , the density of N_2O_4 gas was found to be 30.2. calculate the percentage of NO_2 molecules by wt. and vol.

$$\begin{array}{l} \text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2 \\ 1-\alpha \quad 2\alpha=1+\alpha \end{array} \quad \alpha = \frac{D_0 - D}{(2-1)D} ; \quad \text{The calculated density of } \text{N}_2\text{O}_4 ;$$

$$D_0 = \frac{M}{2} = 46$$

$$= \frac{D_0 - D}{D} \quad \text{Observed density; } D = 30.2$$

$$\text{Hence, } \alpha = \frac{46 - 30.2}{30.2} = 0.523$$

Thus, the fraction of gm-mole of N_2O_4 decomposed = 0.523

Thus, % of NO_2 molecules by wt. = 52.3%

In the mixture, the ratio of gm-moles of NO_2 and N_2O_4

$$\Rightarrow \frac{2\alpha}{1+\alpha} : \frac{1-\alpha}{1+\alpha} \quad \text{This is also the ratio of their volumes.}$$

$$\text{Hence, \% of } \text{NO}_2 \text{, by volume} = \frac{2 \times 0.523}{1 + 0.523} \times 100 = 68.7 \%$$

Dalton's Law of Partial Pressures

If a vessel contains a mixture of two or more gases, then the individual pressures of the different gases will depend upon the relative proportions of the constituents. The individual pr.s are usually expressed as the partial pr.s of the constituents. The partial pr. of a constituent is defined as the pr. it would exert if it alone occupied the entire volume of the vessel at the same temp.

Dalton studied this and stated as

The total pr. of a mixture of gases is equal to the sum of the partial pr.s of the constituent gases at the same temp.

Thus, if a mixture of gases (temp. T) contains n_a, n_b, n_c, \dots moles of diff. gases whose partial pr.s are P_a, P_b, P_c, \dots etc, respectively, the total pr. P of the mixture is

$$P = P_a + P_b + P_c + \dots$$

Since, $P = \frac{n}{V} RT$

$$P_a = \frac{n_a}{V} RT, \quad P_b = \frac{n_b}{V} RT, \quad P_c = \frac{n_c}{V} RT$$

$$\begin{aligned} \text{Hence, } P_a + P_b + P_c + \dots &= (n_a + n_b + n_c + \dots) \frac{RT}{V} \\ &= \frac{n}{V} RT \end{aligned}$$

Therefore, $P = P_A + P_B + P_C + \dots$

$$\text{Also, } P_A = \frac{n_a}{n} P, \quad P_B = \frac{n_b}{n} P, \quad P_C = \frac{n_c}{n} P, \dots$$

Law of Partial volumes (Amagat):

The total vol. of a gas mixture is the sum of the partial volumes of the constituents of the mixture.

$$\text{Thus, } V = U_1 + U_2 + U_3 + \dots$$

V = Total vol. ; U_1, U_2, U_3, \dots are the partial volumes of the constituents.

$$U_1 = \frac{n_1}{P} RT ; \quad U_2 = \frac{n_2}{P} RT, \dots$$

$$\begin{aligned} V = U_1 + U_2 + U_3 + \dots &= (n_1 + n_2 + n_3 + \dots) \frac{RT}{P} \\ &= n \frac{RT}{P} \end{aligned}$$

Moreover, $U_1 = \frac{n_1}{n} V, \quad U_2 = \frac{n_2}{n} V, \dots$