# STATES OF MATTER

## REAL GAS

## ✤ THE IDEAL GAS EQUATION

An ideal gas is defined to be a system in which there are no inter molecular/interatomic forces. Such a system can only exist as a gas. Any real system will approach ideal gas behaviour in the limit that the pressure is extremely low and the temperature is high enough to overcome attractive intermolecular forces.

An ideal gas is a gas to go which the laws of Boyle and Charles are strictly applicable under all conditions of temperatures and pressures.

From Boyle's law we get, V  $\propto 1/P(at \text{ constant } n \text{ and } T)$ 

From charles law we get,  $V \propto T$  (at constant n and P)

From Avogadro's law we get,  $V^{\infty}$  n (at constant T and P)

Combining the above three equations we get

$$V \propto \frac{nT}{P}$$

or 
$$V = R \frac{nI}{n}$$
 [Where R = ideal gas constant]

or 
$$PV = nRT$$

Ideal gas equation is a relation between four variables and it describes the state of any gas. For this reason, it is also called Equation of State.

## Dimension of R

$$R = \frac{PV}{nT} = \frac{Pressure \times Volume}{Mole \times Temperature}$$

$$\frac{(Force / Area) \times (Area \times Length)}{Mole \times Degree (K)}$$

$$= \frac{\text{Force} \times \text{Length}}{\text{Mole} \times \text{Degree (K)}} = \frac{\text{Work or energy}}{\text{Mole} \times \text{Degree (K)}}$$

## • Physical Significance of R

The dimentions of R are energy per mole per kelvin and hence it represents the amount of work (or energy) that can be obtained from one mole of a gas when its temperature is raised by 1K.

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## KEY POINTS Units of R

(i) In lit-atm	$R = \frac{1 \text{ atm} \times 22.4 \text{ lit}}{273 \text{ K}} = 0.0821 \text{ lit-atm mol}^{-1} \text{ K}^{-1}$
(ii) In C.G.S system	$R = \frac{1 \times 76 \times 13.6 \times 980 \text{ dyne } \text{cm}^{-2} \times 22400 \text{ cm}^{3}}{273 \text{ K}}$
	$= 8.314 \times 10^7 \text{ erg mole}^{-1} \text{K}^{-1}.$
(iii)In M.K.S. system	R = 8.314 Joule mole <sup>-1</sup> K <sup>-1</sup> . [10 <sup>7</sup> erg = 1 joule]
(iv)In calories	$R = \frac{8.314 \times 10^7 \text{ ergmole}^{-1} \text{ K}^{-1}}{4.184 \times 10^7 \text{ erg}}$
	= 1.987 2 calorie mol <sup>-1</sup> K <sup>-1</sup> .

- **Ex.** Some spherical balloons each of volume 2 liter are to be filled with hydrogen gas at one atm &  $27^{\circ}$ C from a cylinder of volume 4 liters. The pressure of the H<sub>2</sub> gas inside the cylinder is 20 atm at 127°C. Find number of balloons which can be filled using this cylinder. Assume that temperature of the cylinder is 27°C.
- Sol. No. of moles of gas taken initially  $=\frac{20 \times 4}{R \times 400} = 2.43 \text{ L}$ No. of moles of gas left in cylinder  $=\frac{1 \times 4}{R \times 300} = 0.162 \text{ L}$ No. of moles of gas to be filled in balloons = 2.43 - 0.162 = 2.268 Let we have 'n' balloons that we can fill No. of moles of gas that can be filled in 1 balloon  $=\frac{1 \times 2}{0.082 \times 300} = 0.081$ ∴ 0.081 × n = 2.268
  - $0.061 \times 11 = 2.208$

n = 28 balloons.

## DALTON'S LAW OF PARTIAL PRESSURES

Dalton's law of partial pressure states "at a given temperature, the total pressure exerted by two or more non-reacting gases occupying a definite volume in equal to the sum of the partial pressures of the component gases."

 $P_{Total} = p_1 + p_2 + p_3 + \dots$  (At constant V and T)

$$= (\frac{n_1}{v} + \frac{n_2}{v} + \frac{n_3}{v} + \dots)RT = (n_1 + n_2 + n_3 + \dots)\frac{RT}{v} = \frac{nRT}{v}$$

Where  $n = n_1 + n_2 + n_3 + \dots =$  Total moles, V = Total volume

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$$P_{\text{Total}} = \sum p_i = \frac{RT}{V} \sum n_i$$

Dalton's law of partial pressure is applicable only to non-reacting gases.

If the two non-reacting gases A and B having  ${\sf n}_A$  and  ${\sf n}_B$  number of moles respectively are filled

in a vessels of volume V at temperature T, Then

$$PV = (n_A + n_B) RT \qquad \dots (i)$$

Partial pressure may be calculated as

 $p_A V = n_A RT$ ,  $p_B V = n_B RT$ 

Total pressure  $(p_A + p_B) V = (n_A + n_B)RT$  .....(ii)

from (i) and (ii)

$$P = p_A + p_B$$

$$\frac{p_A}{P} = \frac{n_A RT/V}{(n_A + n_B) RT/V} = \frac{n_A}{n_A + n_B} = x_A \text{ (mole fraction of A)}$$

 $p_A = x_A \times \ \text{P}$  , similarly  $p_B = x_B \times \ \text{P}$ 

Partial pressure of a component = Mole fraction × total pressure.

It has been observed that gases are generally collected over water and therefore are moist.

 $P_{dry gas} = P_{moist gas} - P_{water vapour}$ 

The pressure exerted by water vapour is constant with water at a particular temperature is called as aqueous tension, which varies directly with the temperature and becomes 760 mm at  $100^{\circ}$ C.

Relative Humidity (RH) =  $\frac{Partial pressure of water in air}{Vapour pressure of water}$ 

Pressure of dry gas = Pressure of moist gas – aqueous tension.



**Ex.** A mixture of NO<sub>2</sub> & CO having total volume of 100 ml contains 70 ml of NO<sub>2</sub> at 1 atm, mixture is left for some time and same NO<sub>2</sub> get dimerized to  $N_2O_4$  such that final volume of the mixture become 80 ml at 1 atm, calculate the mole fraction of NO<sub>2</sub> in final equilibrium mixture.

**Sol.** Initial volume of  $NO_2 = 70$  ml

Initial volume of CO = 100 - 70 = 30 ml

Final volume of mixture = 80 ml

Let the volume of  $NO_2$  in final mixture be x

Let 'v' ml NO\_2 be converted to  ${\rm N_2O_4}$ 

$$2NO_2 \longrightarrow N_2O_4$$
  
V V/2

Hence final volume

= volume of CO + volume of NO<sub>2</sub> left + volume of N<sub>2</sub>O<sub>4</sub> formed

= 30 + 70 - V + V/2 = 80

V = 40 ml

Hence volume of NO<sub>2</sub> left = 70 - V = 30 ml

Now as volume  $\propto$  moles

 $\therefore$  mole fraction = volume fraction =  $\frac{30}{80} = \frac{3}{8}$ 

#### AMAGAT'S LAW OF PARTIAL VOLUME

According to this law at constant temperature and pressure, the total volume of mixture of gases which don't react is equal to the sum of partial volumes of each component present in mixture.

 $V_T = V_1 + V_2 + V_3 + \dots$ 

#### Partial Volume

Partial volume of any component is defined as the volume occupied by that particular component measured under the given condition of pressure and temperature.

PV = nRT

V∝ n

#### Partial Volume

Let us consider a three non-reacting gases A, B and C are present in a container which have no. of moles  $n_A, n_B$  and  $n_C$  respectively. For each gas partial volume is

$$V_A = n_A \left(\frac{RT}{P}\right)$$
,  $V_B = n_B \left(\frac{RT}{P}\right)$  and  $V_C = n_C \left(\frac{RT}{P}\right)$ 

Total Volume

$$V_T = V_A + V_B + V_C = (n_A + n_A + n_A) \left(\frac{RT}{P}\right) = n_T \left(\frac{RT}{P}\right)$$

#### **GRAHAM'S LAW OF DIFFUSION AND EFFUSION**

#### Diffusion

The process of mixing of gases by random motion of the molecules is called diffusion.

#### Effusion

When gas is confined to a container at high pressure than in the surrounding atmosphere it will escape from a small hole which is opened in the container until the pressure outside and inside have been equalized. This process is called effusion.

The difference between diffusion and effusion is that in the former case, the gas spontaneously passes through a porous partition while in the case of effusion, the gas is passed out through a small orifice or hole by applying some external pressure.

Graham's law of diffusion states "under the same conditions of temperature and pressure, the rates of diffusion of different gases are inversely proportional to the square roots of their molecular masses or their densities."

Mathematically, 
$$r \propto \sqrt{\frac{1}{M}}$$
 or  $\sqrt{\frac{1}{d}}$  or.  $\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{d_2}{d_1}}$ 

Where  $r_1$  and  $r_2$  are the rates of diffusion of gases 1 and 2.

 $M_1$  and  $M_2$  are their molecular masses.

 $d_1$  and  $d_2$  are their densities.

## Effect of Volume on Rate of Diffusion

Rate of diffusion = 
$$\frac{\text{Volume of gas diffused}}{\text{Time taken for diffusion}}$$
  
or  $r = \frac{V}{t}$ 

Let  $V_1$  be the volume of gas 1 and  $V_2$  be the volume of gas 2, then

$$r_{1} = \frac{V_{1}}{t_{1}} \quad r_{2} = \frac{V_{2}}{t_{2}}$$
$$\therefore \qquad \frac{r_{1}}{r_{2}} = \sqrt{\frac{M_{2}}{M_{1}}} = \frac{V_{1}t_{2}}{V_{2}t_{1}}$$

### (i) Comparison of Times Taken for the Same Volume of Two Gases

Let the times of diffusion for the same volume of two gases be  $\mathsf{t}_1$  and  $\mathsf{t}_2$  respectively. Then,

$$\frac{r_1}{r_2} = \frac{V/t_1}{V/t_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}} \text{ or } \frac{r_1}{r_2} = \frac{t_2}{t_1} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

#### (ii) Comparison of the Volumes of the Gases that Diffuse in Same Time

Let  $V_1$  and  $V_2$  be the volume of two gases that diffuse in same time t. Then,

$$\frac{r_1}{r_2} = \frac{v_1/t}{v_2/t} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}} \text{ or } \frac{r_1}{r_2} = \frac{V_1}{V_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

#### (iii) Effect of Pressure on Rate of Diffusion

Rate of diffusion is proportional to the pressure of the gas in the container.

$$r \propto P$$
; again,  $r \propto \frac{1}{\sqrt{M}}$   
or  $r \propto \frac{P}{\sqrt{M}}$  or  $\frac{r_1}{r_2} = \frac{P_1}{P_2} \sqrt{\frac{M_2}{M_1}}$ 

## Application of Graham's Law of Diffusion in Enrichment of Isotopes Enrichment of Light Component

If a mixture of heavier gas B and a lighter gas A is placed in contact with a porous barrier, the gas passing through will be enriched in lighter component by a factor  $\sqrt{\frac{M_B}{M_A}}$ , called enrichment factor because lighter molecules effuse more rapidly than heavier ones. The remaining gas will be enriched in the heavier component. Each passage gives an enrichment factor equal to  $\sqrt{\frac{M_B}{M_A}}$  and so thousands of such barrier in succession are necessary to provide sufficient enrichment of heavier component.

Thus, enrichment factor for first barrier or operation  $f_1 = \sqrt{\frac{M_B}{M_A}}$ 

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overall separation or enrichment factor 
$$f = \frac{n'_A/n'_B}{n_A/n_B}$$

Where  $n_A$ ,  $n_B$ , and  $n_A$ ,  $n'_B$ , are the concentration of two isotopically different components before and after processing. If required enrichment of gas A is attained in x-operation then,

$$(f_1)^X = \frac{n'_A/n'_B}{n_A/n_B} = f$$

or

....

$$\begin{aligned} x \log f_1 &= \log \left[ \frac{n'_A/n'_B}{n_A/n_B} \right] \\ x \log \left[ \frac{M_B}{M_A} \right]^{1/2} &= \log \left[ \frac{n'_A/n'_B}{n_A/n_B} \right] \end{aligned}$$

 $x = \frac{2\log(\frac{n'_A/n'_B}{n_A/n_B})}{\log(\frac{M_B}{M_A})}$ 

or

or

r 
$$\frac{x}{2}\log[\frac{M_B}{M_A}] = \log\left[\frac{n_A/n_B}{n_A/n_B}\right]$$

#### LIMITATIONS OF THIS LAW

- (i) The laws of diffusion and effusion are applicable only when the pressure difference is very small.
- (ii) Correctly speaking the rate of diffusion and effusion are not constant throughout the time interval, but these rates may be assumed constant for a small-time interval.

#### **Connecting Containers**

- (1) When we are connecting two or more containers then the movement of any component of gas occurs in other container till the final pressure of that component in all the container become equal (that means partial pressure becomes equal).
- (2) To calculate composition of gaseous mixture in any container, we will use law of diffusion.

#### **BAROMETRIC PRESSURE DISTRIBUTION**

In case of air (ideal gas) density depends on pressure. So we cannot calculate pressure difference between two points directly as 'hdg'.

Assume in case of air, composition of air and temperature is constant throughout.

Suppose pressure at height 'h' from the ground level is 'P' and as height increase by 'dh' the pressure decreases by 'dP'. So the pressure difference between two points is :

 $(P - dP) - P = dh \times d \times g$ 

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$$- dP = dh \times \frac{PM}{RT} \times g \quad [PM = dRT]$$

$$\int_{P_0}^{P} \frac{-dP}{P} = \frac{Mg}{RT} \int_0^H dh$$

$$[\ell_n P]_{P_0}^P = \frac{-Mg}{RT} [h]_0^H$$

$$\ell n \frac{P}{P_0} = \frac{-MgH}{RT}$$

$$P = P_0 e^{-\left(\frac{MgH}{RT}\right)}$$

$$M = \text{molar mass of air (kg/mole)}$$

$$g = 9.8 \text{ m/sec}^2$$

H = height in meter

R = 8.314 J/mole/K

## PAYLOAD OF BALLOON

Payload of a balloon is defined as maximum weight which a balloon can carry with it upward direction.

V = Volume of Balloon,  $d_{out} = density of outside air$ ,



 $d_{in} = density of gas inside, m = mass of balloon.$ 

 $Payload = d_{out} \times V \times g - [d_{in} V \times g + mg]$ 

= [Buoyancy force] – [effective wt. of Balloon]

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Ex. Calculate payload of a balloon having volume 100 liter. It is filled with helium gas at 0.2486 atm pressure and 300 K. Density of air is 1.3 gm./liter and mass of material of balloon is 20 gm.

Sol. 
$$PM = dRT$$
  
 $d_{in} = \frac{PM_{He}}{RT} = \frac{0.2486 \times 4}{0.0821 \times 300} = \frac{1}{25}$   
Payload =  $1.3 \times 100 \times 10 - [\frac{1}{25} \times 100 \times 10 + 20 \times 10]$   
 $= \frac{13}{10} \times 100 \times 10 - [4 \times 10 + 200] = 1300 - 240 = 1060$ 

## (A) CALCULATION OF PAYLOAD OF BALLOON AT CONSTANT HEIGHT

(1) At constant volume of balloon

Payload = 
$$d_{out}$$
 V.g - [w]  
 $d_{out} = d_0 e^{(-\frac{Mgh}{RT})}$ 

Payload = d<sub>0</sub>  $e^{\left(-\frac{Mgh}{RT}\right)}$  V.g - w

Density of outside air decreases with increase in height so buoyancy force decreases and payload of balloon decreases with increase in height.

(2) At variable volume of balloon

$$PV = nRT$$

$$PV = constant$$

$$P_0V_0 = P_h \times V_h$$

$$P_0V_0 = P_0e^{(-\frac{Mgh}{RT})} \times V_h$$

$$V_h = V_0 e^{(-\frac{Mgh}{RT})}$$

Now payload =  $d_{out} \times V \times g - w$ 

$$= d_0 e^{\left(-\frac{Mgh}{RT}\right)} V_0 e^{\left(-\frac{Mgh}{RT}\right)} xg - w$$
$$= d_0 V_0 g - w$$
$$= \text{constant}$$

In this case buoyancy force at any height is same so payload will remain constant throughout.

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#### (B) MAXIMUM HEIGHT AT WHICH BALLOON WILL BURST

Maximum volume =  $V_{max}$ 

$$V_{max} = V_0 e^{\left(\frac{Mgh_{max}}{RT}\right)}$$
$$\frac{V_{max}}{V_0} = e^{\left(\frac{Mgh_{max}}{RT}\right)}$$
$$\lambda n \left(\frac{V_{max}}{V_0}\right) = \left(\frac{Mgh_{max}}{RT}\right)$$

 $h_{max} = \frac{RT}{Mg} ln(\frac{V_{max}}{V_0})$ 

**Ex.** Calculate the payload of balloon of diameter 20-meter weight 100 kg. If it is filled with, He at 1.0 atm and 27°C. Density of air is 1.2 kgm<sup>-3</sup>. [R = 0.082 dm<sup>3</sup> atm K<sup>-1</sup> mol<sup>-1</sup>]

Sol. Weight of balloon = 100 kg = 10 × 10<sup>4</sup> g Volume of balloon =  $\times \frac{4}{3}\pi r^3 = \frac{4}{3} \times \frac{22}{7} \times (\frac{20}{2} \times 100)^3$ = 4190 × 10<sup>6</sup> cm<sup>3</sup> = 4190 × 10<sup>3</sup> liters Weight of gas (He) in balloon =  $\frac{PV}{RT} = \frac{1 \times 4190 \times 10^3 \times 4}{0.082 \times 300} = 68.13 \times 10^4 \text{ g}$ Total weight of gas and balloon =  $68.13 \times 10^4 + 10 \times 10^4 = 78.13 \times 10^4 \text{ g}$ Weight of air displaced =  $\frac{1.2 \times 4190 \times 10^6}{10^3} = 502.8 \times 10^4 \text{ g}$   $\therefore$  Payload = wt. of air displaced - (wt. of balloon + wt. of gas)  $\therefore$  Payload = 502.8 × 10<sup>4</sup> - 78.13 × 10<sup>4</sup> = 424.67 × 10<sup>4</sup> g = 4.2467 × 10<sup>6</sup> g

## CALCULATION OF VAPOUR DENSITY OF MIXTURE IN REACTION

It is given that initially only reactant A is present with vapour density (D). It has degree of dissociation  $\alpha$  and finally vapour density 'd'

 $A_n \longrightarrow nB$ 

Moles before dissociation 1 0 Moles after dissociation  $1 - \alpha$   $n\alpha$  $\therefore$  total no. of moles after dissociation =  $1 + (n - 1)\alpha$ Since, mol. wt.  $\propto \frac{1}{n0. \text{ of particles present}}$ 

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 $\therefore \quad \frac{1}{\text{Normal mol. wt}} \propto \text{no. of particles before dissociation}$ 

 $\therefore \quad \frac{1}{\text{Experimental mol. wt}} \propto \text{no. of particles after dissociation}$ 

$$\therefore \frac{\text{Normal mol. wt.}}{\text{Experimental mol. wt}} \propto \frac{\text{no. of particles after dissociation}}{\text{no. of particles before dissociation}}$$
$$\therefore \frac{M_{\text{Normal}}}{M_{\text{exp}}} = \frac{1 + (n-1)\alpha}{1}$$

The entire conclusion can be represented in a general way as -

 $\frac{P_{Normal}}{P_{experimental}} = \frac{D_{Normal}}{D_{experimental}} = \frac{M_{Normal}}{M_{experimental}} = 1 + (n-1)\alpha$