

PROPERTIES OF GASES & GAS MIXTURES* Avogadro's Law

A mole of a substance has a mass numerically equal to the molecular weight of the substance.

$$n = \frac{m}{M}, \text{ where } n \rightarrow \text{no of moles (kgmol)}$$

$m \rightarrow$ mass of substance.

$M \rightarrow$ molecular weight of substance

* Equation of state of a gas.

The functional relationship among the properties Pressure P , molar volume \bar{V} and temperature T is known as equation of state.

$$f(P, \bar{V}, T) = 0 \quad \text{or} \quad f(P, V, T) = 0$$

* Ideal Gas and Ideal Gas equation of state

A hypothetical gas which obeys the law $P\bar{V} = R_u T$ at all pressures and temperatures is called an ideal gas.

Where $P \rightarrow$ pressure, \bar{V} - molar volume.

$R_u \rightarrow$ universal gas constant

$T \rightarrow$ Temperature (k)

Ideal gas equation is valid when (Assumptions)

1) molecules do not occupy any volume.

2) No attractive force between molecules.

Ideal Gas Equation of state

$$P\bar{V} = R_U T \rightarrow P V = n R_U T$$

where molar volume, $\bar{V} = \frac{V}{n}$.

V - Total volume.

P → pressure.

$$PV = n R_U T$$

We have $n = \frac{m}{M}$ where m - mass of substance.
M → molecular weight of substance

n → Another way of expressing mass of substance as fraction of molecular weight.

$$PV = \frac{m}{M} R_U T$$

Also we have $R_U = M R$ where R - characteristic gas constant

$$\therefore PV = m R T \rightarrow \frac{PV}{m} = R T$$

$$P v = R T \quad v - \text{specific volume.}$$

Important Points

- At low pressure ($P \rightarrow 0$) and high temperature ($T \rightarrow \infty$) density of gas decreases and the real gas behaves as ideal gas under these conditions.
- In the range of practical interest, many familiar gases such as air, N_2 , O_2 , H_2 , He, Ar, Neon, krypton and even heavier gases such as CO_2 can be treated as ideal gas with negligible error.

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3. Dense gases such as water vapour in steam power plants and refrigerant vapour in refrigerators should not be treated as ideal gases. Instead, the property tables should be used for these substances.

Real Gases

Real gases are gases which deviate appreciably from ideal gas behaviour. In case of real gas, the following two effects should be considered while modelling the equation of state for real gases.

1) molecular force of attraction

2) volume occupied by molecules is significant

* Vanderwaals equation of state

Vanderwaals intended to improve ideal gas equation of state by considering 2 effects which was not considered in ideal gas model.

1. Intermolecular force of attraction.

2. volume occupied by the molecules is significant.

Let $b \rightarrow$ ^{molar} volume occupied by gas molecules.

Free volume available for molecular motion
 $= \bar{V} - b$.

where \bar{V} - molar volume.

The Van der Waal introduced 2 correction terms in the ideal gas equation of state and is modified as.

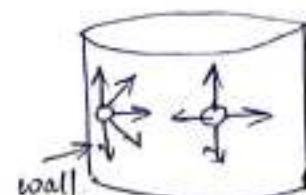
$$\left(P + \frac{a}{V^2}\right) (V - b) = RT.$$

$\frac{a}{V^2}$ → pressure correction term (force of cohesion)
The coeff a was introduced to account for the resistance of mutual attraction between the molecules.

P → ideal pressure.

$$P' = \left(P + \frac{a}{V^2}\right) \rightarrow \underline{\text{observed pressure}}$$

$$\text{i.e } P' - P = \frac{a}{V^2}$$



Application → liquid, gas and mixture.

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

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

Finding values of a and b

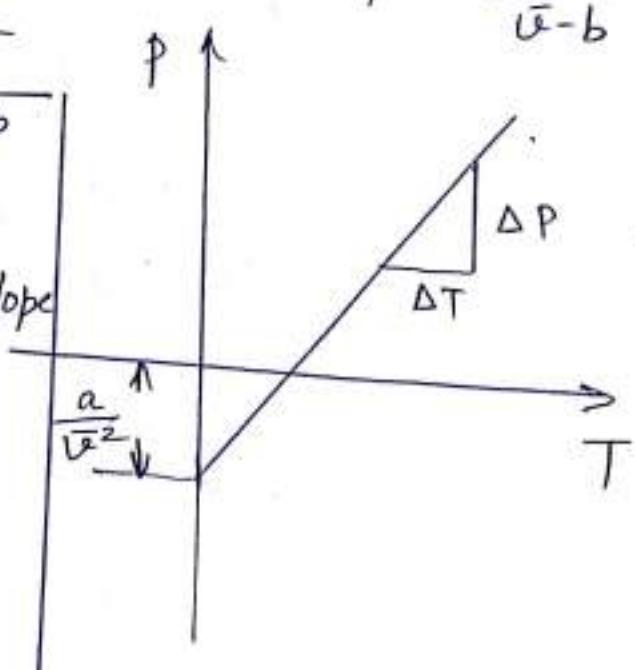
$$1) \text{ we have } P = \frac{RT}{V-b} - \frac{a}{V^2}$$

2) At critical pt for gases, the slope and curvature = 0.

$$\left(\frac{\partial P}{\partial V}\right)_{Tc} = 0 \quad \text{--- (1)}$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{Tc} = 0 \quad \text{--- (2)}$$

Solving, we get a & b.



* Virial Equation of state (3)

The equation of state can be expressed in a power series form as

$$\frac{P\bar{V}}{R_u T} = 1 + \frac{B}{\bar{V}} + \frac{C}{\bar{V}^2} + \frac{D}{\bar{V}^3} + \dots$$

where $B \rightarrow$ second virial coefficient

$C \rightarrow$ third virial coefficient

$D \rightarrow$ fourth virial coefficient

$$\frac{P\bar{V}}{R_u T} = 1 \rightarrow \text{Ideal gas equation of state}$$

- * Virial coefficients describes how it is different from ideal gas behaviour.
- * The PVT data accuracy can be improved by including more virial coefficients.
- * The experimental value of 2nd virial coefficient for no of gases are available.
- * The value of 3rd virial coefficient is not known for several gases.
- * The virial equation has a strong theoretical base.

* Compressibility factor

When a gas is not ideal, $P\bar{V} \neq R_u T$ or $PV \neq RT$. The deviation of real gas from ideal gas law can however be rectified by incorporating a correction factor in the ideal gas law.

The correction factor is denoted by z .

$$z = \frac{PV}{RT} \quad \text{or} \quad z = \frac{PV}{RT}$$

$$z = \frac{\text{Actual volume}}{\text{Ideal volume}} = \frac{\bar{V}}{RT/p} = \frac{V}{RT/p}$$

Compressibility factor at a particular temperature and pressure gives an indication of the extent of deviation of gas from ideal gas behaviour.

For an ideal gas, $z=1$ and for real gas the compressibility factor (z) approaches unity as the pressure is reduced.

The compressibility factor is not really a constant since it is different for each gas and varies with both pressure and temperature.

* Compressibility Factor Chart

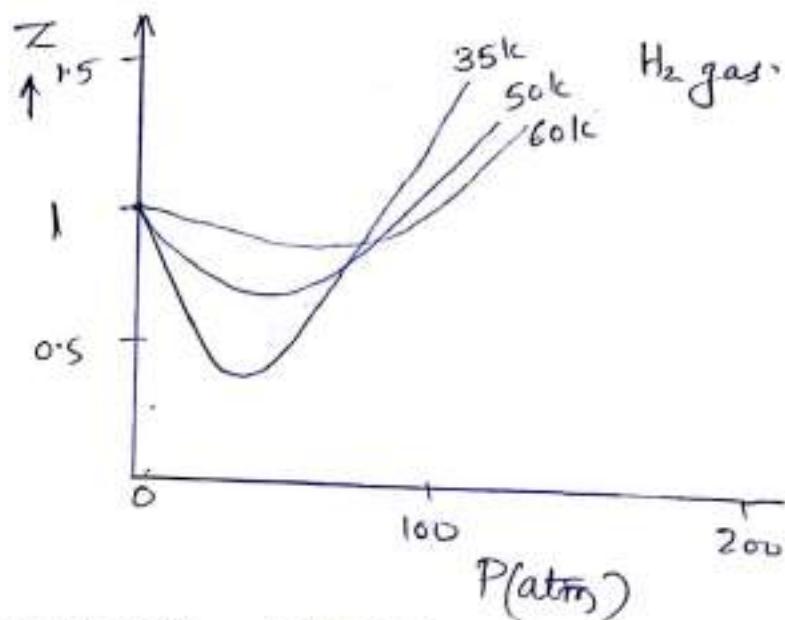
For a certain gas, the compressibility factor z is a function of P & T .

$$z = f(P, T)$$

The compressibility factor chart is a chart where constant temperature lines are plotted as a function of pressure and compressibility factor.

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From this plot, \bar{z} can be obtained for any value of P & T and the volume can be determined from the equation $P\bar{V} = \bar{z}RT$.



* LAW OF CORRESPONDING STATES

Note: A different compressibility factor chart is needed for each substance. It would be very convenient if one generalised compressibility chart could be used for all substances. The basis for this is law of corresponding states.

The equation of state when expressed in terms of reduced variables (properties) is a universal equation valid for all substances.

* Reduced properties

The general shape of the vapour dome and the constant $\overset{\text{temp}}{\sim}$ curves on the p-v plot are similar for all substances. However the scale may be different for

diff substances. This similarity^P can be utilised with application of dimensionless properties called reduced properties.



* Reduced property is the ratio of the existing property (λ) to the critical property (λ_c) of the substance

$$x_R = \frac{\lambda}{\lambda_c}$$

Sl. No	Reduced property	Symbol
1.	Reduced pressure	$p_R = \frac{p}{p_c}$
2.	Reduced Temperature	$T_R = \frac{T}{T_c}$
3.	Reduced specific volume	$v_R = \frac{v}{v_c}$

It is found from experimental data that at the same reduced pressure and reduced temperature, the reduced volume of different gases are approximately ^{the same.} (compressibility factors are nearly the same)

Mathematically it can be expressed in the form , $Z = f(Z_c, p_R, T_R)$

Experimental values of Z_c for most substances

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fall within a narrow range of 0.2 to 0.3. Therefore z_c may be taken to be a constant i.e. $z = f(P_R, T_R)$

The relation among the reduced properties T_R, P_R and V_R is known as the law of corresponding states. This equation of state when expressed in terms of reduced properties is a universal equation valid for all substances.

* Generalised Compressibility Chart

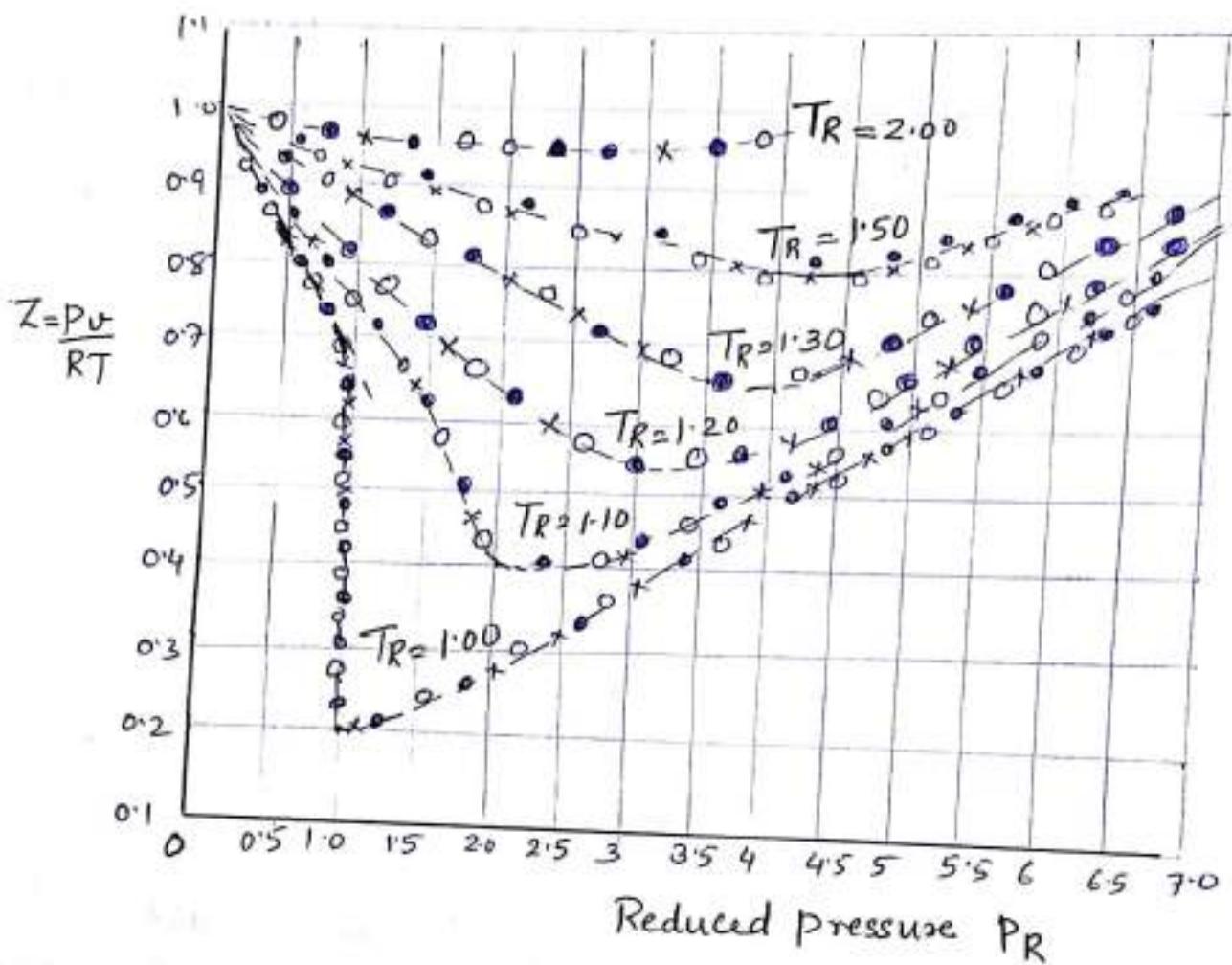
Law of Corresponding State is the basis of generalised compressibility chart.

If the actual values of z are plotted against the values of P_R for constant T_R , one would get the same curve for all substance. Such a plot is known as generalised compressibility chart.

Observations

- At all temperatures, as $P_R \rightarrow 0, z \rightarrow 1$
- The compressibility factor at critical point for all substances, $z_c = \frac{P_c V_c}{R T_c} = \frac{P_c V_c}{R_0 T_c} = 0.375$
- At the temperature equal to twice the critical point temperature ($T_R=2$) and above

$Z=1$ over a wide range of pressure up to 5 times the critical pressure ($PR=5$)



X - Methane.

● - CO_2

○ - N_2 .

Generalised Compressibility Chart

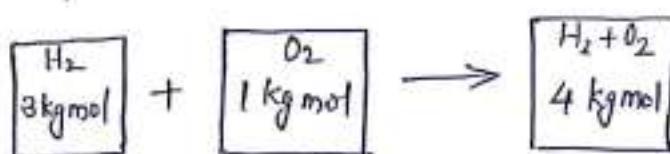
(6) MIXTURE OF IDEAL GASES



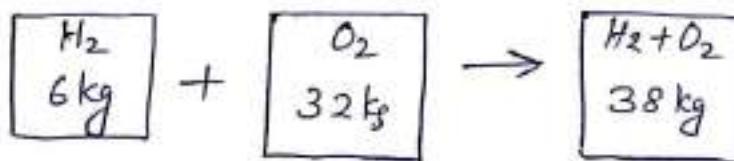
Composition of a gas mixture

To determine the properties of mixture, we need to know the composition of the mixture as well as the properties of individual components.

- * Method of describing composition of mixture
 - 1) Molar analysis: Composition of mixture can be described in terms of number of moles of each component.
 - 2) Gravimetric analysis: Composition of mixture can be described in terms of mass of each component.



no of moles of a non reacting mixture = sum of the no of moles of its components



mass of a mixture = sum of the masses of its components.

- * mole fraction of a component, $y_i = \frac{\text{no of moles of component}}{\text{Total no of moles in mixture}} = \frac{n_i}{n_m}$

- * mass fraction of a component, $m_f = \frac{\text{mass of component}}{\text{Total mass of mixture}} = \frac{m_i}{m_m}$
- $i \rightarrow \text{Component}$

The sum of mole fraction & mass fraction of a mixture = 1

$$\sum_{i=1}^k m_{fi} = 1$$
$$\sum_{i=1}^k y_i = 1$$

$$H_2 + O_2$$
$$y_{H_2} = 0.75$$
$$y_{O_2} = \frac{0.25}{1.00}$$

Characteristic Gas constant for mixture

$$R_{\text{m}} = \frac{R_u}{M_m}$$

$$n = \frac{m}{M}$$

$$M_m = \frac{m_m}{n_m}$$

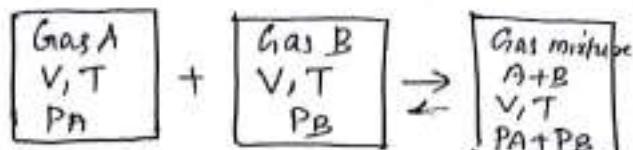
PVT Behaviour of Ideal Gas Mixtures

* Dalton's Law of Additive pressure / Partial Pressure

The pressure of a gas mixture is equal to the sum of the pressures each gas would exert if it existed alone at the mixture temperature and volume.

Dalton's law states that the total pressure of a mixture of ideal gases is equal to the sum of partial pressures.

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$$P_A V = n_A R_u T \quad \text{--- (1)}$$

$$P_B V = n_B R_u T \quad \text{--- (2)}$$

$$\vdots \qquad \vdots \\ P_k V = n_k R_u T \quad \text{--- (k)}$$

where P_A, P_B, \dots, P_k are partial pressure.

Adding,

$$(P_A + P_B + \dots + P_k) V = (n_A + n_B + \dots + n_k) R_u T.$$

$$P_m \cdot V = n_m R_u T$$

\therefore Mixture pressure (total pressure), $P_m = P_A + P_B + \dots + P_k$

$$P_m = \sum_{i=1}^k P_i$$

Similarly $n_m = n_A + n_B + \dots + n_k$

For i^{th} component, we have

$$P_i V = n_i R_u T \quad \text{--- (1)}$$

Also, we know $P_m V = n_m R_u T \rightarrow R_u T = \frac{P_m V}{n_m}$ --- (2)

Sub. the value of $R_u T$ in (1)

$$P_i V = n_i \frac{P_m V}{n_m} \rightarrow \frac{P_i}{P_m} = \frac{n_i}{n_m}$$

P_i - partial pressure of component ; n_i - no. of moles of i^{th} component

P_m - total pressure of mixture ; n_m - total no. of moles of mixture

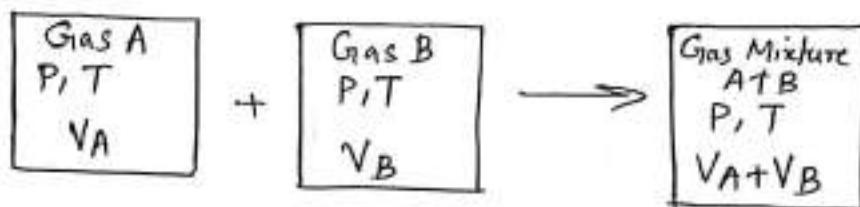
$\frac{P_i}{P_m}$ - pressure fraction ; $\frac{n_i}{n_m}$ - mole fraction

$$P_i = P_m \times \text{mole fraction}$$

* Amagat's Law of Additive / Partial Volumes.

Amagat's Law of Additive / Partial volume states that the total volume of a mixture of ideal gases is equal to the sum of partial volumes.

i.e. total volume of a gas mixture is equal to the sum of the volumes each gas would occupy if it existed alone at the mixture temperature and pressure.



$$P \cdot V_m = n_m \cdot R_u T$$

Mixture volume, $V_m = V_A + V_B + \dots + V_k$
(total volume)

$$V_m = \sum_{i=1}^k V_i$$

Volume fraction = $\frac{V_i}{V_m}$, $V_i \rightarrow$ component volume.

Component volume \rightarrow volume of component occupied if it existed alone at mixture T & P .

For ideal gas, component volume = partial volume.

$$PV_i = n_i R_u T \quad \text{--- } ①$$

Also we have $P V_m = n_m R_u T \rightarrow R_u T = \frac{P V_m}{n_m}$ --- ②

Sub ② the value of $R_u T$ in ①

$$PV_i = n_i \cdot \frac{P V_m}{n_m} \rightarrow$$

$$V_i = y_i \cdot V_m$$

$$\frac{V_i}{V_m} = \frac{n_i}{n_m}$$

$$\frac{n_A}{n_m} = y_A$$

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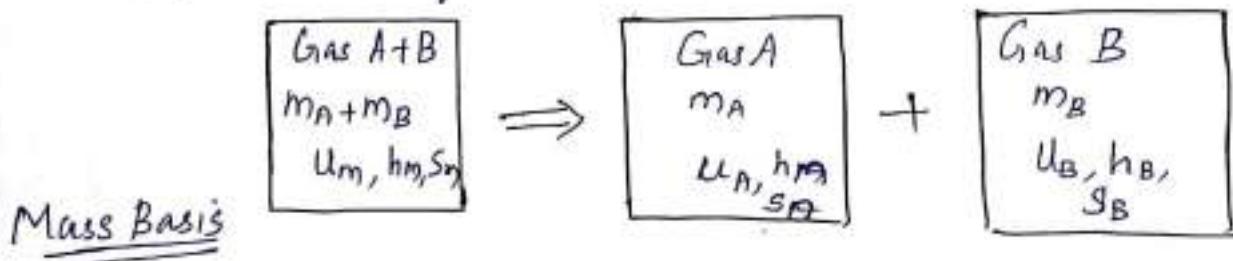
* Gibbs Dalton Law (Gibbs Theorem)

Internal Energy, Enthalpy, Entropy & specific heats of gas mixtures

Note:

When gases at equal pressures and temperatures are mixed adiabatically without work, as by interdiffusion in a constant volume container, the first law requires that the internal energy of the gaseous system remains constant, and experiments show that temperature remains constant.

* The internal energy, Enthalpy, Entropy, specific heat (C_V, C_P), F & G of the mixture of gases is equal to the sum of the internal energy, Enthalpy, Entropy etc of the individual components, each taken at the temperature and volume of mixture is known as Gibbs Theorem



$$m_m \cdot U_m = m_A U_A + m_B U_B$$

$$(m_A + m_B) U_m = m_A U_A + m_B U_B$$

$U_m = \frac{m_A U_A + m_B U_B}{m_A + m_B}$ Average specific internal energy of mixture
--

III^{ly} total enthalpy of mixture

$$m h_m = m_A h_A + m_B h_B$$

$$(m_A + m_B) h_m = m_A h_A + m_B h_B$$

Average specific enthalpy of mixture, $h_m = \frac{m_A h_A + m_B h_B}{m_A + m_B}$

III^{ly} Average sp. entropy of mixture, $s_m = \frac{m_A s_A + m_B s_B}{m_A + m_B}$

II Spheat of mixture, $c_{Vm} = \frac{m_A c_{V_A} + m_B c_{V_B}}{m_A + m_B}$

$$c_{pm} = \frac{m_A c_{p_A} + m_B c_{p_B}}{m_A + m_B}$$

Characteristic Gas

Const of Mixture, $R_m = \frac{m_A R_A + m_B R_B}{m_A + m_B}$

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INTRODUCTION TO IDEAL BINARY SOLUTION

Solution : It is a homogeneous mixture of two or more substances in same or different physical phases. The substances forming the solution are called components of solution.

$$\boxed{\text{solute} + \text{solvent} = \text{solution}}$$

Binary Solution : A solution containing only two components.

→ 1 solute + 1 solvent.

In a binary solution, solvent is the component which is present in large quantity, while the other component is known as solute.

Classification of solutions on the basis of physical state of solute + solvent

SL. No	Solute	Solvent	Example
Solid Solution	solid	solid	Alloys
	liquid	solid	Hydrated salts
	gas	solid	Dissolved gases in mineral
Liquid Solution	Solid	Liquid	salt/sugar soln in water
	Liquid	Liquid	Alcohol in water
	Gas	Liquid	Aerated drink in water
Gaseous Solution	Solid	gas	iodine vapour in air
	Liquid	gas	water vapour in air
	Gas	Gas	Air ($O_2 + N_2$)

Note

If water is used as solvent, the solution is called aqueous solution and if not, the solution is called non-aqueous solution.

Classification of solution based on the amount of solute dissolved in solvent

1) unsaturated soln: A solution in which more solute can be dissolved without raising temperature is called an unsaturated solution.

2) saturated soln: A solution in which no solute can be dissolved further at a given temperature is called saturated solution.

3) supersaturated solution: A solution which contains more solute than that would be necessary to saturate it at a given temperature is called supersaturated solution.

Solubility:

The maximum amount of solute that can be dissolved in a given amount of solvent at a given temperature is called its solubility at that temperature.

Solubility depends on the following factors

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- 1) Nature of solute
- 2) Nature of solvent
- 3) Temperature of solution
- 4) Pressure (in case of gases)

* Concentration of Solutions

Concentration of solution is defined as the relative amount of solute present in a solution. On the basis of concentration of solution, there are 2 types of solutions.

- 1) Dilute solution
- 2) Concentrated solution

* Method of Expressing concentration of solution

1) percentage by weight : It is defined as amount of solute present in solution.

$$w/w \% = \frac{\text{weight of solute}}{\text{weight of soln}} \times 100$$

2) percentage by volume = $\frac{\text{volume of solute}}{\text{volume of solution}} \times 100$

3) mole fraction (y) : It is defined as the ratio of the number of moles of a component to the total number of moles of the components

$$y_A = \frac{n_A}{n_A + n_B}$$

$$y_B = \frac{n_B}{n_A + n_B}$$

$$y_A + y_B = 1$$

5) parts per million (ppm) : It is defined as the parts of component per million parts (10^6) of the solution. It is widely used when a solute is present in trace quantities.

* HENRY'S LAW

Henry's Law states that at constant temperature, the concentration of gas that is dissolved in a given liquid (mole fraction of the gas in the solution) is proportional to the partial pressure of the gas above the fluid. Mathematical expression for Henry's Law is given by,

$$P = k_H \cdot y$$

k_H → Henry's law constant.

y → mole fraction (y) of the gas in the solution (solubility of gas at a fixed temperature in a solvent)

* If $k_H \uparrow$ higher the solubility of gas in soln.

As k_H decreases, k_{Hd} value decreases.

* As temperature increases, k_{Hd} value decreases.

Applications of Henry Law

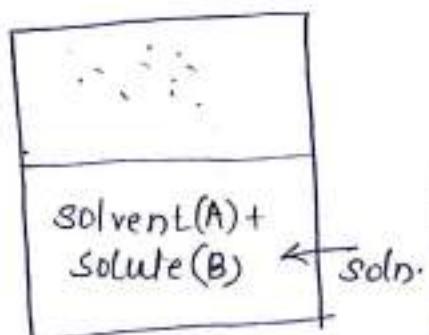
1. Aquatic species are more comfortable in cold water (more dissolved O_2) rather than in warm water.
2. In manufacture of soft drinks and soda water, CO_2 is passed at high pressure to increase its solubility.
3. At high altitudes, the partial pressure of O_2 is less than that at the ground level. This leads to low concentration of O_2 in the blood of climbers which causes anoxia.

* Raoult's Law

It states that for a solution of volatile liquids, the partial vapour pressure of each component (volatile) of the solution is proportional to the mole fraction of that component present in the solution.

For solution containing two liquids A + B, the partial vapour pressure of liquid A is

$$P_A \propto Y_A$$



$$\text{ie } P_A = k \cdot y_A \rightarrow P_A = P_A^\circ y_A$$

when $y_A = 1$, $k = P_A^\circ \leftarrow$ partial vapour pressure of pure liquid.

$$\text{Hence } P_B = P_B^\circ y_B$$

$$P_{\text{total}} = P_A + P_B$$

$P_A \leftarrow$ partial vapour pressure of component A

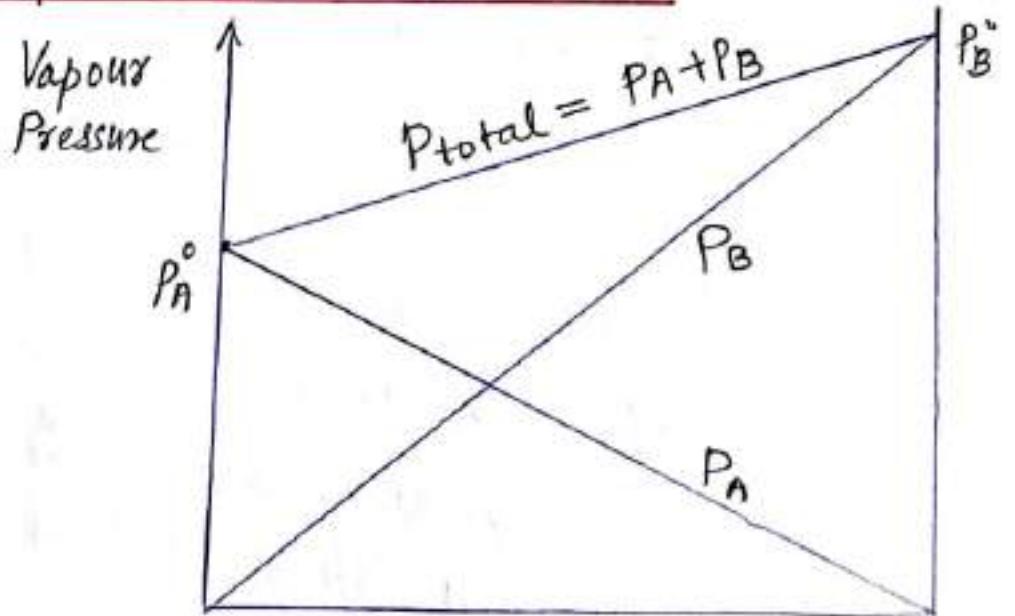
$P_B \leftarrow$ partial vapour pressure of component B

$$P_{\text{total}} = P_A + P_B = P_A^\circ y_A + P_B^\circ y_B$$

$$P_{\text{total}} = P_A^\circ (1 - y_B) + P_B^\circ y_B$$

(since $y_A + y_B = 1$)

* Graphical Representation of Raoult's Law



$$\begin{aligned} y_B &= 0 \\ y_A &= 1 \end{aligned}$$

→ mole fraction of
(y_B)
mole fraction (y_A)

$$\begin{aligned} y_B &= 1 \\ y_A &= 0 \end{aligned}$$

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* Limitations of Raoult's Law.

1. It is applicable only to ideal liquid solutions.
2. The results obtained for some complex, concentrated solutions that have significant intermolecular forces vary considerably from the law.

* Ideal Solution

Those solutions in which solute-solute (B-B) and solvent-solvent (A-A) interactions are almost similar to solvent-solute (A-B) interaction are called ideal solution. These solutions satisfy the following conditions:

- 1) Solution must obey Raoult's Law.
- 2) $\Delta H_{\text{mix}} = 0$ (No energy evolved or absorbed)
- 3) $\Delta V_{\text{mix}} = 0$ (No expansion or contraction on mixing)

* Nonideal Solutions

Those solutions which show deviation from Raoult's Law is called non-ideal solution.

For such solution, $\Delta H_{\text{mix}} \neq 0$
 $\Delta V_{\text{mix}} \neq 0$.

a) Nonideal solution showing +ve deviation

In such a case, solvent-solute (A-B) interactions are weaker than solvent-solvent (A-A) and solute-solute (B-B) interactions.

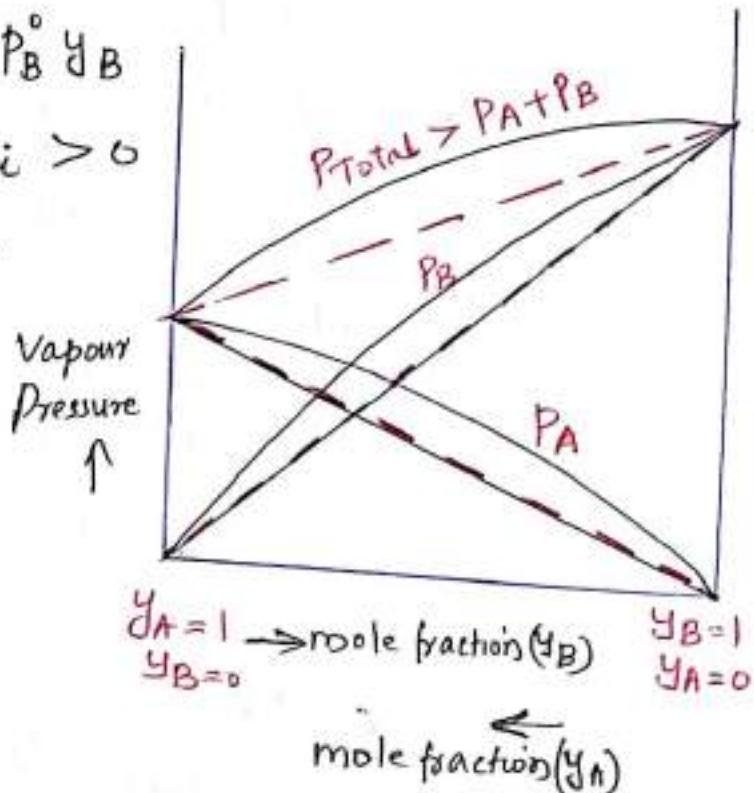
and the observed vapour pressure of each component and the total vapour pressure are greater than that predicted by Raoult's law.

$$\text{i.e. } P_A > P_A^\circ y_A, \quad P_B > P_B^\circ y_B$$

$$P_{\text{total}} > P_A^\circ y_A + P_B^\circ y_B$$

$$\Delta H_{\text{mix}} > 0, \quad \Delta V_{\text{mix}} > 0$$

e.g. Ethanol + water



(b) Non ideal solns showing negative deviation

In such a case, (A-B) solution-solvent interactions are stronger than solvent-solvent (A-A) or solute-solute (B-B) interactions and the observed vapour pressure of each component and the total vapour pressure are lesser than that predicted by Raoult's law.

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$$P_A < P_A^\circ y_A \quad ; \quad P_B < P_B^\circ y_B$$

$$P_{\text{Total}} < P_A^\circ y_A + P_B^\circ y_B$$

For such solns, $\Delta H_{\text{mix}} < 0$, $\Delta V_{\text{mix}} < 0$

e.g. $\text{H}_2\text{O} + \text{HCl}$

