ST. LAWRENCE HIGH SCHOOL

A JESUIT CHRISTIAN MINORITY INSTITUTION

STUDY MATERIAL FOR CHEMISTRY (CLASS-12)

TOPIC- SOLUTION

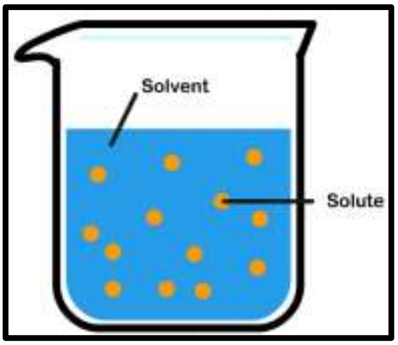
PREPARED BY: MR. ARNAB PAUL CHOWDHURY

SET NUMBER-04

DATE: 22.08.2020

A solution is a homogeneous mixture of two (or more) substances, the composition of which may vary between certain limits. A solution consisting of two components is called ***binary solution.*** The component which is present in large quantity is called ***solvent*** and the component which is small in quantity is called ***solute***. If both components are in same physical state.

Type of Solutions



A

All the three states of matter (gas, liquid or solid) may behave either as solvent or solute. Depending on the state of solute or solvent, mainly there may be the following seven types of binary solutions.

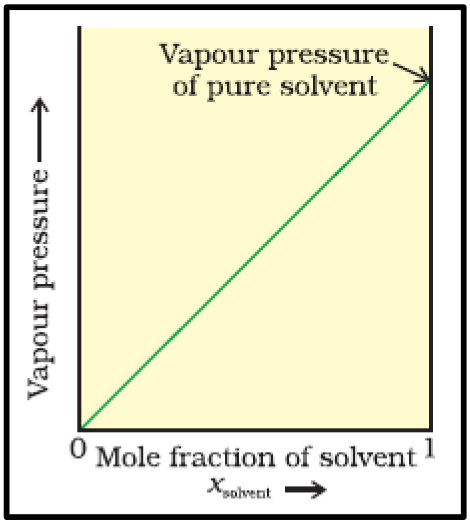
S.No.	Solute	Solvent	Example
1	Gas	Gas	Air
2	Gas	Liquid	Aerated water ($CO_2 + H_2O$)
3	Gas	Solid	Hydrogen in palladium
4	Liquid	Liquid	Alcohol in water, benzene in toluene
5	Liquid	Solid	Mercury in zinc amalgam
6	Liquid	Gas	CO_2 dissolved in water
7	Solid	Liquid	Sugar in water, common salt in water
8	Solid	Gas	Smoke
9	Solid	Solid	Various alloys

Vapour Pressure:

- The pressure exerted by vapours over the liquid surface at equilibrium is called ***vapour pressure*** of the liquid.
- If solute is non volatile solid or liquid the vapour pressure of solution is equal to partial vapour pressure of solvent in the solution.
- If the solute is volatile solid or liquid, then vapour pressure will be equal to the sum of partial vapour pressure of solute and that of solvent.

Raoult's Law:

***"The partial vapour pressure of any component in the solution is directly proportional to its mole fraction"*.**



For a binary solution of two components A and B,

$P_A = X_A$
$P_B = X_B$

Where

P^0_A = vapour pressure of component A in pure state.
P_A = vapour pressure of component A in the solution.
P^0_B = vapour pressure of component B in pure state.
P_B = vapour pressure of component B in the solution

Limitations of Raoult's Law

- Raoult's law is applicable only to very dilute solutions.
- It is applicable to solutions containing non-volatile solute only.
- It is not applicable to solutes which dissociate or associate in a particular solution

Raoult's Law in Combination with Dalton's Law of Partial Pressure:

$P_T = X_A P^0_A + X_B P^0_B = P^0_B + (P^0_A - P^0_B) X_A$

Where

P_T = Total Vapour Pressure of the Solution.

Ideal and Non-Ideal Solutions:

These solutions obey Raoult's law at all compositions of solute in solvent at all temperature

Two liquids A and B form and ideal solution when A –A and B–B molecular attractions will be same and hence A–B molecular attraction will be almost same as A–A and B–B molecular attraction.

For Ideal Solution:

1. $dH_{mixing} = 0$, i.e. no heat should be absorbed or evolved during mixing
2. $dV_{mixing} = 0$, i.e. no expansion or contraction on mixing

Examples , Ethyl chloride and ethyl bromide, n–hexane and n–heptane , CCl_4 and $SiCl_4$

Non-Ideal Solution:

These solutions deviate from ideal behaviour and do not obey Raoult's law over entire range of composition.

For non ideal solutions,

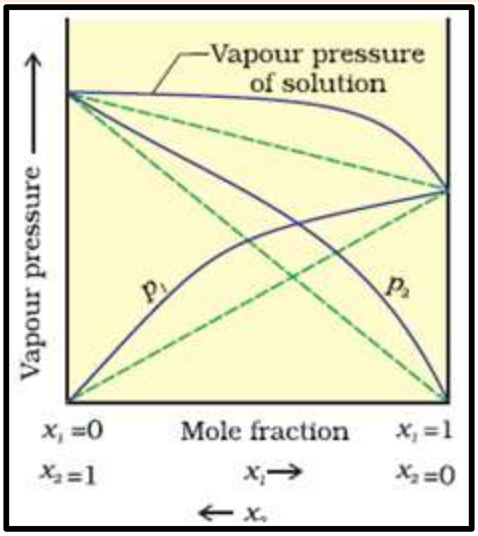
1. $dH_{mixing} \neq 0$
2. $dH_{mixing} \neq 0$

Here we may have two cases

A) Positive Deviation*:*

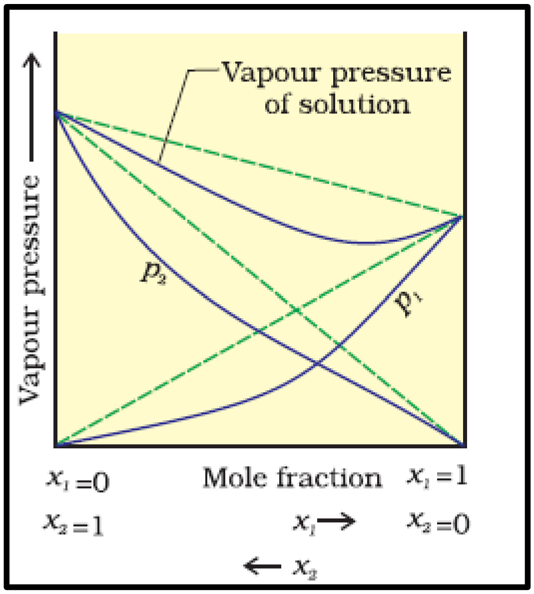
1. $P_A > X_A$ **&** $P_B > X_B$
2. $dH_{mix} > 0$
3. $dV_{mix} > 0$

Example: Cyclohexane and Ethanol



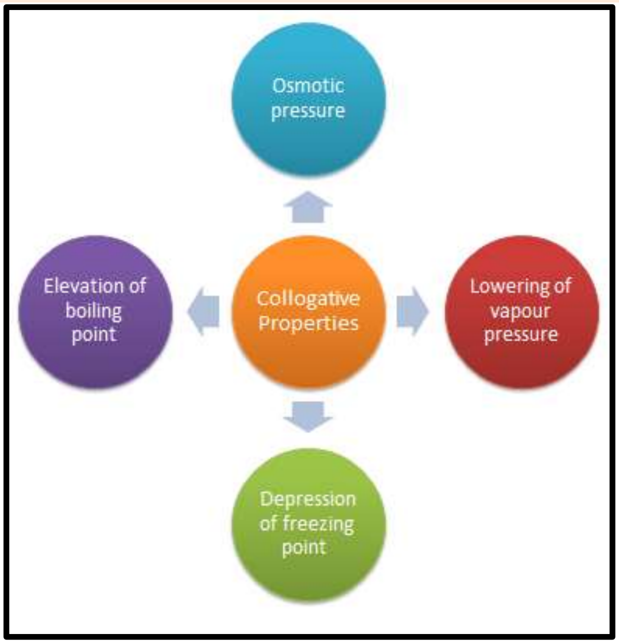
B) Negative Deviation:

1. $P_A > X_A$ **&** $P_B > X_B$
2. $dH_{mix} < 0$
3. $dV_{mix} < 0$



Colligative Properties

The properties of dilute solutions which depend only on number particles of solute present in the solution and not on their identity are called ***colligative properties*** (denoting depending upon collection).



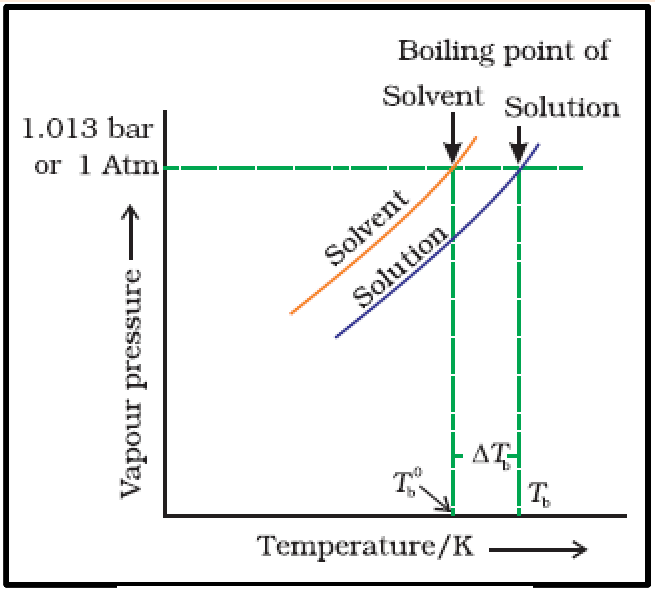
Lowering of Vapour Pressure by a Non-Volatile Solute

The relative lowering of vapour pressure of a solution containing a non-volatile solute is equal to the mole fraction of the solute present in the solution.

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{w_2 \times M_1}{M_2 \times w_1}$$

Elevation of Boiling Point by a Non-Volatile Solute :

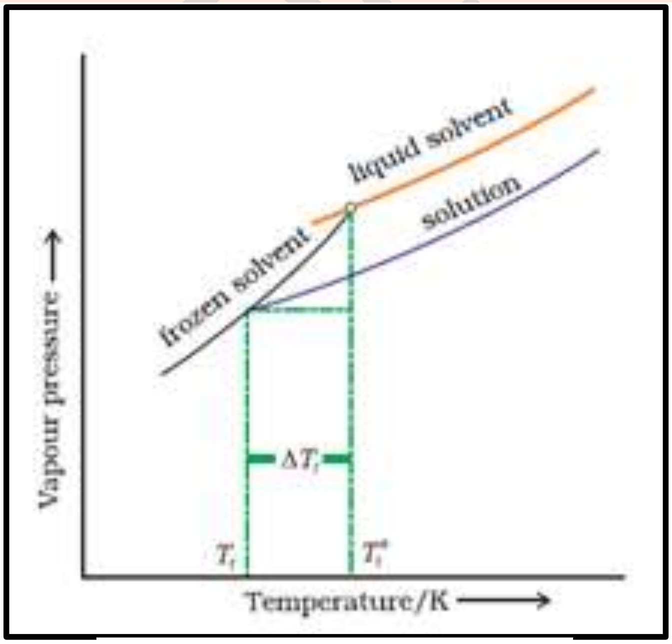
Since the addition of a non-volatile solute lowers the vapour pressure of the solvent, the vapour pressure of a solution is always lower than that of the pure solvent, and hence it must be heated to a higher temperature to make its vapour pressure equal to atmospheric pressure.



$$\Delta T_b = \frac{K_b \times 1000 \times w_2}{M_2 \times w_1}$$

where M_1 = molecular weight of solute and w_2 and w_1 are weights of solute and solvent

Depression of Freezing Point by a Non-Volatile Solute:



$$\Delta T_f = \frac{K_f \times w_2 \times 1000}{M_2 \times w_1}$$

where M_1 = molecular weight of solute and w_2 and w_1 are weights of solute and solvent

Osmosis and Osmotic Pressure:

- **Osmosis:** The phenomenon of the passage of pure solvent from a region of lower concentration (of the solution) to a region of its higher concentration through a semi-permeable membrane.
- **Osmotic Pressure:** Excess pressure which must be applied to a solution in order to prevent flow of solvent into the solution through the semi-permeable membrane.

$\pi V = nRT$

Where,

π = Osmotic pressure

V = volume of solution

n = no. of moles of solute that is dissolved

R = Gas constant

T = Absolute temperature

Isotonic Solutions: A pair of solutions having same osomotic pressure is called isotonic solutions.

Abnormal Molecular Weight and Van't Hoff Factor:

Van't Hoff Factor:

Van't Hoff, in order to account for all abnormal cases introduced a factor **i** known as the Van't Hoff factor, such that

$$i = \frac{\text{Observed colligative property (actual)}}{\text{Theoretical colligative property (expected)}}$$

$$= \frac{\text{No. of molecules actually present}}{\text{No. of molecules expected to be present}}$$

Degree of Association:

The fraction of the total number of molecules which combine to form bigger molecule

$$nA \rightleftharpoons (A)_n$$

Let a be the degree of association, then,

The number of unassociated moles = $1-\alpha$
The number of associated moles = α/n
Total number of effective moles = $1-\alpha+\alpha/n$

$$i = \frac{1-\alpha+\alpha/n}{1}$$

$$i = 1- \alpha\,(1-1/n)$$

Obviously, $i < 1$

Degree of Dissociation

The fraction of the total number of molecules which dissociates in the solution, that is, breaks into simpler molecules or ions.

$KCl \leftrightarrow K^+ + Cl^-$
$1-\alpha \qquad \alpha \quad \alpha$
Thus, the total number of moles after dissociation $= 1-\alpha+\alpha+\alpha = 1+\alpha$
Hence, $i = (1+\alpha)/1$
$i = 1+ \alpha = 1+ (2-1)\alpha$
In general, $\mathbf{i = 1+ (n-1)\,\alpha}$**,**

Where, n = number of particles (ions) formed after dissociation

From the above formula, it is clear that $\mathbf{i > 1}$

GLOSSARY ON SOLUTION

- **Solutions:** Solutions are the homogeneous mixtures of two or more than two components.
- **Binary solution:** A solution having two components is called a binary solution.
- Components of a binary solution.
  It includes solute and solvent.

1. When the solvent is in solid state, solution is called solid solution.
2. When the solvent is in liquid state, solution is called liquid solution.
3. When the solvent is in gaseous state, solution is called gaseous solution.

- **Concentration:** It is the amount of solute in given amount of solution.
- **Mass by volume percentage (w/v):** Mass of the solute dissolved in 100 mL of solution.
- **Molality** (m) is the number of moles of solute present in 1kg of solvent.
- **Molarity** (M) is the number of moles of solute present in 1L of solution.
- **Normality(N)** is the number of gram equivalent of solute dissolved per litre of solution.
- **Solubility:** It is the maximum amount that can be dissolved in a specified amount of solvent at a specified temperature.
- **Saturated solution:** It is a solution in which no more solute can be dissolved at the same temperature and pressure.
- In a nearly saturated solution if dissolution process is an endothermic process, solubility increases with increase in temperature.

- In a nearly saturated solution if dissolution process is an exothermic process, solubility decreases with increase in temperature.
- **Henry’s Law:** It states “at a constant temperature the solubility of gas in a liquid is directly proportional to the pressure of gas”. In other words, “the partial pressure of gas in vapour phase is proportional to the mole fraction of the gas in the solution”.
- When a non-volatile solute is dissolved in a volatile solvent, the vapour pressure of solution is less than that of pure solvent.
- **Raoult’s law:** It states that “for a solution of volatile liquids the partial vapour pressure of each component in the solution is directly proportional to its mole fraction”.
- Using Dalton’s law of partial pressure the total pressure of solution is calculated.

- Comparison of Raoult’ law and Henry’s law: It is observed that the partial pressure of volatile component or gas is directly proportional to its mole fraction in solution. In case of Henry’s Law the proportionality constant is KH and it is different from p10 which is partial pressure of pure component. Raoult’s Law becomes a special case of Henry’s Law when KH becomes equal to p10 in Henry’s law.
- Classification of liquid–liquid solutions: It can be classified into ideal and non-ideal solutions on basis of Raoult’s Law.
- **Ideal solutions:**
  1. The solutions that obey Raoult’s Law over the entire range of concentrations are known as ideal solutions.
  2. The intermolecular attractive forces between solute molecules and solvent molecules are nearly equal to those present between solute and solvent molecules i.e. A-A and B-B interactions are nearly equal to those between A-B.
- **Non-ideal solutions:**
  1. When a solution does not obey Raoult’s Law over the entire range of concentration, then it is called non-ideal solution.
  2. The intermolecular attractive forces between solute molecules and solvent molecules are not equal to those present between solute and solvent molecules i.e. A-A and B-B interactions are not equal to those between A-B
- **Types of non- ideal solutions:**
  1. Non ideal solution showing positive deviation
  2. Non ideal solution showing negative deviation
- **Non ideal solution showing positive deviation**
  1. The vapour pressure of a solution is higher than that predicted by Raoult’s Law.

2. The intermolecular attractive forces between solute-solvent molecules are weaker than those between solute-solute and solvent-solvent molecules i.e., A-B < A-A and B-B interactions.

- **Non ideal solution showing negative deviation**

1. The vapour pressure of a solution is lower than that predicted by Raoult's Law.
2. The intermolecular attractive forces between solute-solvent molecules are stronger than those between solute-solute and solvent-solvent molecules i.e. A-B > A-A and B-B interactions.

- **Azeotopes**: These are binary mixtures having same composition in liquid and vapour phase and boil at constant temperature. Liquids forming azeotrope cannot be separated by fractional distillation.
- **Types of azeotropes:** There are two types of azeotropes namely,

1. Minimum boiling azeotrope
2. Maximum boiling azeotrope

- The solutions which show a large positive deviation from Raoult's law form minimum boiling azeotrope at a specific composition.
- The solutions that show large negative deviation from Raoult's law form maximum boiling azeotrope at a specific composition.
- **Colligative properties**: The properties of solution which depends on only the number of solute particles but not on the nature of solute are called colligative properties.
- **Types of colligative properties**: There are four colligative properties namely,

1. Relative lowering of vapour pressure
2. Elevation of boiling point
3. Depression of freezing point
4. Osmotic pressure

- **Relative lowering of vapour pressure:** The difference in the vapour pressure of pure solvent and solution represents lowering in vapour pressure .
- Relative lowering of vapour pressure: Dividing lowering in vapour pressure by vapour

  pressure of pure solvent is called relative lowering of vapour pressure
- Relative lowering of vapour pressure is directly proportional to mole fraction of solute. Hence it is a colligative property.

- **Elevation of boiling point:**

- For a dilute solution elevation of boiling point is directly proportional to molal concentration of the solute in solution. Hence it is a colligative property.
- **Depression of freezing point**: The lowering of vapour pressure ofsolution causes a lowering of freezing point compared to that of pure solvent.The difference in freezing point of the pure solvent and solution is called the depression in freezing point.
- For a dilute solution depression in freezing point is a colligative property because it is directly proportional to molal concentration of solute.
- Osmosis: The phenomenon of flow of solvent molecules through a semi permeable membrane from pure solvent to solution is called osmosis.
- **Osmotic pressure:** The excess pressure that must be applied to solution to prevent the passage of solvent into solution through a semipermeable membrane is called osmotic pressure.
- Osmotic pressure is a colligative property as it depends on the number of solute particles and not on their identity.
- For a dilute solution, osmotic pressure is directly proportional to the molarity (C) of the solution.
- Osmotic pressure can also be used to determine the molar mass of solute using the equation.
- **Isotonic solution:** Two solutions having same osmotic pressure at a given temperature are called isotonic solution.
- **Hypertonic solution:** If a solution has more osmotic pressure than other solution it is called hypertonic solution.
- **Hypotonic solution**: If a solution has less osmotic pressure than other solution it is called hypotonic solution.
- **Reverse osmosis**: The process of movement of solvent through a semipermeable membrane from the solution to the pure solvent by applyingexcess pressure on the solution side is called reverse osmosis.
- Colligative properties help in calculation of molar mass of solutes.
- Abnormal molar mass: Molar mass that is either lower or higher than expected or normal molar mass is called as abnormal molar mass.
- **Van’t Hoff factor**: Van’t Hoff factor (i)accounts for the extent of dissociation or

  association.
- Value of i is less than unity in case solute undergo association and the value of i is greater than unity in case solute undergo dissociation.
- Inclusion of van’t Hoff factor modifies the equations for colligative properties as:

-

Van't Hoff factor, 'i' is used to express the extent of association or dissociation of solutes in solution. It is die ratio of the normal and observed molar masses of the solute, i.e.

$$i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}}$$

$$\text{or} \quad i = \frac{\text{Calculated molar mass}}{\text{Experimental molar mass}}$$

In case of association, observed molar mass being more than the normal, the factor 'T has a value less than one. But in case of dissociation, the van't Hoff factor is more than one because the observed molar mass has a less value.
In case of solutes which do not undergo any association or dissociation in a solvent, the Vant Hoff factor, 'i', will be equal to one because the observed and normal molar masses will be same.
Inclusion of van't Hoff factor, 'F, modifies the equations for colligative properties as follows:

Elevation in boiling point, $\Delta T_b = iK_b m$
Depression in freezing point, $\Delta T_f = iK_f m$
Osmotic pressure, $\pi = iCRT$