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An Initiative by अमरउजाला

LIQUID SOLUTION

PHYSICAL CHEMISTRY

JEE/NEET-2020

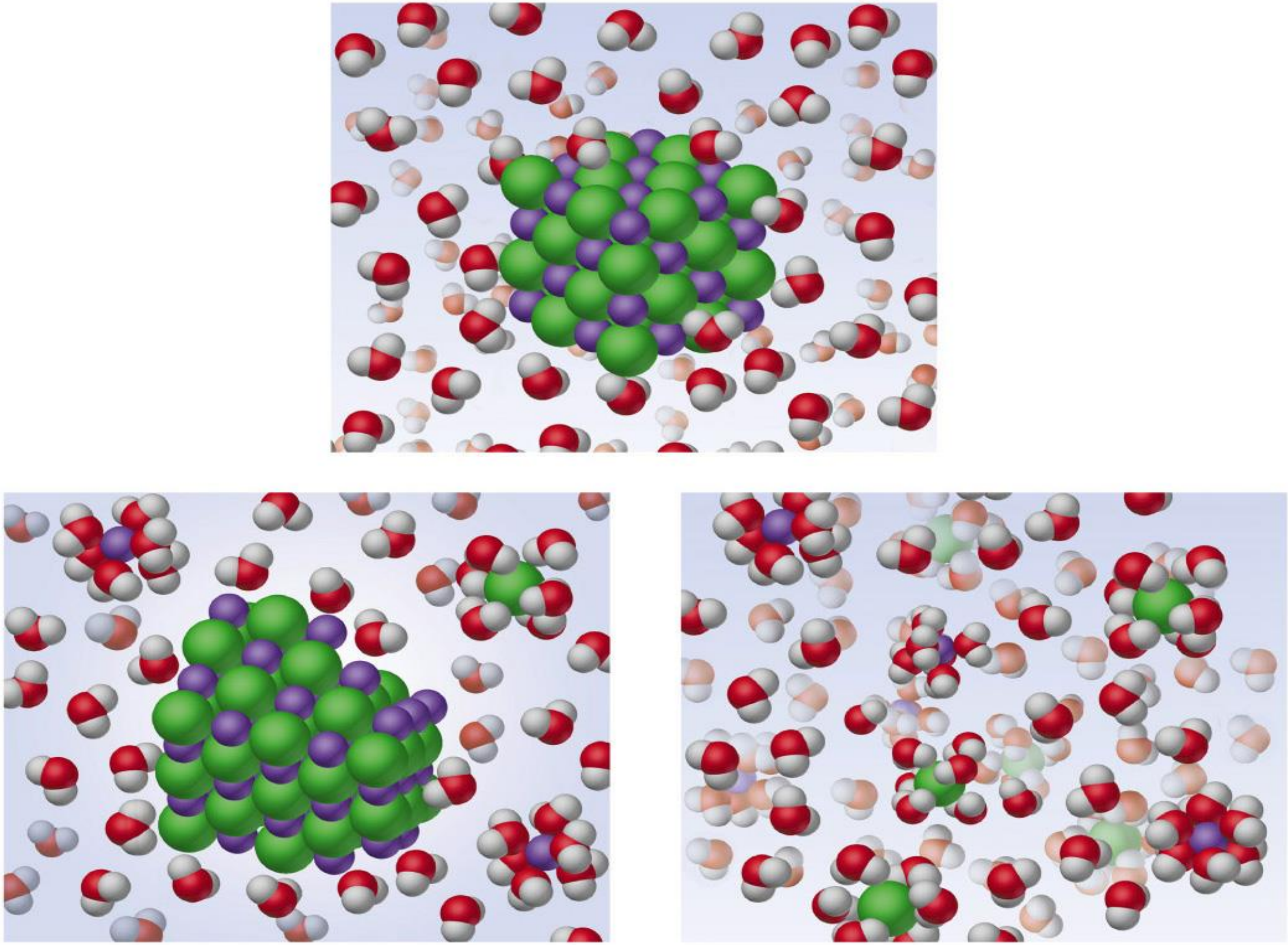
Liquid Solution

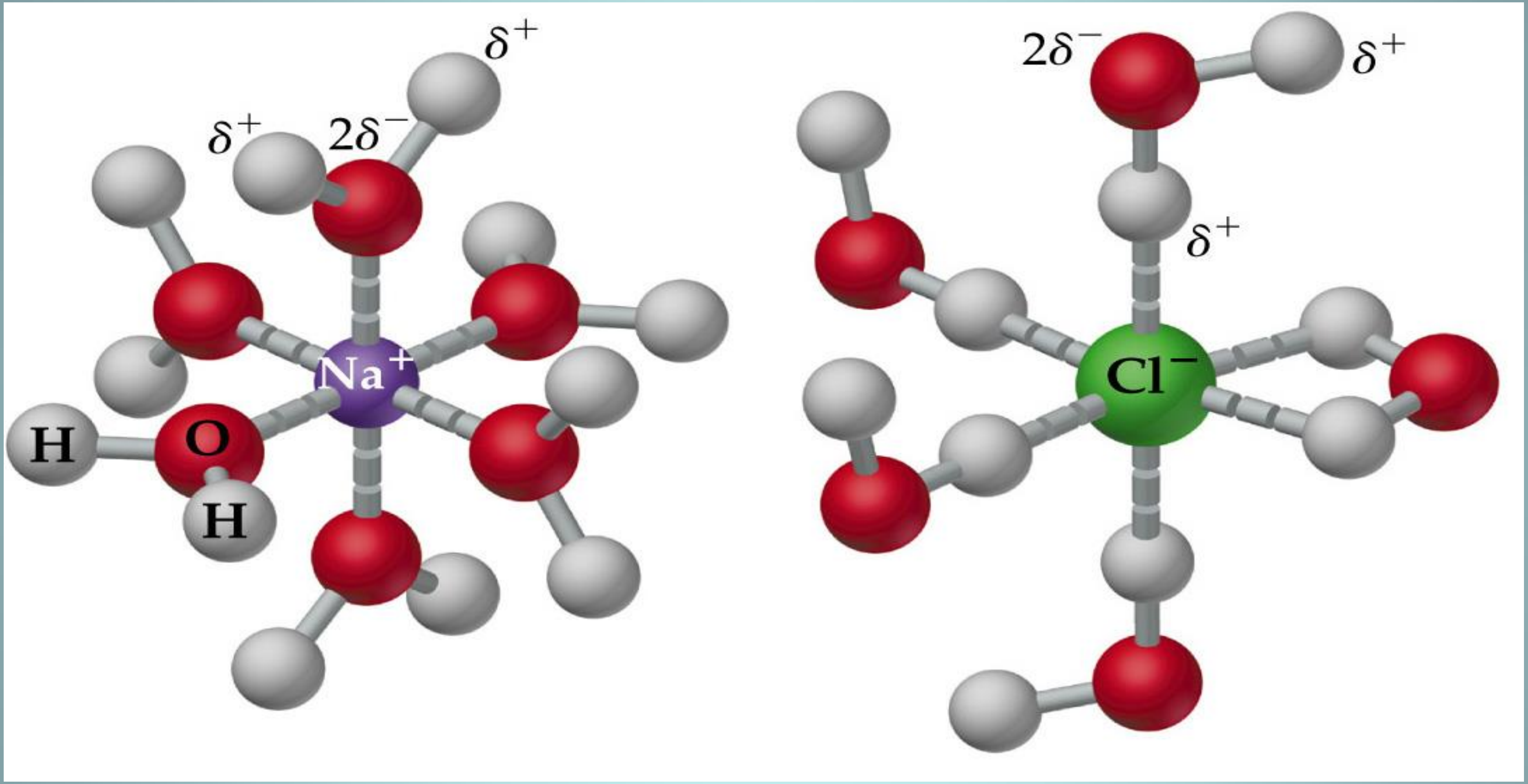
- Solution - homogeneous mixture of solute and solvent.

(Solute + solvent = solution)

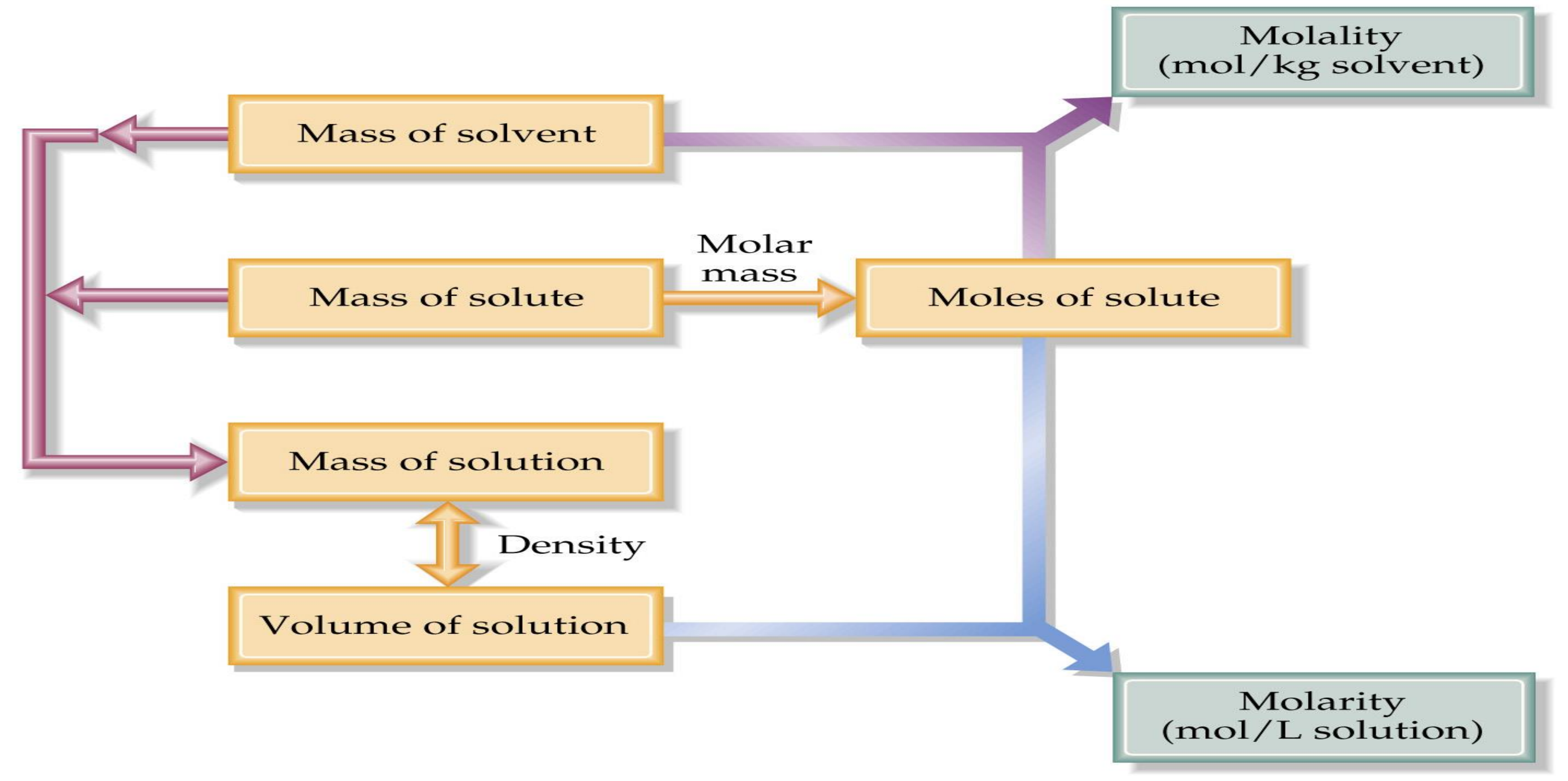
- In solutions, intermolecular forces become rearranged.

Saturated Solution : A solution that is in equilibrium with pure solid solute. No more solute can be dissolved in it.




δ+
δ+
2δ−
Na+
H
O
H
2δ−
δ+
δ+
Cl−

Ways of Expressing Concentration



The concentration of a solution can be expressed in a number of ways. The important methods are:

(i) Mass percentage or per cent by mass:

$$\%(w/w) \text{ Mass percentage of solute} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$$

$$= \frac{\text{Mass of solute}}{\text{Mass of solute} + \text{Mass of solvent}}$$

$$= \frac{\text{Mass of solute}}{\text{Volume of solution} \times \text{Density of solution}}$$

(ii) Percent mass by volume:

$$\%(w/v) = \frac{\text{Mass of solute}}{\text{Volume of soltuion}} \times 100$$

(iii) Parts per million (ppm) :

$$\text{ppm} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$$

(iv) Mole fraction:

Let n moles of solute (A) and N moles of solvent (B) be presnet in a solution.

Mole fraction of solute = $\frac{n}{N+n} = X_A$, Mole fraction of solvent = $\frac{N}{N+n} = X_B$

In binary solution, $X_A + X_B = 1$

Mole fraction is independent of temperature of the solution.

(v) Molality

$$\text{Molality } (m) = \frac{\text{No. of moles of solute}}{\text{weight (in kg) of solvent}}$$

Let w_A grams of the solute of molecular mass m_A be present in w_B grams of the solvent, then

$$\text{Molality } (m) = \frac{w_A}{m_A \times w_B} \times 1000$$

Relation between mole fraction and Molality :

$$\frac{X_A \times 1000}{X_B \times m_B} = m = \frac{w_A \times 1000}{w_B \times m_B}$$

Note: (i) Molality is the most convenient method to express the concentration because it involves the mass of liquids rather than their volumes. It is also independent of the variation in temperature.

(vi) Molarity (Molar concentration)

$$\text{Molarity (M)} = \frac{\text{No. of moles of solute}}{\text{Volume (in litre) of solution}}$$

$$\text{Molarity of the solution} = \frac{w_A}{m_A \times V} \text{ x } 1000$$

Relation between molarity and % solute by mass :

Let d = density of solution in g/mL and let it contains x% (w/w) solute by mass.

Number of moles of solute in 1 litre

$$= \frac{\text{mass of solute in gram} \quad \text{grams}}{\text{molecular mass of solute} \quad \underline{x \times d \times 10}} = \frac{x \times d \times 10}{\text{M}_{\text{solute}}}$$

$$\text{M} = \quad m_{\text{A}}$$

Molarity of dilution:

Before dilution $M_1V_1 = M_2V_2$ After dilution

Molarity of mixing:

$$M_1V_1 + M_2V_2 + M_3V_3 = M_R(V_1 + V_2 + V_3)$$

M_R = resultant molarity

Relationship between molality and molarity :

$$\text{Molality (m)} = \frac{\text{molarity}}{d - \text{molarity} \times m_{\text{solute}}} = \frac{1000 \times M}{1000 \times d - M \times M_{\text{solute}}}$$

Illustration 1. The is density of a solution containng 13% by mass of sulphric acid 1.09 g/mL. Calculate the molarity of the solution.

Solution: In solving such numericals, the following formula can be applied:

$$\text{Molarity} = \frac{\%\ \text{strength of soln.} \times \text{density of soln.} \times 10}{\text{Mol. mass}}$$

$$M = \frac{13 \times 1.09 \times 10}{98} = 1.445\ M$$

Illustration 2. ***The density of a 3 M sodium thiosulphate solution ($Na_2S_2O_3$) is 1.25 g/mL. Calculate***

(i) the percentage by mass of sodium thiosulphate,

(ii) the mole fraction of sodium thiosulphate

2–

Solution: $M = \frac{x \times d \times 10}{m_A} \Rightarrow 3 = \frac{x \times 1.25 \times 10}{158}$

$\therefore \quad x = 37.92$

(ii) No. of moles of $Na_2S_2O_3 = \frac{474}{158} = 3$

Mass of water = (1250 – 474) = 776 g ,

No. of moles of water = $\frac{776}{18} = 43.1$

Mole fraction of $Na_2S_2O_3 = \frac{3}{43.1+3} = \frac{3}{46.1} = 0.065$

Illustration 3. ***One litre of sea water weighs 1030 g and contains about 6 × 10^{-3} g of dissolved O_2. Calculate the concentration of dissolved oxygen in ppm.***

Solution: Mass of O_2 in mg = $6 \times 10^{-3}\,\text{g} \times 10^{3}\,\text{mg/g} = 6\,\text{mg}$

ppm of O_2 in 1030 g sea water = $\dfrac{\text{Mass of } O_2 \text{ in mg}}{\text{Mass of sea water in kg}} = \dfrac{6}{(1030/1000)\text{kg}}$

$$= \frac{6 \times 1000}{1030} = 5.8\,\text{ppm}$$

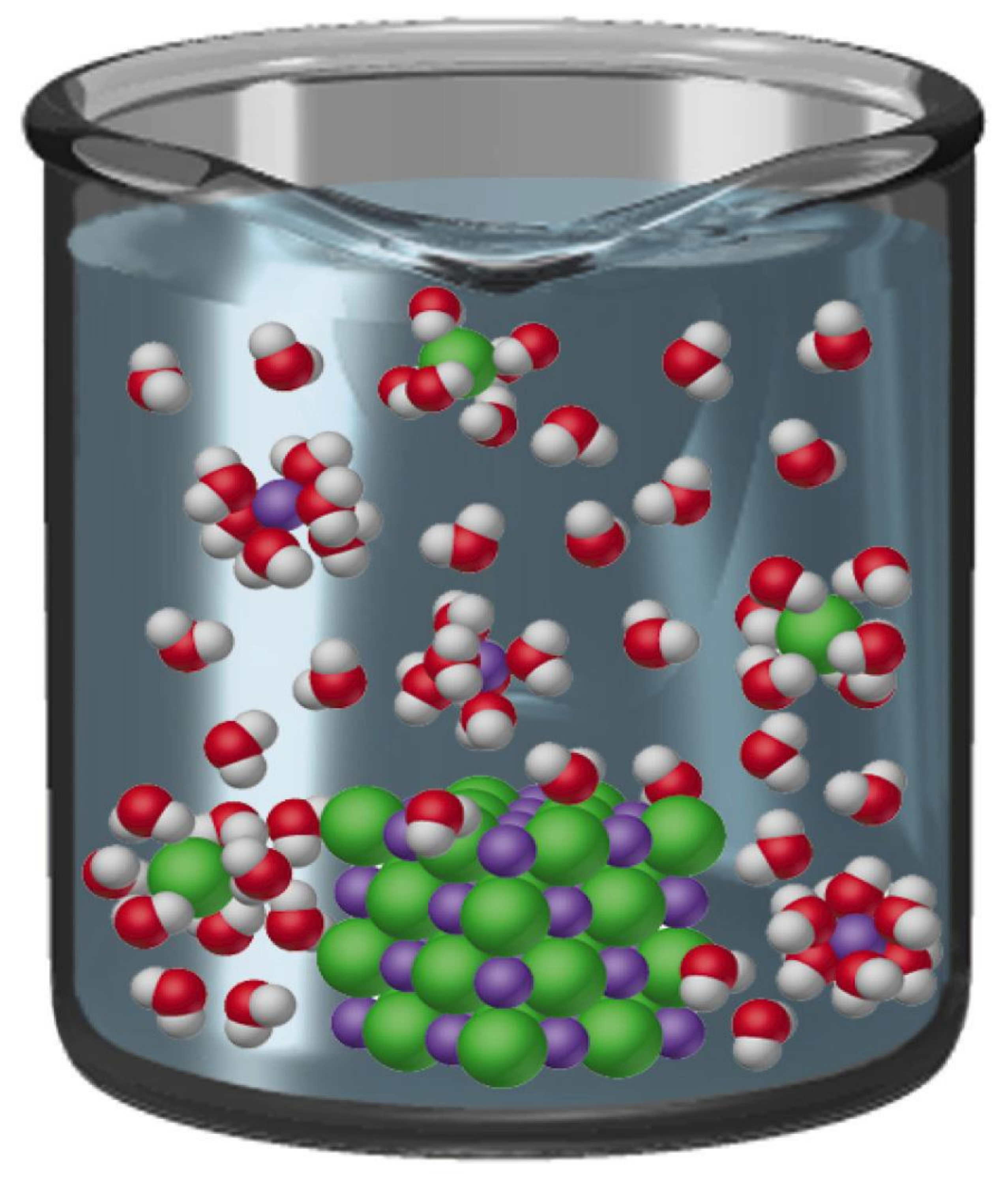
Solubility of a substance is its maximum amount that can be dissolved in a specified amount of solvent. It depends upon the nature of solute and solvent as well as temperature and pressure. Let us consider the effect of these factors in solution of asolid or a gas in a liquid.

Solubility of Gases

Gases are completely miscible with each other. Gases also dissolve in liquids and solids.Gasses are soluble in liquid to different extents e.g., solubility of hydrochloric acid gas in water is much more than the solubility of oxygen in water.

Solubility of gas in a liquid depends on the following factors:

1) Nature of the gas and the liquid
2) Temperature
3) Pressure.

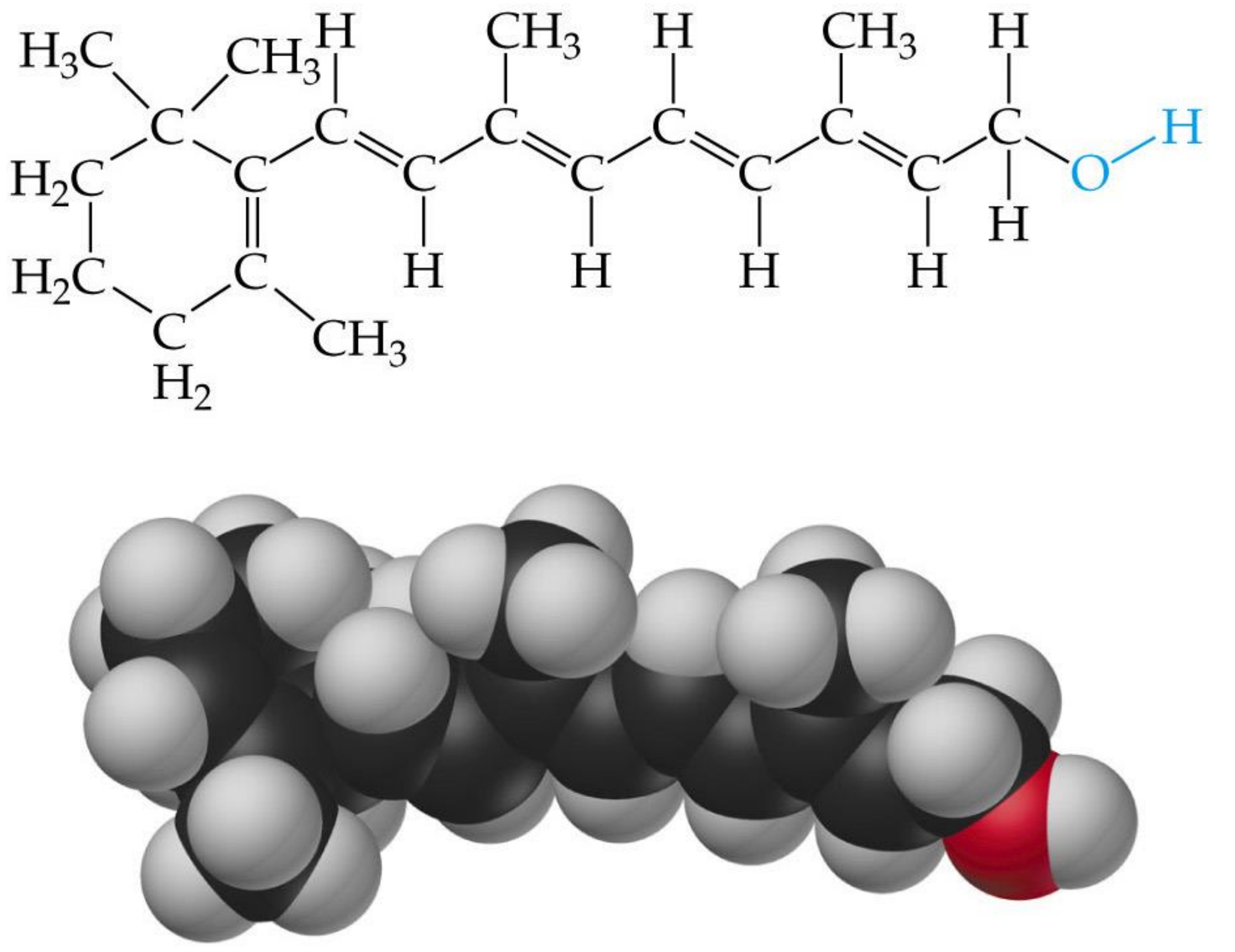


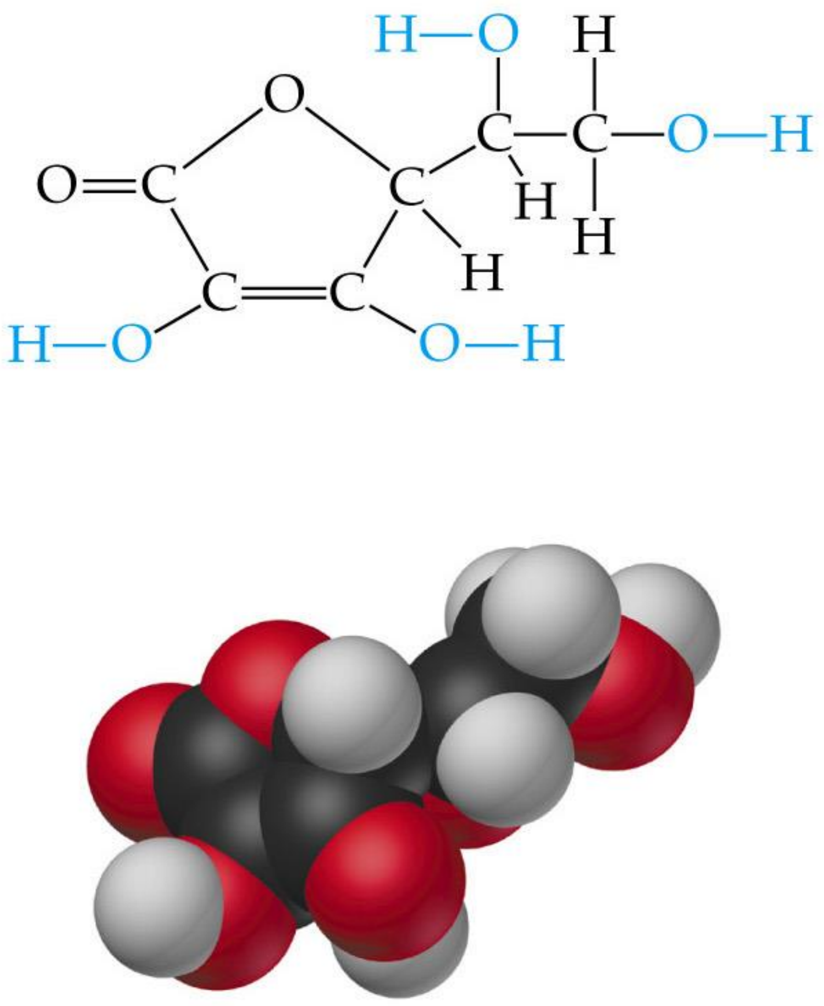
Nature of the gas and the liquid

Solubility of nonpolar bromine is much more Soluble in nonpolar solvents like carbondisulphide or carbontetrachloride than in water.

LIKE DISSOLVE LIKES

Which of these two would be more soluble in water?


Vitamin A


Vitamin C

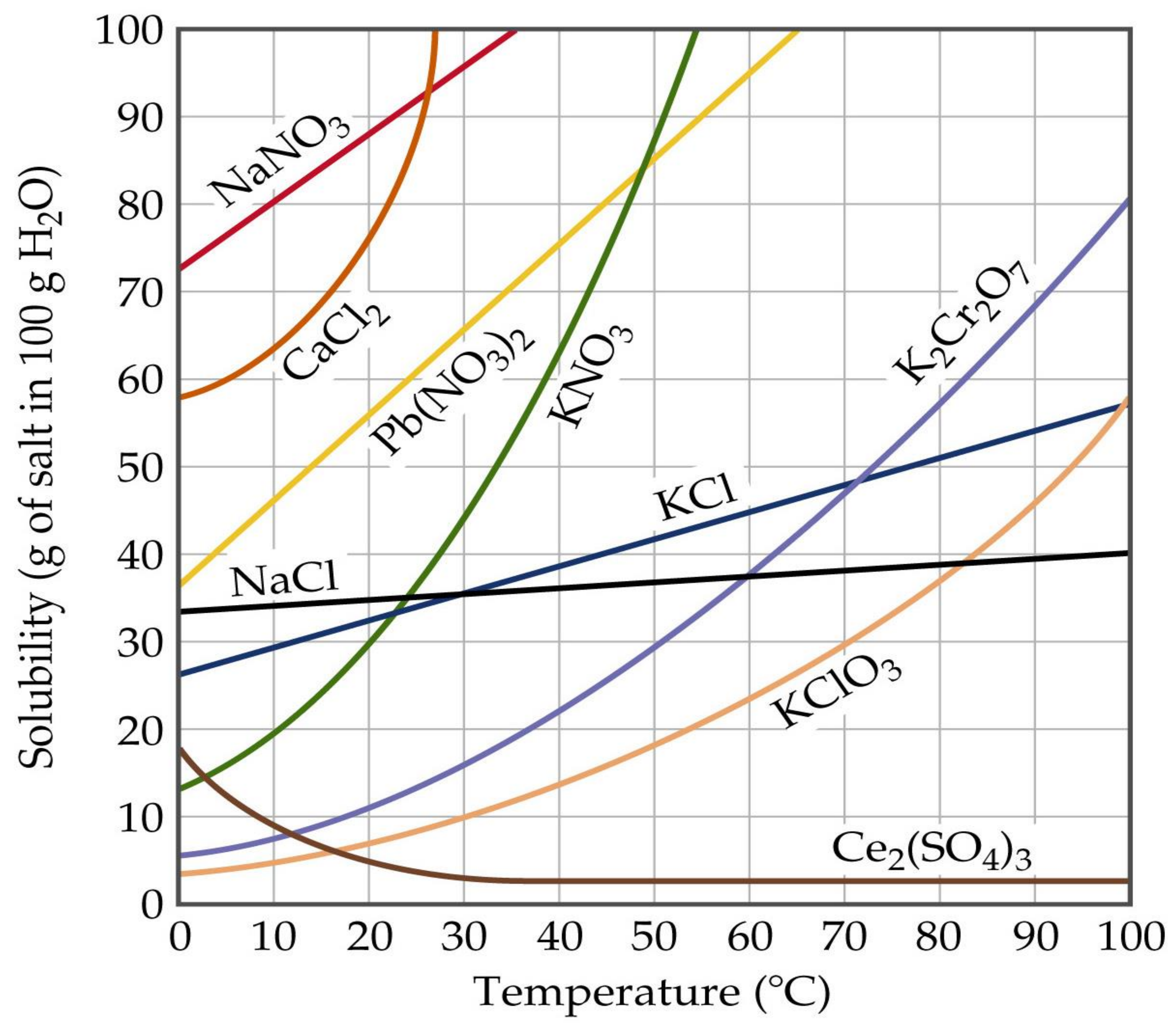
Temperature

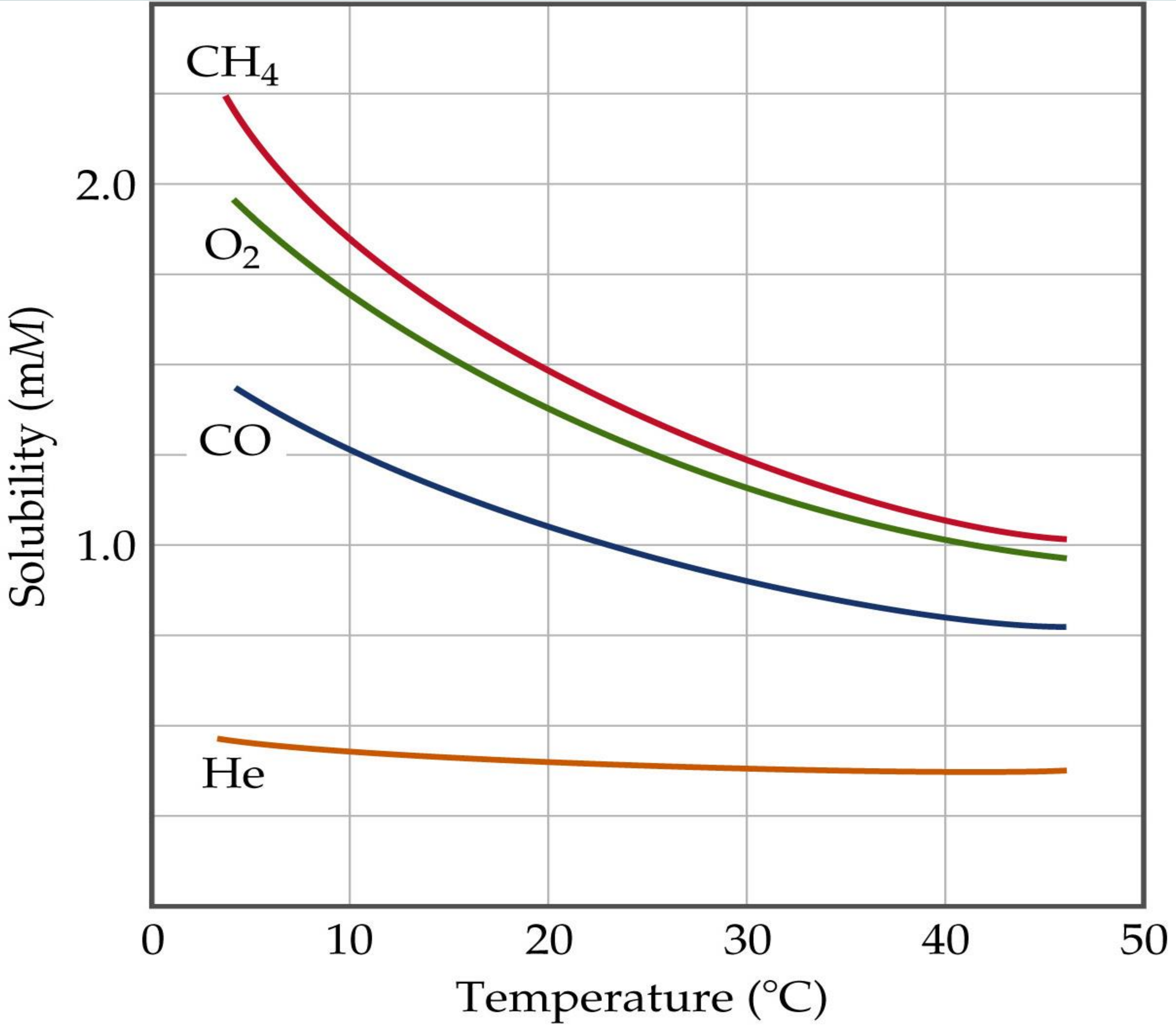
Solubility of a gas in a liquid generally decreases with increase in temperature.

The solubility of a gas decrease with increases in temp. The dissolution of a gas in liquid is an exothermic process i.e, it is accompanied by evolution of heat i.e.

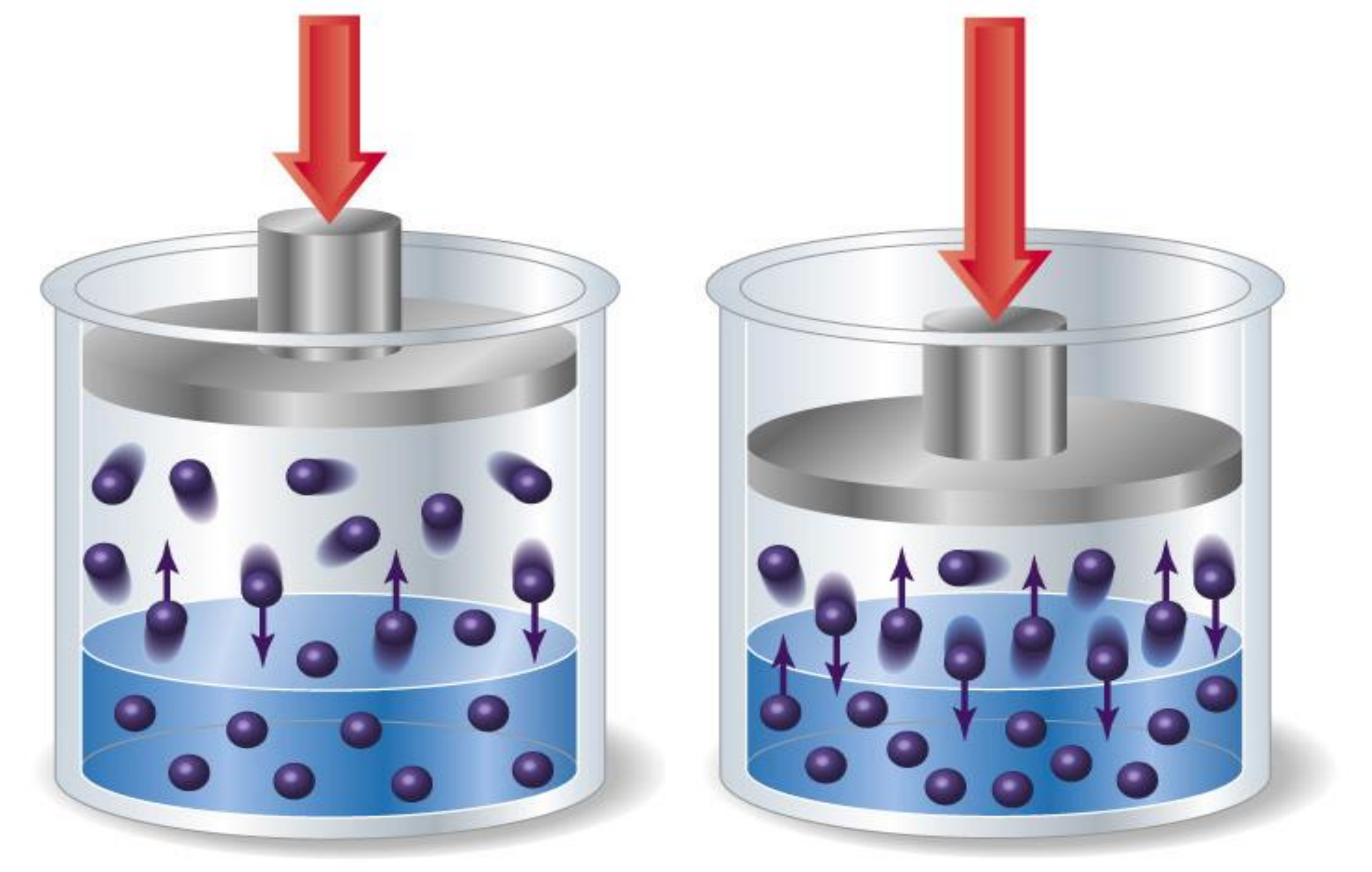
Gas + Solvent = Solution + Heat

Applying Le Chatelier's principle, it is evident hat increases of temp. would shift the equilibrium in the backward direction i.e. , the solubility would decreases.


NaNO3
CaCl2
Pb(NO3)2
KNO3
K2Cr2O7
KCl
NaCl
KClO3
Ce2(SO4)3
Solubility (g of salt in 100 g H2O)
100
90
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
70
80
90
100
Temperature (°C)


CH$_4$
O$_2$
CO
He
2.0
1.0
Solubility (m*M*)
0
10
20
30
40
50
Temperature (°C)

Pressure Effects



Henry’s Law gives:

$$\boxed{S_g = kP_g}$$

where 'S' is the mass of the gas dissolved in a unit volume of the solvent. p is the pressure of the gas in equilibrium with the solvent.
k is the proportionality constant called Henry's law constant characteristic of the nature of the solvent and the natures of the gas, also the temperature.

Example

27g of acetylene, C_2H_2, dissolves in 1L of acetone at 1.0 atm pressure. If the partial pressure of acetylene is increased to 12 atm, what is the solubility in acetone?

Solution:

$S_1 = kP_1$…………(1)

$S_2 = kP_2$…………(2)

Ans: 3.2×10^2 g

Dalton also concluded independently that, solubility of a gas in liquid solution is a function of the partial pressure of the gas.

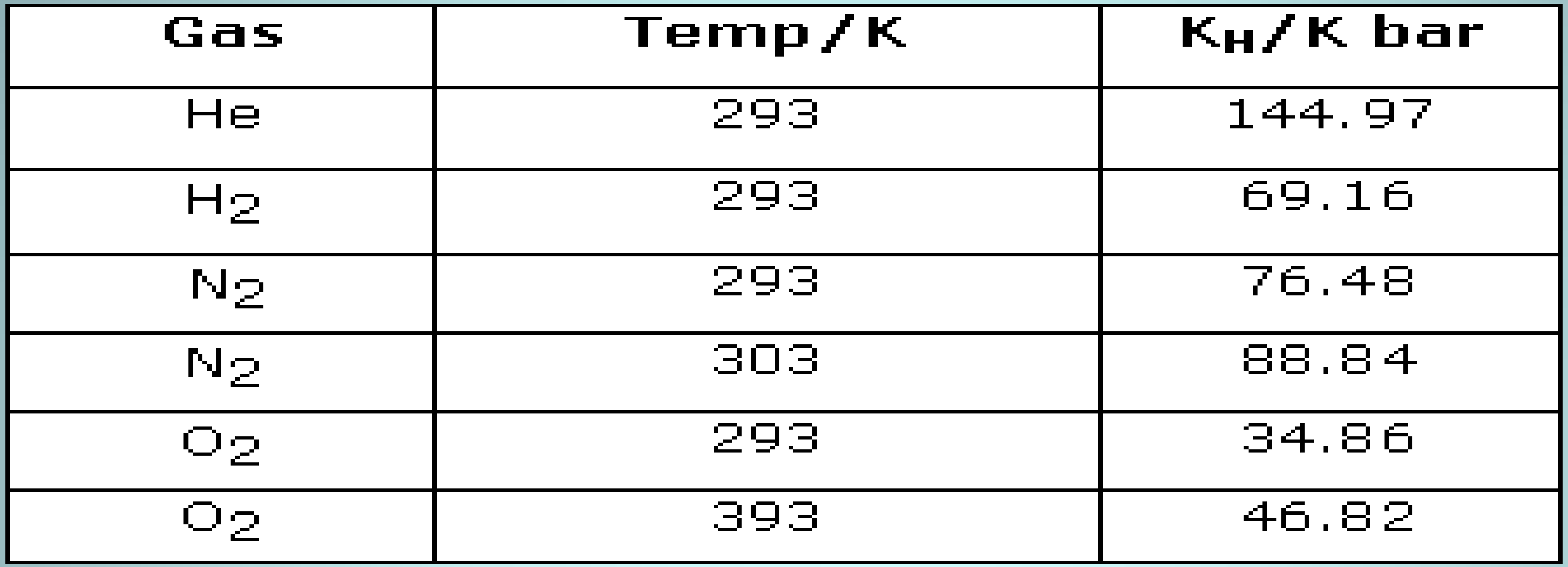
If mole fraction is used to represent the solubility of the gas in the solution, then

Partial pressure of the gas in solution $\propto$ mole fraction of the gas in solution.

$$\text{or } p \propto K_H \, x$$

where, p is the partial pressure of the gas in solution, x is the mole fraction of the gas in solution and K_H is Henry's law constant.

Here are the values of Henry's Law Constant (K_H) for some selected gases in water



Gas	Temp / K	K_H / K bar
He	293	144.97
H_2	293	69.16
N_2	293	76.48
N_2	303	88.84
O_2	293	34.86
O_2	393	46.82

It is obvious from the above table that the value of K_H increases with temperature, indicating that solubility of gases decreases with increase in temperature.

Henry's Law explains many biological phenomena and also has several applications in industries, like:

To increase the solubility of CO_2 in soft drinks and soda water, the bottle is sealed under high pressure.

In lungs the partial pressure of oxygen is high so haemoglobin combines with. oxygen to form oxohaemoglobin. But in the tissues the partial pressure of oxygen is low therefore oxohaemoglobin releases oxygen for utilization in cellular activities.

The breathing gas for deep sea divers consists of oxygen diluted with less soluble helium gas. This is to minimize the painful effects of deep sea divers due to decompression.
For e.g., concentration of CO_2 which is dissolved in a carbonated beverage.
Example: Soda water is dependant directly on the partial pressure of CO_2 in the gas phase.

Hydrogen bonding or dipole-dipole interaction between molecules of gas and molecules of the liquid. For e.g., dissolution of acetylene in acetone and dissolution of HCl in ether are due to hydrogen bonding.

Limitation of Henry’s Law:-

(i)The pressure should be low and the temp should be high i.e, the gas should behave like an ideal gas.

The gas should not undergo compound formation with the solvent or association or dissociation in the solvent.

Application of Henry’s law:-

(i)In the function of lungs:- When air enters the lungs, partial pressure of oxygen is high. This oxygen combines with haemoglobin to form oxyhaemoglobin. Hence here O_2 is released from oxyhaemoglobin which is utilized for functions of the cells.

In the production of carbonated beverages:- To inc the solubility of Co_2in soft drinks, soda water , beer, champagne etc, the bottles are sealed under high pressure. When the bottle is opened to air, the partial pressure of CO_2 above the sol. dec. and CO_2 bubbles out.

Question :

H_2S, a toxic gas with rotten egg like smell, is used for the qualitative analysis. If the solubility of H_2S in water at STP is 0.195 m, calculate Henry's law constant.

It is given that the solubility of H_2S in water at STP is 0.195 m, i.e., 0.195 mol of H_2S is dissolved in 1000 g of water.

Moles of water = $\frac{1000g}{18g\ mol^{-1}} = 55.56$ mol

$$\therefore \text{Mole fraction of } H_2S,\ x = \frac{\text{Moles of } H_2S}{\text{Moles of } H_2S + \text{Moles of water}} = \frac{0.195}{0.195 + 55.56} = 0.0035$$

At STP, pressure (p) = 0.987 bar

According to Henry's law:

$p = K_H x$

$$\Rightarrow K_H = \frac{p}{x} = \frac{0.987}{0.0035} \text{ bar} = 282 \text{ bar}$$

Question :

Henry's law constant for CO_2 in water is 1.67×10^8 Pa at 298 K. Calculate the quantity of CO_2 in 500 mL of soda water when packed under 2.5 atm CO_2 pressure at 298 K.

It is given that:

$K_H = 1.67 \times 10^8$ Pa $\quad p_{CO_2} = 2.5$ atm $= 2.5 \times 1.01325 \times 10^5$ Pa $= 2.533125 \times 10^5$ Pa

According to Henry's law:

$$p_{CO_2} = K_H.x$$

$$\Rightarrow x = \frac{p_{CO_2}}{K_H} = \frac{0.533125\times10^5}{1.67\times10^8}$$

$= 0.00152$

We can write, $\quad x = \dfrac{n_{CO_2}}{n_{CO_2} + n_{H_2O}} \approx \dfrac{n_{CO_2}}{n_{H_2O}}$

[Since, n_{CO_2} is negligible as compared to n_{H_2O}]

In 500 mL of soda water, the volume of water = 500 mL

[Neglecting the amount of soda present] We can write:

500 mL of water = 500 g of water

$= \frac{500}{18}$ mol of water

= 27.78 mol of water

Now, $\frac{n_{CO_2}}{n_{H_2O}} = x$

$$\frac{n_{CO_2}}{27.78} = 0.00152$$

$$n_{CO_2} = 0.042\,\text{mol}$$

Hence, quantity of CO_2 in 500 mL of soda water = (0.042 × 44)g

= 1.848 g

<u>Question :</u>

Why do gases always tend to be less soluble in liquids as the temperature is raised?

Solubility of gases in liquids decreases with an increase in temperature. This is because dissolution of gases in liquids is an exothermic process.

$$\text{Gag} + \text{Liquid} \longrightarrow \text{Solution} + \text{Heat}$$

Therefore, when the temperature is increased, heat is supplied and the equilibrium shifts backwards, thereby decreasing the solubility of gases.

Question 2.35:

Henry’s law constant for the molality of methane in benzene at 298 Kis 4.27×10^5 mm Hg. Calculate the solubility of methane in benzene at 298 Kunder 760 mm Hg.

Here,

$p = 760$ mm Hg

$k_H = 4.27 \times 10^5$ mm Hg

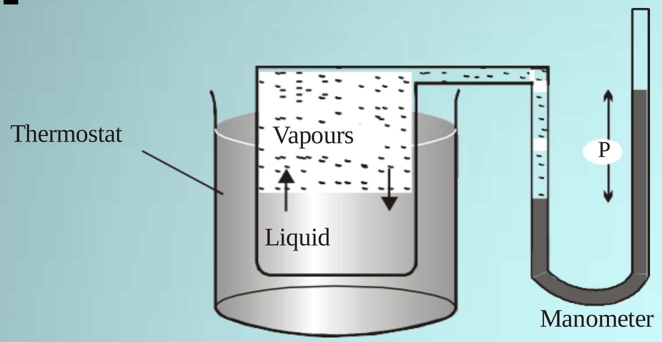
According to Henry’s law,

$p = k_H x$

$$\Rightarrow x = \frac{p}{k_H} = \frac{760 \text{ mm Hg}}{427 \times 10^5 \, mm \text{ Hg}} = 177.99 \times 10^{-5} = 178 \times 10^{-5} \text{ (approximately)}$$

Hence, the mole fraction of methane in benzene is 178×10^{-5}.

Vapour Pressure



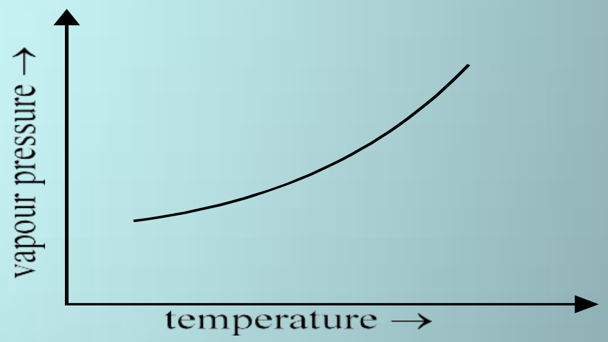
Physical equilibrium between liquid $\rightleftharpoons$ vapours

The pressure exerted by the vapour (molecules in the vapour phase) over the surface of the liquid at the equilibrium at given temperature is called the vapour pressure of the liquid.

Factors affecting vapour pressure

(i) Temperature :

Vapour pressure $\propto$ Temperature



The temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure is called its ***boiling point.***

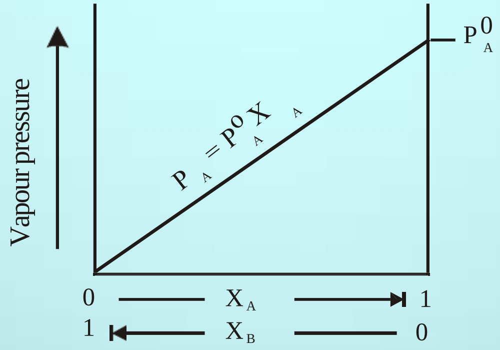
(ii) Nature of liquid:

$$\text{Vapour pressure of liquid} \propto \frac{1}{\text{The strength of intermolecular forces acting between molecules}}$$

For example, ethyl alcohol has higher vapour pressure because of the weak intermolecular forces acting between its molecules than water which has stronger intermolecular forces acting between water molecules of volatile liquid has lower boiling point than a non-volatile liquid.

(i) Vapour Pressure of a Solution Containing Non Volatile Solute - Raoult's Law :

Raoult's Law : Acccording to this law, the partial pressure of any volatile constituent of a soltuion at a constant temperature is equal to the vapour pressure of pure constituent multiplied by the mole fraction of that constituent in the solution.



$$P_A \propto X_A \Rightarrow P_A = P^0_A X_A \qquad \text{.......(1)}$$

Relative Lowering of vapour pressure: For a solution of a non-volatile solute in a liquid, the vapour pressure contribution by the non-volatile solute is negligible. Therefore, the partial vapour pressure of a solution containing a non-volatile solute is equal to the product of vapour pressure of the pure liquid

(solvent P°_A) and its mole fraction in the solution.

Let X_A be the mole fraction of solvent A, then (Here p^0_B = negligible as solute is non-volatile)

$$P_A = P^{\circ}_A X_A$$

If X_B be the mole fraction of the solute B, then

$$X_A + X_B = 1 \Rightarrow X_A = 1 - X_B$$

hence $P_A = P^{\circ}_A(1 - X_B) = P^{\circ}_A - P^{\circ}_A X_B \Rightarrow \mathbf{P^o_A X_B = P^o_A - P_A}$ ......(2)

($P^o_A - P_A$ is known as lowering of vapour pressure)

$$\mathbf{\frac{P^o_A - P_A}{P^o_A} = X_B} \quad \left(\frac{P^{\circ}_A - P_A}{P^{\circ}_A} \text{ is called relative lowering of vapour pressure, } \mathbf{(RLVP)} \right) \quad .....(3)$$

Therefore, Raoult's law states that the relative lowering of vapour pressure $\left(\frac{P^\circ_A - P_A}{P^\circ_A}\right)$, for a non-volatile solute is equal to the mole fraction of the solute when the solvent alone is volatile.

***Illustration 4:** The vapour pressure of pure water at 37°C is 47.1 torr. What is the vapour pressure of an aqueous solution at 37°C containing 20 g of glucose dissolved in 500 gm of water. Also calculate vapour pressure lowering.*

Solution: $n_{H_2O} = \frac{500}{18} = 27.78\,\text{mol}$, $n_{(glucose)} = \frac{20}{180} = 0.11\,\text{mol}$

$$X_{H_2O} = \frac{n_{H_2O}}{n_{H_2O} + n_{(glucose)}} = \frac{27.78}{27.78 + 0.11} = \frac{27.78}{27.89} = 0.996$$

According to Raoult's law,

$$P_{H_2O} = P^o_{H_2O} X_{H_2O} = 47.1 \times 0.996 = 46.9\,\text{torr}$$

Vapour pressure of solution

$$P^o_{H_2O} - P_{H_2O} = 47.1 - 46.9 = 0.2\,\text{torr}$$

Lowring of vapour pressure

5. ***The vapour pressure of ethyl alcohol at 25°C is 59.2 torr. The vapour pressure of a solution of urea in ethyl alcohol is 51.3 torr. What is the molality of the solution?***

Solution: Given: $P_A^o = 59.2$ torr, $pA = 51.3$ torr

By RLVP ⇒ $X_{solute} = \frac{7.9}{59.2} = .1334$

$\because$ (molality) $m = \frac{X_B}{X_A} \times \frac{1000}{M_{solvent}} = \frac{X_B}{(1-X_B)} \times \frac{1000}{M_{solvent}}$ $\quad (\because X_A + X_B = 1)$

$m = \frac{0.1334}{0.8666} \times \frac{1000}{46} = 3.346$ molal

6. ***Calculate relative lowering of vapour pressure of 0.161 molal aqueous solution.***

Solution : we know Molality = $\frac{X_B \times 1000}{(1-X_B) \times m_{solvent}}$ $\Rightarrow 0.161 = \frac{X_B \times 1000}{(1-X_B) \times 18}$

$X_A = 0.00289 \Rightarrow$ RLVP $= X_A = 0.00289$

(ii) Vapour Pressure of a Solution Containing Two Volatile Liquids

Raoult's law states that the partial vapour pressure of a component of a solution of two miscible liquids A and B at a given temperature is equal to the product of the vapour pressure of the pure component at that temperature and its mole fraction in the solution.

Mathematical Expression: Let us assume that a solution has n_A moles of liquid A and n_B moles of liquid B. Let P_A be the vapour pressure of the pure liquid A and P_B is the vapour pressure of the pure liquid B.

Mole fraction of A, $X_A = \dfrac{n_A}{n_A + n_B}$, Mole fraction of B, $X_B = \dfrac{n_B}{n_A + n_B}$

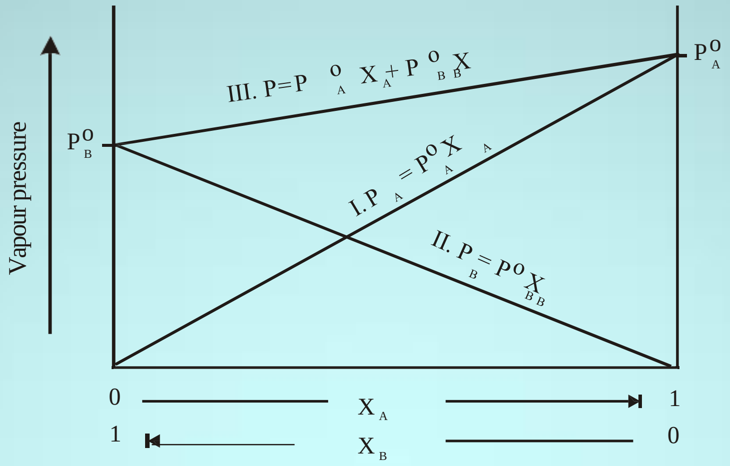
According to Raoult's law,

$P_A = P^\circ_A X_A$ (where P_A is the partial vapour pressure of liquid A in the solution)

Similarly, $P_B = P^\circ_B X_B$ (P_B - partial vapour pressure of B in the solution)

The total vapour pressure of an ideal solution containing components A and B is the sum of partial vapour pressures of all the components (Dalton's law of partial pressures)

$$\mathbf{P = P_A + P_B = P^0_A X_A + P^0_B X_B} \qquad ......(1)$$



$\because\ X_A + X_B = 1 \quad \Rightarrow \quad X_A = 1 - X_B$

$\therefore \quad P = P^o_A(1 - X_B) + P^o_B X_B \quad \Rightarrow \quad P^o_A - P^o_A X_B + P^o_B X_B$

$\mathbf{P = P^o_A + (P^o_B - P^o_A)X_B}$ ......(2)

About relation shows that graph between P and XB is a straight line having slope $\mathbf{P^o_B - P^o_A}$ and intercept $\mathbf{P^o_A}$

Similarly $\mathbf{P = P^o_B + (P^o_A - P^o_B)X_A}$ ....(3)

Above figure shows the relationship between partial vapour pressure and mole fraction of an ideal solution at constant temperature.

1. Straight line I represents the plot of vapour pressure of liquid A (P_A) and its mole fraction (X_A). According to Raoult's law this should be a straight line when

   $X_A = 0 \quad P_A = 0, \qquad X_A = 1, \quad P_A = P^o_A$

   When mole fraction of liquid A is $X_A = 1$, the liquid A is pure and its vapour pressure is equal to P^o_A as shown by line (I)

2. Straight line II represents the plot of partial vapour pressure of liquid (B) P_B and its mole fraction (X_B). According to Raoult's law, this should be a straight line. when

   $X_B = 0 \quad P_B = 0, \qquad X_B = 1, \quad P_B = P^o_B$

   When mole fraction of liquid B is $X_B = 1$, the liquid B is pure and its vapour pressure is equal to P^o_B as shown by line (II).

3. Straight line (III) represents the total vapour pressure, P, of the solution for any composition and is given by the sum of the partial vapour pressure of liquids of A and B.

$$P = P_A + P_B$$

7. An aqueous solution containing 28% by mass of a liquid A (mol. mass = 140) has a vapour pressure of 160 mm at 37ºC. Find the vapour pressure of the pure liquid A. (The vapour pressure of water at 37ºC is 150 mm.)

Solution : For two miscible liquids,

$$P_{total} = P_A + P_B = P^o_A X_A + P^o_B X_B \qquad n_A = \frac{28}{140} = 0.2,$$

Liquid B is water. Its mass is (100–28), i.e. 72. Total number of moles = 0.2 + 4.0 = 4.2

$$n_B = \frac{72}{18} = 4.0$$

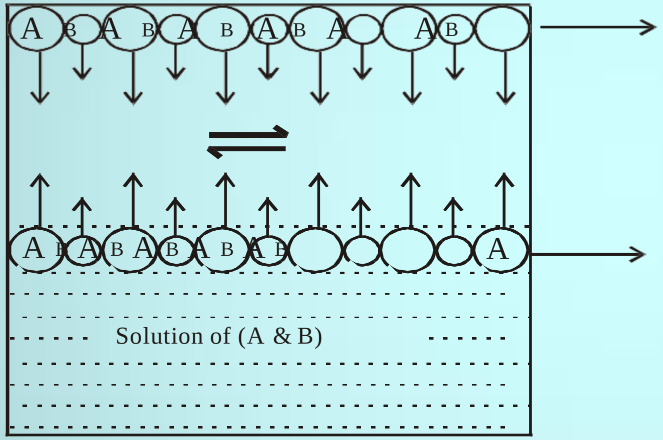
Given $P_{total} = 160$ mm, $P^0_B = 150$ mm

So $$160 = \frac{0.2}{4.2} \times P^0_A + \frac{4.0}{4.2} \times 5.0$$

$$p^0_A = \frac{17.15 \times 4.2}{0.2} = 360.15\text{mm}$$

Dalton’s Law v/s Raoult’s Law:

The composition of the vapour in equilibrium with the solution can be calculated applying Daltons’ law of partial pressures. Let the mole fractions of vapours A and B be Y_A and Y_B respectively. Let p_A and p_B be the partial pressure of vaours A and B respectively and total pressure P.



vapours (Dalton's law)
y_A = more fraction of A in vapour phase
y_B = more fraction of B in vapour phase

$(Y_A + Y_B = 1)$

solution (Raoult's law)
X_A = more fraction of A in liquid phase
X_B = more fraction of B in liquid phase

$(X_A + X_B = 1)$

From Raoult's law $P = P^o_A X_A + P^o_B X_B$

$P_A = P^o_A X_A$ and $P_B = P^o_B X_B$

From Dalton's law,

Partial pressure = Mole fraction × Total pressure For A

$$P_A = y_A \times P$$

$$P^o_A X_A = y_A \times P \quad \Rightarrow \mathbf{y_A} = \frac{\mathbf{P^o_A X_A}}{\mathbf{P}} \qquad .....(1)$$

Above formula is used for calculation of mole fraction of A in vapour phase For B,

$$P_B = y_B \times P$$

$$P^o_B X_B = y_B \times P \quad \Rightarrow \mathbf{y_B} = \frac{\mathbf{P^o_B X_B}}{\mathbf{P}} \qquad .....(2)$$

Above formula is used for calculation of mole fraction of B in vapour phase

From (1) , $X_A = \frac{P \times y_A}{P^o_A}$ From (2) $X_B = \frac{P \times y_B}{P^o_B}$

on adding $X_A + X_B = \frac{P \times y_A}{P^o_A} + \frac{P \times y_B}{P^o_B} = 1$

$$\Rightarrow \frac{\mathbf{1}}{\mathbf{P}} = \frac{\mathbf{y_A}}{\mathbf{P^o_A}} + \frac{\mathbf{y_B}}{\mathbf{P^o_B}} \qquad .....(3)$$

Above formula is used to calculate total vapour pressure when mole fractions are given in vapoure phase

Avoid confusion

$P = P^{o}_{A}X_{A} + P^{o}_{B}X_{B}$ ⇒ This formula is used to calculate total pressure when mole fraction are given in liquid phase

$\frac{1}{P} = \frac{y_A}{P^o_A} + \frac{y_B}{P^o_B}$ ⇒ This formula is used to calculate total pressure when mole fraction are given in vapour phase

Note: Thus, in case of ideal solution the vapour phase is phase is richer with more volatile component i.e., the one having relatively greater vapour pressure.

8. The vapour pressures of ethanol and methanol are 44.5 mm and 88.7 mm Hg respectively. An ideal solution is formed at the same temperature by mixing 60 g of ethanol with 40 g of methanol. Calculate the total vapour pressure of the solution and the mole fracion of methanol in the vapour.

Solution: No. of moles of $C_2H_5OH = \frac{60}{46} = 1.304$, No. of moles of $CH_3OH = \frac{40}{32} = 1.25$

'X_A' of ethyl alcohol = $\frac{1.304}{1.304+1.25} = 0.5107$

'X_B' of methyl alcohol = $\frac{1.25}{1.304+1.25} = 0.4893$

Partial pressure of ethyl alcohol = $X_A.P_A^0 = 0.5107 \times 44.5 = 22.73$ mm Hg

Partial pressure of methyl alcohol = $X_B.P_B^0 = 0.4893 \times 88.7 = 43.40$ mm Hg

Total vapour pressure of solution = 22.73 + 43.40 = 66.13 mm Hg

Mole fraction of methyl alcohol in the vapour = $\frac{\text{Partial pressure of } CH_3OH}{\text{Total vapour pressure}}$

$$= \frac{43.40}{66.13} = 0.6563$$

(i) Ideal Solution

An ideal solution may be defined as the one which obeys Raoult’s law over all concentration ranges at a given temperature. The total vapour pressure of an ideal solution containing liquids A and B is given by the following equation.

$$P_A = P_B + P_A = P_A^o X_B + P_B^o X$$

benzene + toluene,
ethyl bromde + ethyl iodide; ethyl alcohol + methyl alcohol

chlorobenzene + bromobenzene;
n-butyl chloride + n-butyl bromide

Energy Changes and Solution Formation

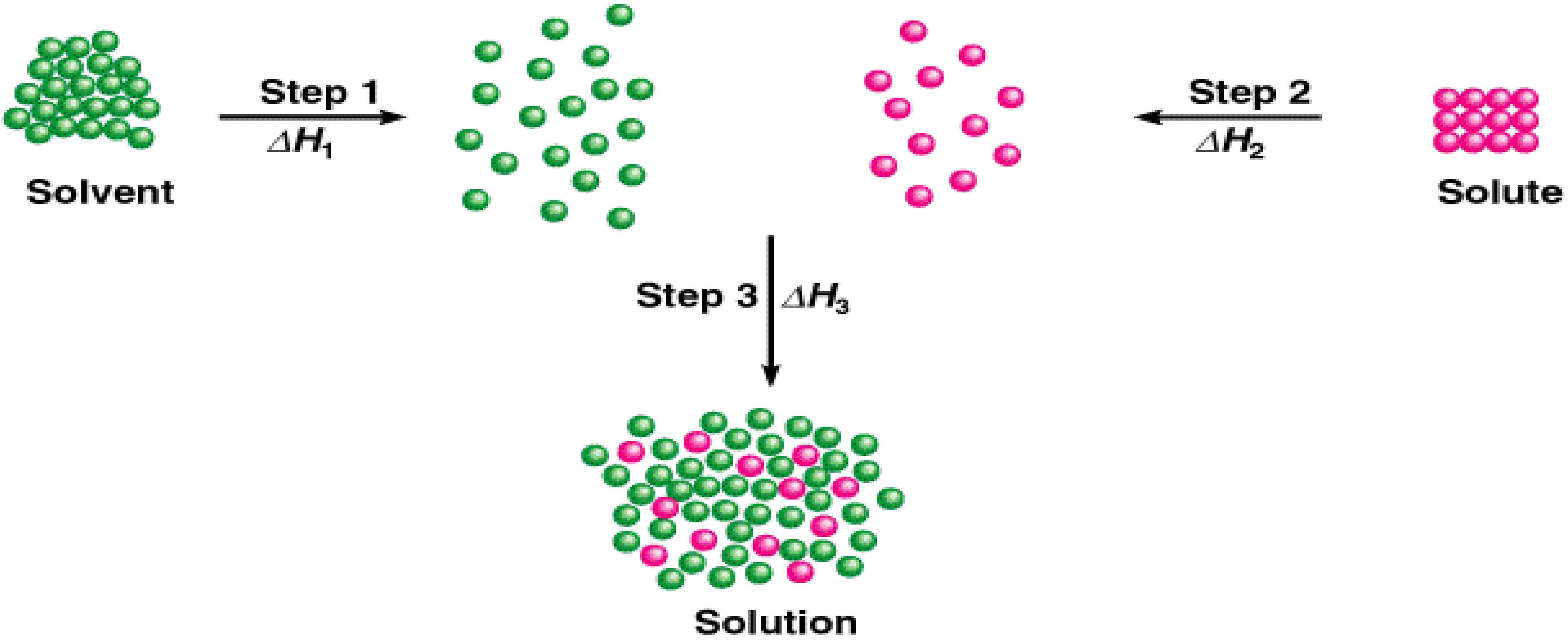
3 energy steps in forming a solution:

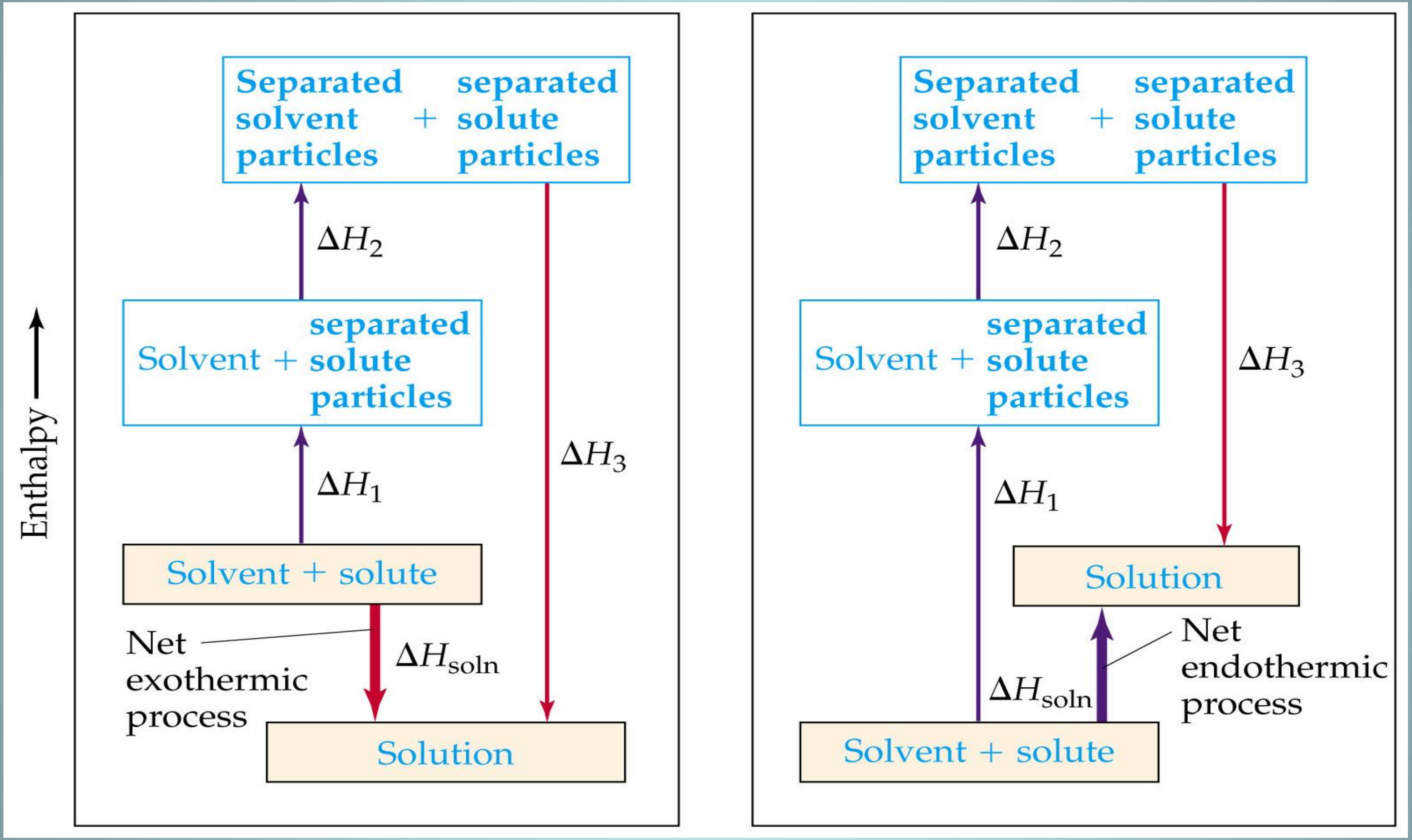
- separation of solute molecules ($\Delta H1$),
- separation of solvent molecules ($\Delta H2$), and
- formation of solute-solvent interactions ($\Delta H3$).

$$\Delta H_{soln} = \Delta H_1 + \Delta H_2 + \Delta H_3.$$

- ΔH_{soln} can be +ve or -ve depending on the intermolecular forces.

Molecular View of the Solution Process




Enthalpy
Separated solvent particles + separated solute particles
ΔH_2
Solvent + separated solute particles
ΔH_1
ΔH_3
Solvent + solute
Net exothermic process
ΔH_{soln}
Solution
Separated solvent particles + separated solute particles
ΔH_2
Solvent + separated solute particles
ΔH_3
ΔH_1
Solution
Net endothermic process
ΔH_{soln}
Solvent + solute

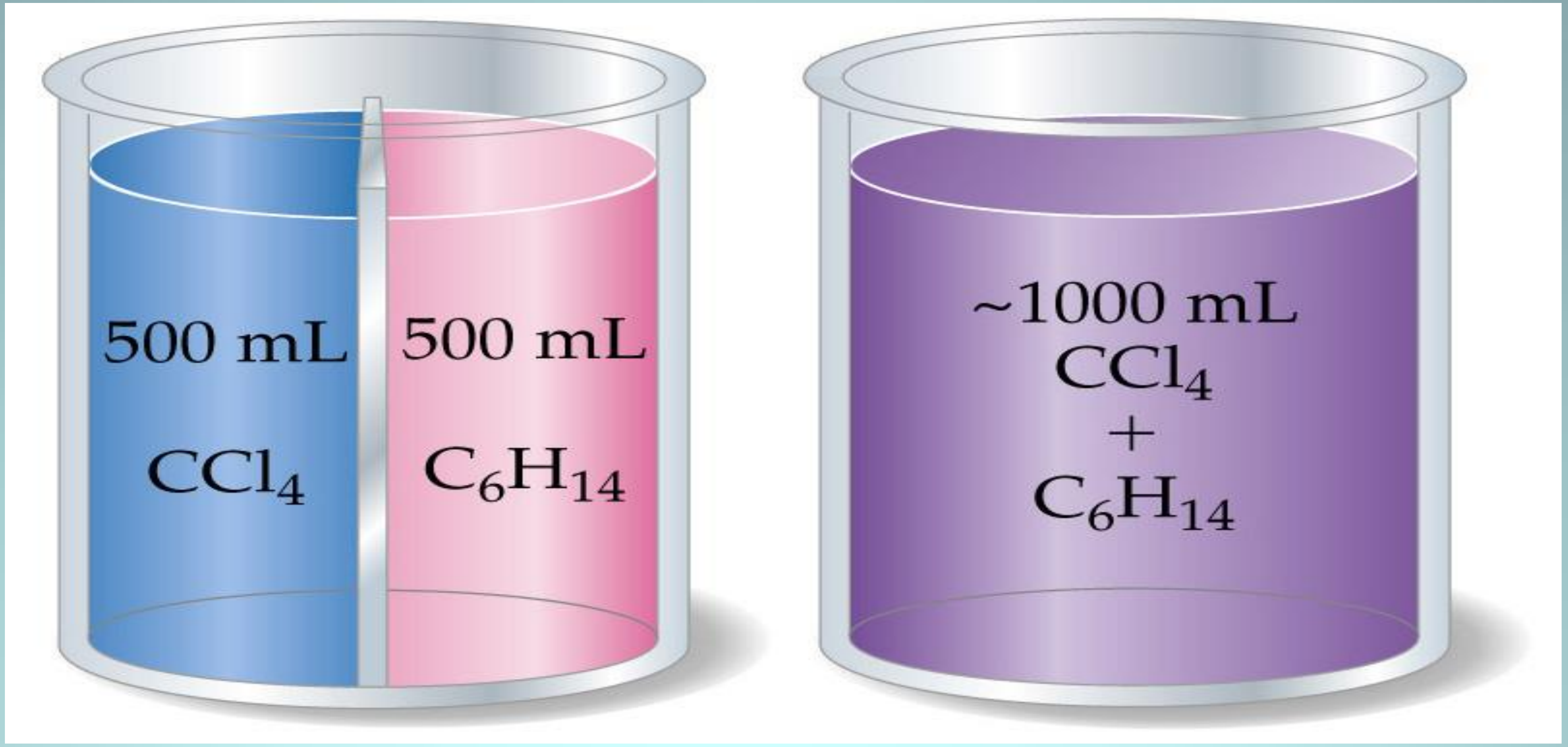
Conditions for Forming Ideal Solution: Two liquids on mixing form an ideal solution only when

1. both have similar structures and polarity so that they have similar molecular environment.
2. both have similar molecular sizes.
3. both have identical intermolecular forces.

Characteristics Of Ideal Solution:

Mixing of two substances results in an ideal solution only when:

1. They obey Raoult's Law
2. $\Delta H_{mixing} = 0 \Rightarrow$ that is no heat is absorbed or released during dissolution
3. $\Delta V_{mixing} = 0 \Rightarrow$ that is the total volume of the solution is equal to the sum of the volume of the pure liquids mixed to form the solution.

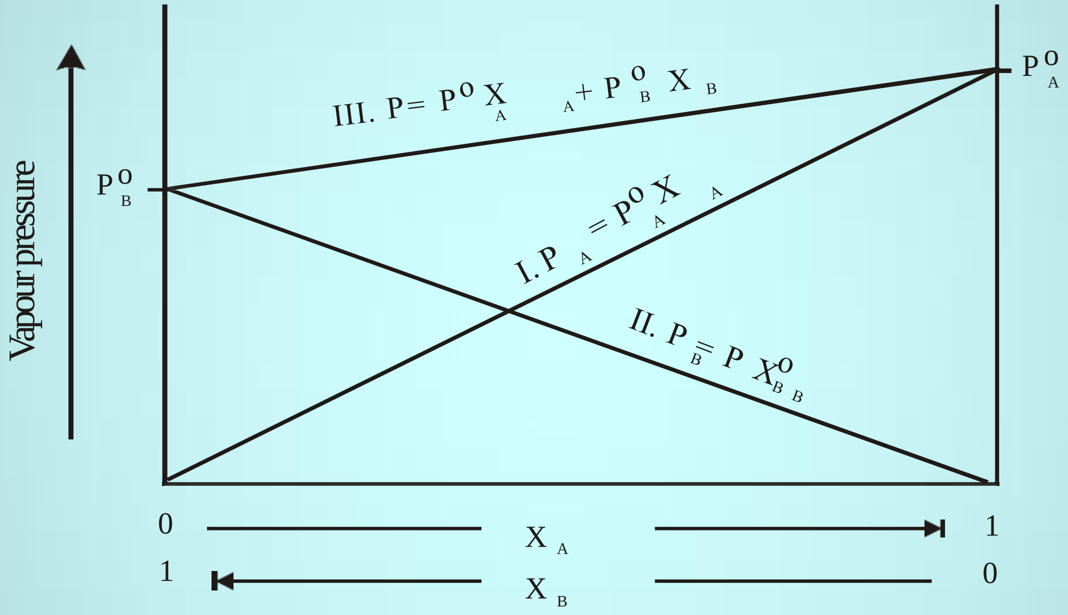


- Ideal solution - obeys Raoult's law
- Raoult's law is to solutions what the ideal gas law is to gases
- Raoult's law breaks down when the solvent-solvent and solute-solute intermolecular forces are greater than solute-solvent intermolecular forces
- For liquid-liquid solutions where both components are volatile, a modified form of Raoult's law applies:

$$P_{total} = P_A + P_B = X_A P^o{}_A + X_B P^o{}_B$$

Graphical Representation of Vapour Pressure of Ideal Solutions:

Figure shows the relationship between partial vapour pressure and mole fraction of an ideal solution at constant temperature.



Note : Components of ideal solution can be saperated in pure form by fractional distillation

(ii) Non-Ideal Solutions

Solutions which do not obey Raoult’s law over all concentration ranges at constant temperature are called non-ideal solutions.

Characteristic of nonideal solution

(i) $P_A \neq P^o_A X_A + P_B \neq P^o_B X_B$, $P \neq P^o_A X_A + P^o_B X_B$

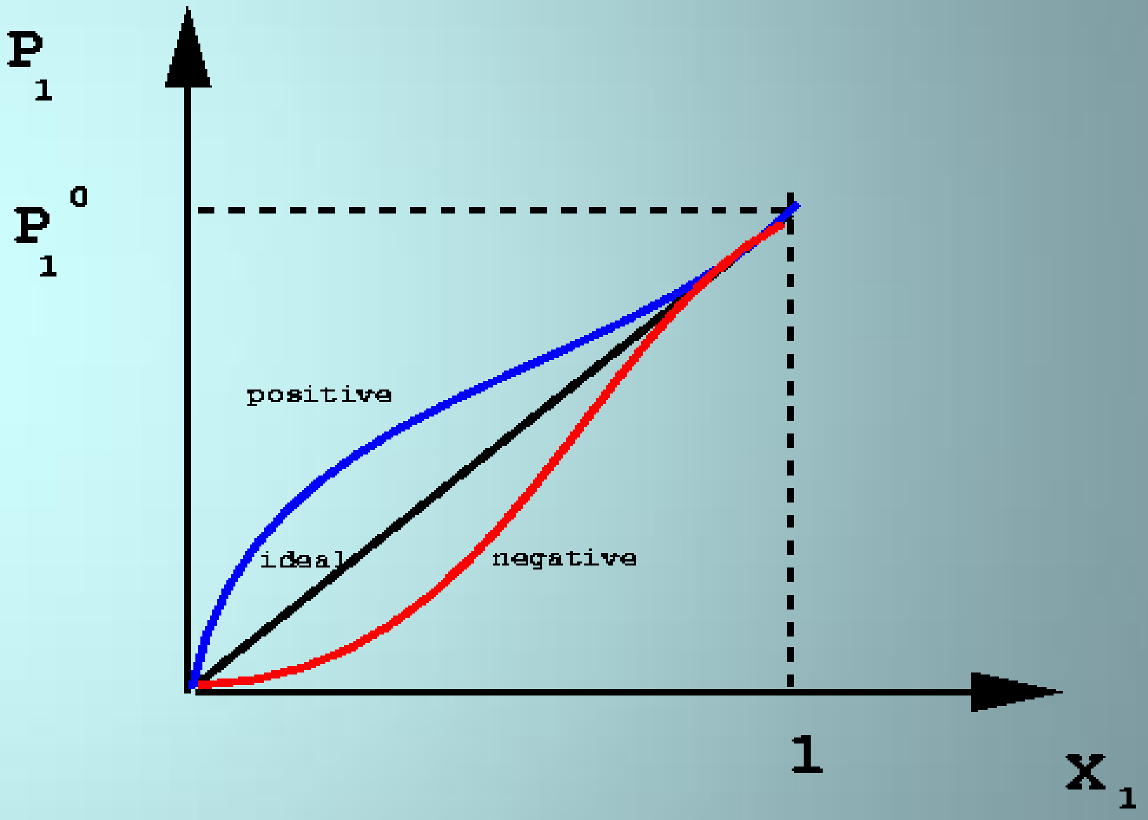
(ii) $\Delta V_{mix} \neq 0$,

(iii) $\Delta H_{mix} \neq 0$

Types of Non-Ideal Solutions

1. Non ideal solutions showing +ve deviation
2. Non ideal solutions showing –ve deviation.

1. Non ideal solutions showing +ve deviation



Condition for forming non-ideal solution showing +ve deviation from Raoult's law.

Tow liquids A and B on mixing form this type of solution when

1. A—B attractive force should be weaker than A—A and B—B attractive forces.
2. 'A' and 'B' have different shape, size and charater.
3. 'A' and 'B' escape easily showing higher vapour pressure than the expected value.

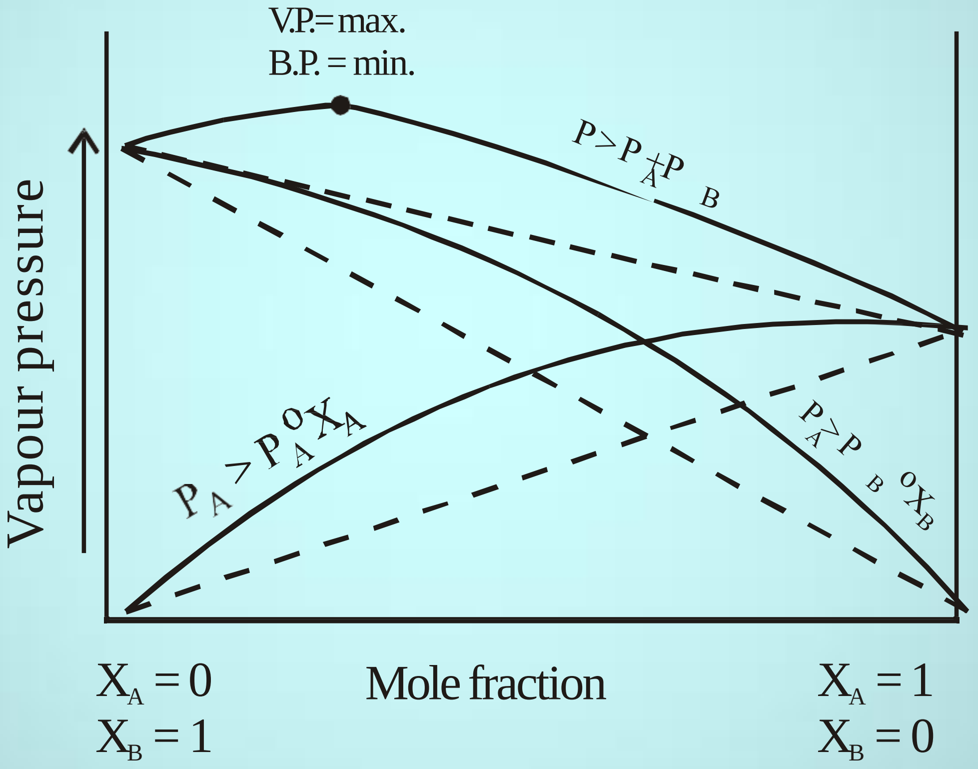
Characteristic of non-ideal solution showing +ve deviation

1. Do not obey Raoult's law
2. $\Delta H_{mix} > 0$. (endothermic dissolution heat is absorbed.)
3. ΔV mix > 0. (Volume is increased after dissolution)
4. $p_B > p_B^0 X_B$; $p > p^o X_A$, $_B \therefore p_A + p_A > p^o X_B + _B p^o X$ A A A

Example :

acetone + ethanol acetone + CS_2 water + methanol; water + ethanol; CCl_4 + toluene; $CCl_4 + CHCl_3$; acetone + benzene; CCl_4 + CH_3OH; cyclohexane + ethanol

Graphical representation of vapour of non-ideal solution showing +ve deviation



2. Non ideal solutions showing –ve deviation.

Condition for forming non-ideal solution showing +ve deviation from Raoult’s law.

Two liquids A and B on mixing form this type of solution when

1. A—B attractive force should be greater than A—A and B—B attractive forces.
2. ‘A’ and ‘B’ have different shape, size and character
3. Escaping tendency of both components ‘A’ and ‘B’ is lowered showing lower vapour pressure than expected ideally.

Characteristic of non-ideal solution showing +ve deviation

1. Do not obey Raoult’s law.
2. $\Delta H_{mix} < 0$. (Exothermic dissolution; heat is evolved.)
3. $\Delta V_{mix} < 0$. (Volume is decreased during dissoluton)
4. $p_A < P_A^0 X_A$; $p_B < p_B^0 X_B$; $\therefore p_A + p_B < p_A^o X_A + p_B^o X_B$

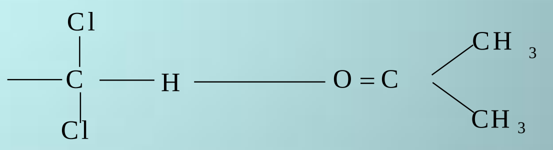
Example

acetone + aniline; chlorofrom + diethyl ether,

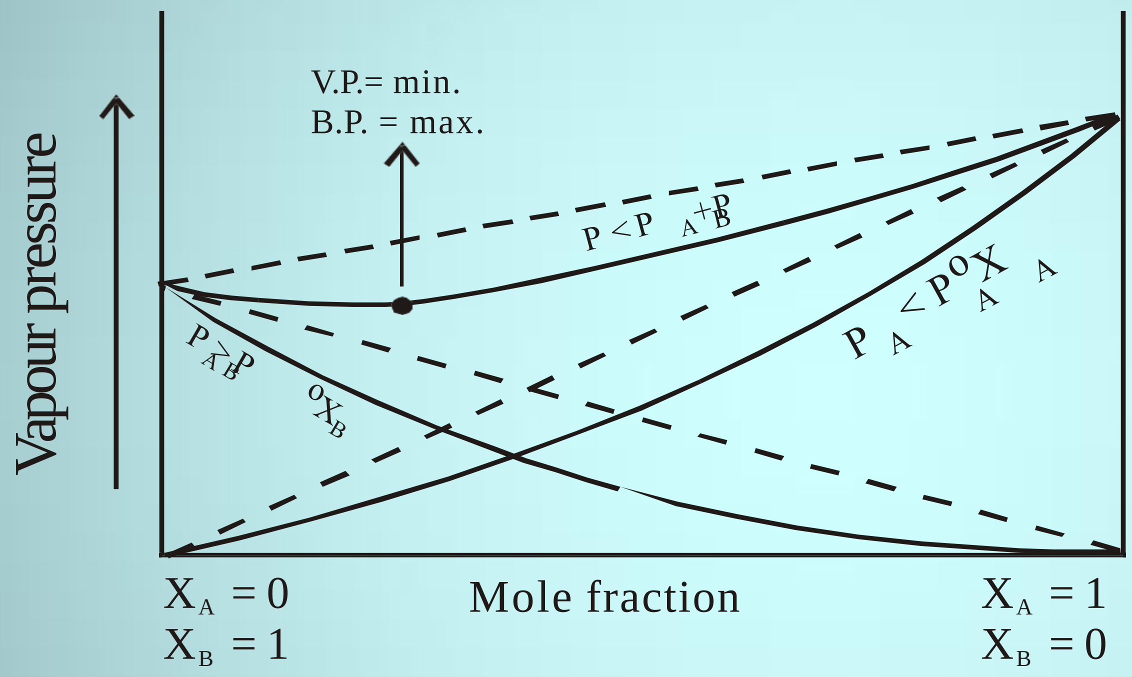
$CH_3OH + CH_3COOH$; acetic acid + pyridine;

chloroform + benzene

$H_2O + HNO_3$; water + HCl acetone + chloroform; C l



Graphical representation of vapour of non-ideal solution showing +ve deviation



(iii) Azeotropes

The non-ideal solution showing large deviations from Raoult’s law can not be purified by distillation. A solution at certain composition which continues to boil at constant temperature without change in the composition of the solution and its vapour is called an AZEOTROPE or constant boiling mixture. Azeotropes are of two types:

1. **Azeotropes with Max. vapour pressure and Min. BP :** When liquid in a solution do not have great chemical affinity for each other (+ve deviation from ideality) their higher escape tendencies increase the vapour pressure much more than expected on the basis of Raoult’s law. In many cases, the deviations are so extreme as to lead to a maximum in the curve. The point of maximum vapour pressure means that the bp at this composition will be minimum and constant.

Example of Minimum Boiling Azeotrope

Components			**Boiling point (K)**		
A	**B**	**Mass% of B**	**A**	**B**	**Azeoterope**
H_2O	C_2H_5OH	95.57	373	351.3	351.10
H_2O	C_3H_7OH	71.69	373	370.0	350.72
$CHCl_3$	C_2H_5OH	67.00	334	351.3	332.30

2. **Azeotropes with Min. vapour pressure and Max. bp :** When liquids in solution form chemical bonds (–ve deviation from ideality), their escape tendencies and hence the vapour pressure decreases than expected on the basis of Raoult's law. In many cases, the maximum in the temperature composition curve is obtained. The point of minimum vapour pressure in the curve means that the bp of this composition will be max. and constant.

Examples of Max. Boiling Azeotrope

Components			**Boiling point (K)**		
A	**B**	**Mass% of B**	**A**	**B**	**Azeoterope**
H_2O	HCl	20.3	373	188	383
H_2O	HNO_3	58.0	373	359	393.5
H_2O	$HClO_4$	71.6	373	383	476

Colligative Properties

- Colligative properties - depend only on the number of particles in solution and not on their identity.
- So $NaCl(s) \rightarrow Na^{+}(aq) + Cl^{-}(aq)$
- $K_2SO_4(s) \rightarrow 2K^{+}(aq) + SO_4^{2-}(aq)$
- $C_{12}H_{22}O_{11}(s) \rightarrow C_{12}H_{22}O_{11}(aq)$

Type of colligative properties

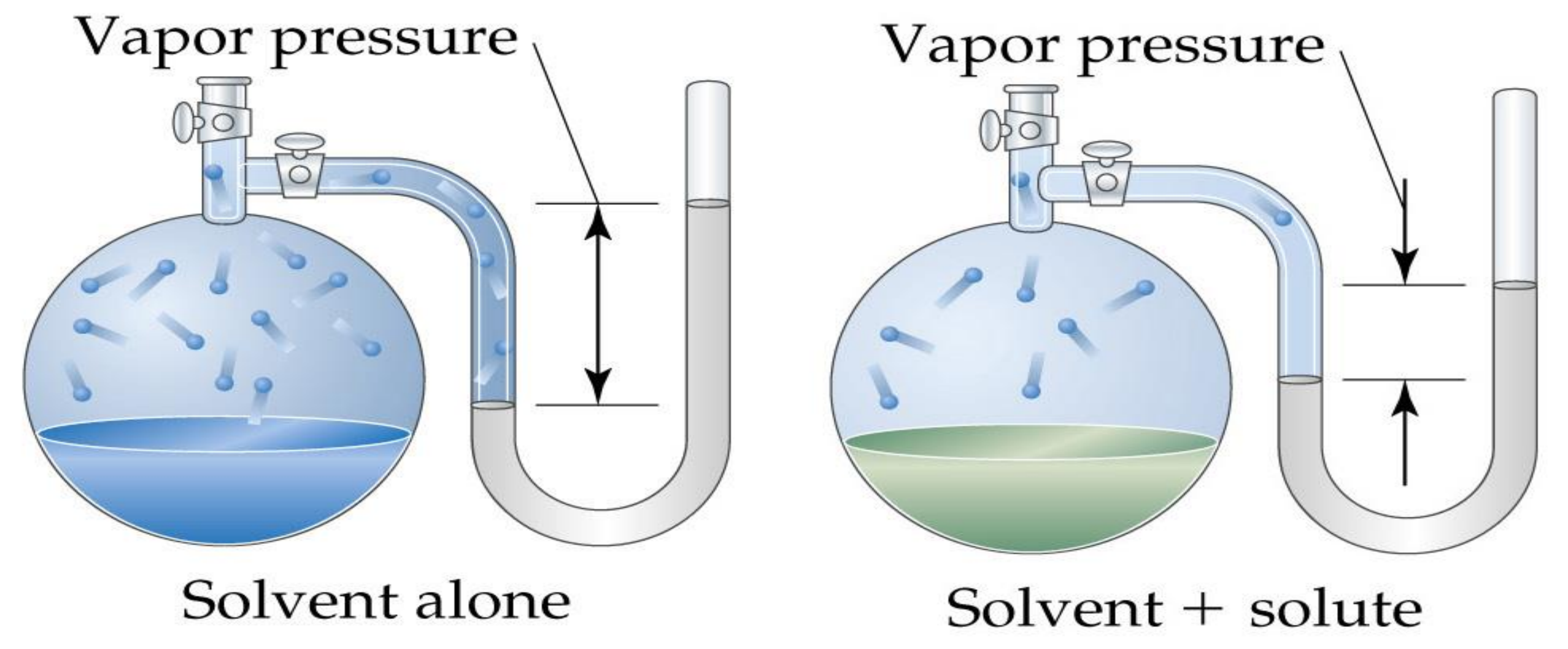
(i) Lowering of vapour pressure (ii) Elevation of Boiling point
(iii) Depression of Freezing point (iv) Osmotic Pressure

Factors that Affect the Colligative Property: The no. of solute particles in solution.

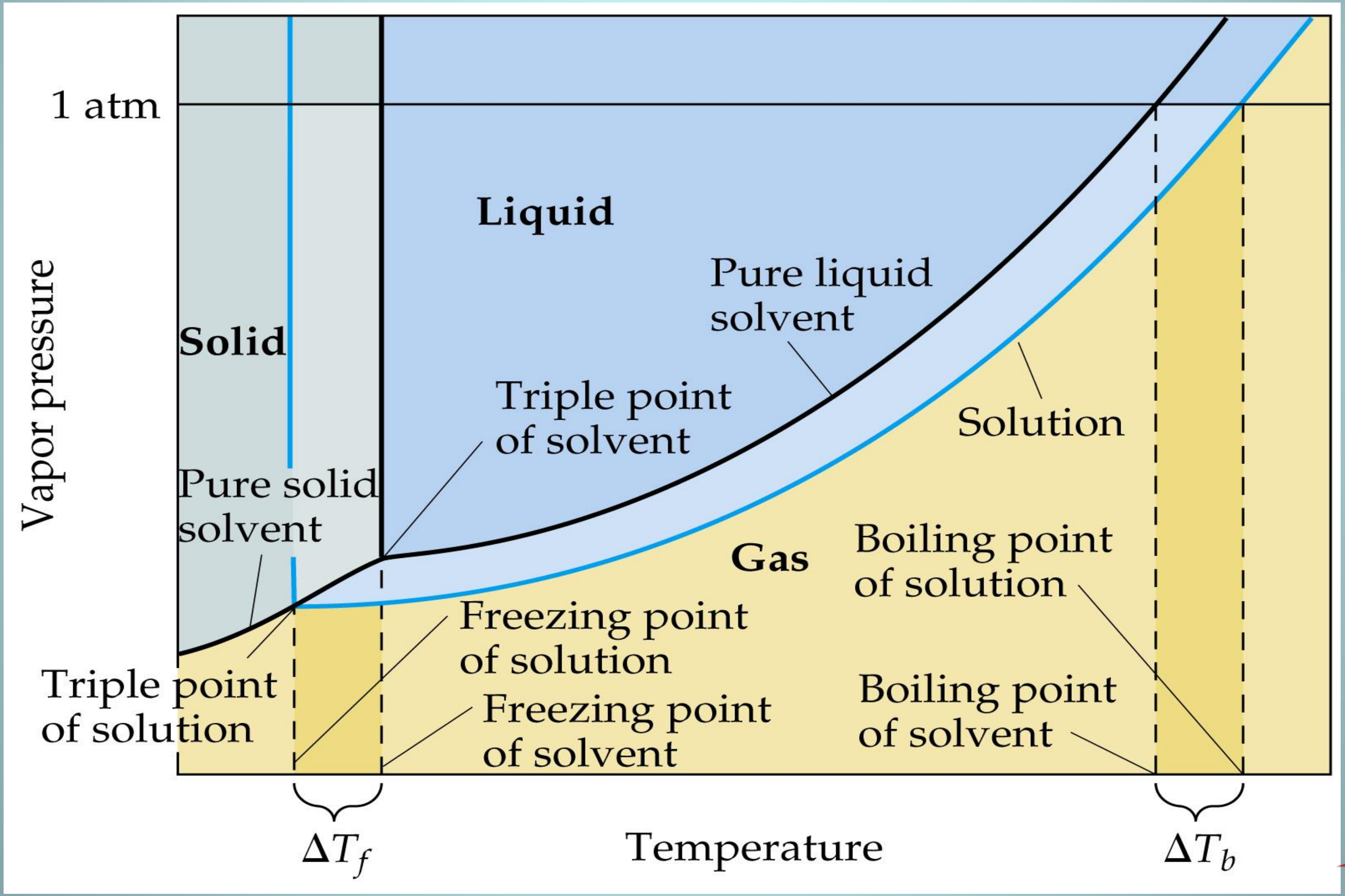
(1) Nature of the solvent
(2) Independent of the nature of the solute
(3) Extent of association and dissociation of solute particles in solution.

(i) Lowering of Vapour Pressure: Vapour pressure lowering of a solution has already been explained under Raoult' Law. It was derived that the relative lowering of vapour pressure is given by the equation

$$\frac{P_A^o - P_A}{P_A^o} = X_B = \frac{n_B}{n_A + n_B}$$



(ii) Elevation of Boiling Point: The boiling point of a liquid is the temperature at which its vapour pressure becomes equal to the atmospheric pressure. When the atmospheric pressure is 1 atm, boiling point is called the normal boiling point.



The vapour pressure of a liquid decreases when a non-volatile solute is dissolved in it. The decreased vapour-pressure means that the solution would have to be heated to a higher temperature so that its vapour pressure becomes equal to the atmospheric pressure. In other words, the boiling point of the solution T_b is higher than the boiling point of the pure solvent T_b^0. The difference $T_b^s -$ T_b^0 is called the boiling point elevation and denoted by ΔT_b.

$$\mathbf{\Delta T_b = T_b - T_b^0} \qquad ......(1)$$

$$\Delta T \propto m \quad \Rightarrow \quad \mathbf{\Delta T = K_b . m_b} \qquad ......(2)$$

.

Molal Elevation Constant or Ebullioscopic Constant: When molality of the solution is 1m, (1 mole of the solute is dissolved in 1 kg of the solvent) the above equation reduces to

$$\Delta T_b = K_b \times 1m = K_b$$

This indicates that molal elevation constant of a liquid (K_b) is equal to elevation of boiling point when molality of the solution is 1 m. the unit of K_b is Km_{-1}. K $(mol/kg)_{-1}$ = K kg mol_{-1}.

Determination of K_b of solvent :

$$K_b = \frac{RT_b^2}{1000L_v} \qquad ....(3)$$

where R is molar gas constant, T_b is the boiling point of the solvent on Kelvin scale and L_v the latent heat of vaporization of solvent in calories per gram.

For water $K_b = \frac{2\times(373)^2}{1000\times540} = 0.515$ K-kg/mol

Illustration 9. Estimate the boiling point of a solution of 25.0g of urea NH_2CONH_2 plus 25.0g of thiourea NH_2CSNH_2 in 500g of chloroform, $CHCl_3$. The boiling point of pure chloroform is 61.2°C, K_b of chloroform = 3.63 Km^{-1}.

Solution: Moles of urea $= \frac{\text{Mass of urea}}{\text{Molecular mass of urea}} = \frac{25.0g}{60g/mol} = 0.42mol$

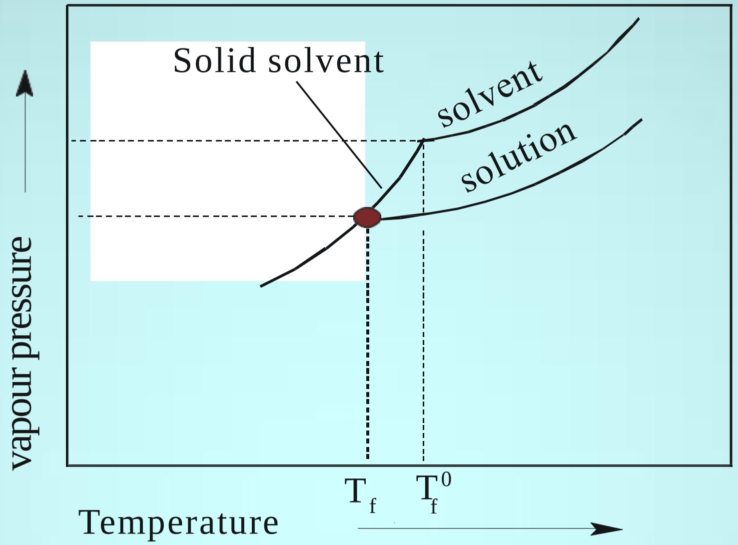
Moles of thiourea $= \frac{25.0}{76\ g/mol} = 0.33mol$ $\qquad \therefore$ Total moles of solute = 0.42 + 0.33 = 075

$$\text{Molality, m} = \frac{\text{Moles of solute}}{\text{Mass of solvent in kg}} = \frac{0.75\text{mol}}{(500\text{g}/1000\text{g})\text{kg}} = 1.50\text{m}$$

$$\Delta T_b = T_b - T_b^0 = K_b \cdot m \quad = 3.63 \times 1.50 \quad = 5.44\text{K} \quad = 5.445°\text{C}$$

$$T_b = 5.445°\text{C} + T_b^0 \quad = 5.445°\text{C} + 61.2°\text{C} \quad = 66.645°\text{C}$$

(iii) Depression in Freezing Point: The freezing point of a liquid is the temperature at which it begins to freeze and the crystallized solid and liquid are in equilibrium. At freezing point, the vapour pressure of the solid is equal to the vapour pressure of the liquid. When a dilute solution is cooled to freezing point, it is assumed that crystals of pure solvent always separate out first.



Plot of variation of vapour pressure of a solution with temperature and depression in freezing point.

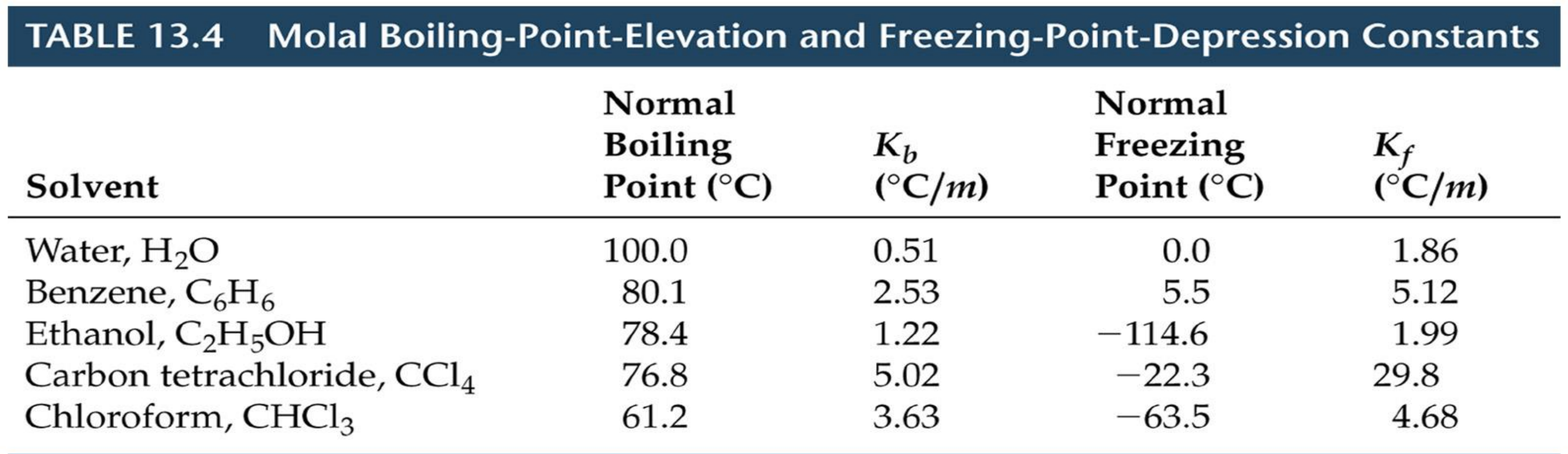


TABLE 13.4 Molal Boiling-Point-Elevation and Freezing-Point-Depression Constants

Solvent	Normal Boiling Point (°C)	K_b (°C/m)	Normal Freezing Point (°C)	K_f (°C/m)
Water, H_2O	100.0	0.51	0.0	1.86
Benzene, C_6H_6	80.1	2.53	5.5	5.12
Ethanol, C_2H_5OH	78.4	1.22	−114.6	1.99
Carbon tetrachloride, CCl_4	76.8	5.02	−22.3	29.8
Chloroform, $CHCl_3$	61.2	3.63	−63.5	4.68

$$\Delta T_f = T_f^0 - T_s \qquad ....(1)$$

$$\Delta T_f = K_f \cdot m \qquad ....(2)$$

where m is the molality of the solution and K_f is a constant for a given solvent known as molal depression constant or cryoscopic constant.

Molal Depression Constant or Cryoscopic Constant: When molality of the solution is 1m, (1 mole of the solute is dissolved in 1 kg of the solvent) the above equation reduces to

$$\Delta T_f = K_f \times 1m = K_f$$

unit: Km^{-1}. $K\ (mol/kg)^{-1} = K\ kg\ mol^{-1}$.

Determination of K_f of solvent

K_f is characteristic of a particular solvent and can be calculated from the thermodynamical relationship.

$$K_f = \frac{\square_f\ RT^2}{1000L_f} \qquad \text{......(3)}$$

where T_f is the freezing point of solvent in absolute scale and L_f the latent heat of fusion in calories per gram of the solvent. For water,

$$K_f = \frac{0.002 \times (273)^2}{80} = 1.86 \quad \text{K-kg/mole}$$

Ex. What is the percent by mass of iodine needed to reduce the freezing point of benzene to 3.5°C? The freezing point and cryoscopic constant of pure benzene are 5.5°C and 5.12 K/m respectively.

Solution: $\Delta T_f = T_f^0 - T_f = K_f \, . \, m$

$5.5°C - 3.5°C = 5.12 \times m$

$$m = \frac{2}{5.12} = 0.39 \text{ molal}$$

∴ Mass of iodine needed for 1000g of benzene = m × molecular mass of iodine I_2

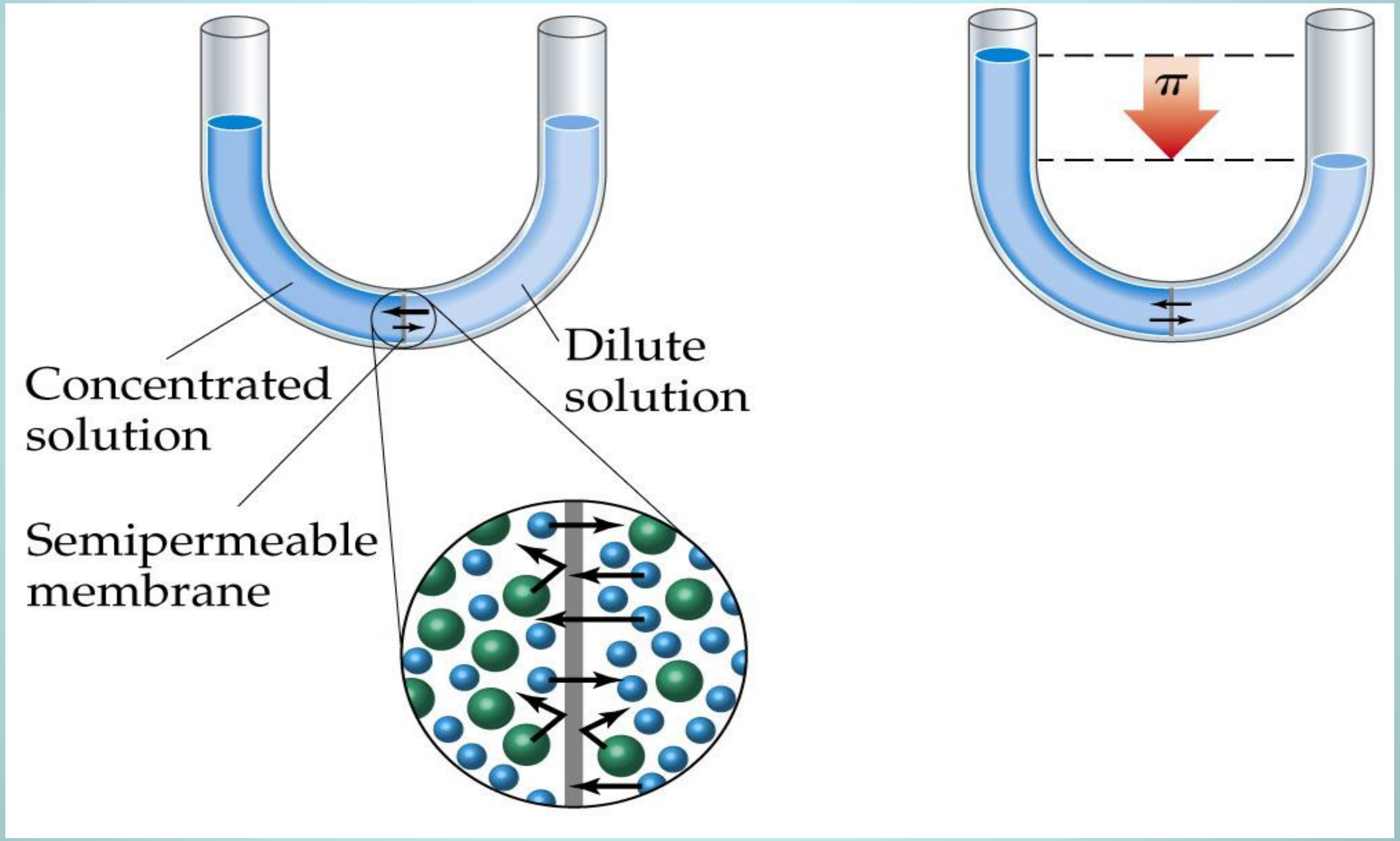
= 0.39 mol/kg × 254 g/mol = 99.06 g/kg

∴ 1000g + 99.06g solution contains 99.06g I_2

100g solution contains $\frac{99.06\text{g} \times 100}{1099.06\text{g}} = 9.01\%$

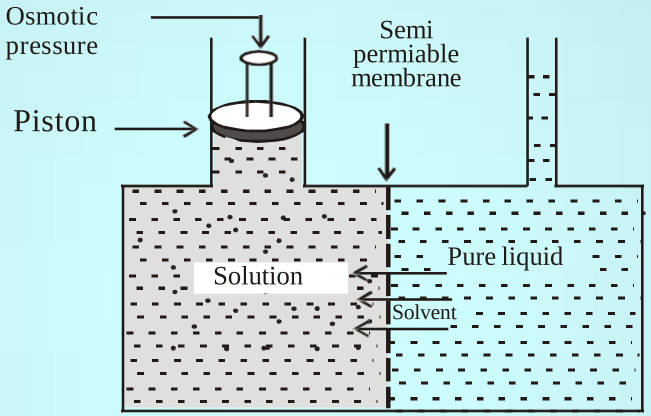
Osmosis

- Eventually the pressure difference between the arms stops osmosis.



Osmosis:

Spontaneous flow of solvent molecules through a semipermeable membrane from a pure solvent to the solution (or from a dilute solution to a concentrated solution) is termed as osmosis.



Osmotic Pressure (π):

For dilute solutions

$$\pi V = nRT$$

$$\pi = \left(\frac{n}{V}\right)RT$$

$$= CRT$$

=hρg (hydrostatic pressure)

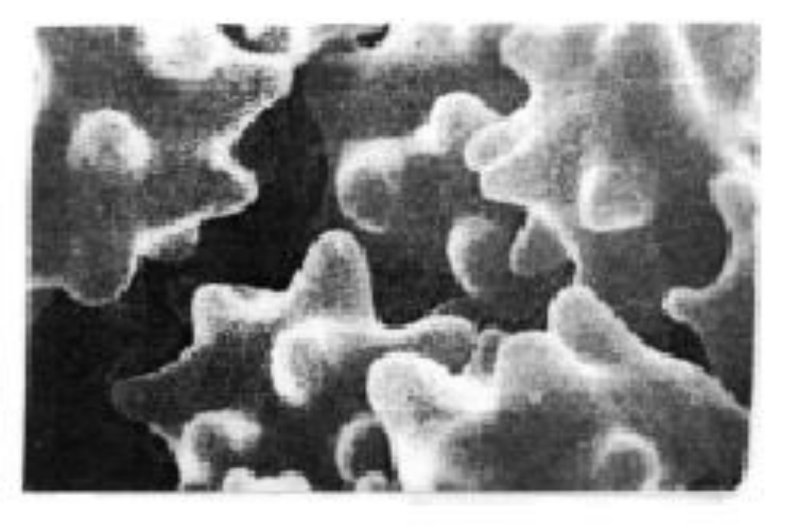
Where C is the total molar concentration of all the free species present in the solution, h is the height developed by the column of the concentrated solution and ρ is the density of the solution in the column. On the basis of osmotic pressure, *the solutions can be classified in three classes.*

(a) **Hypertonic solution:** When two solutions are being compared, then the solution with higher osmotic pressure is termed as hypertonic.

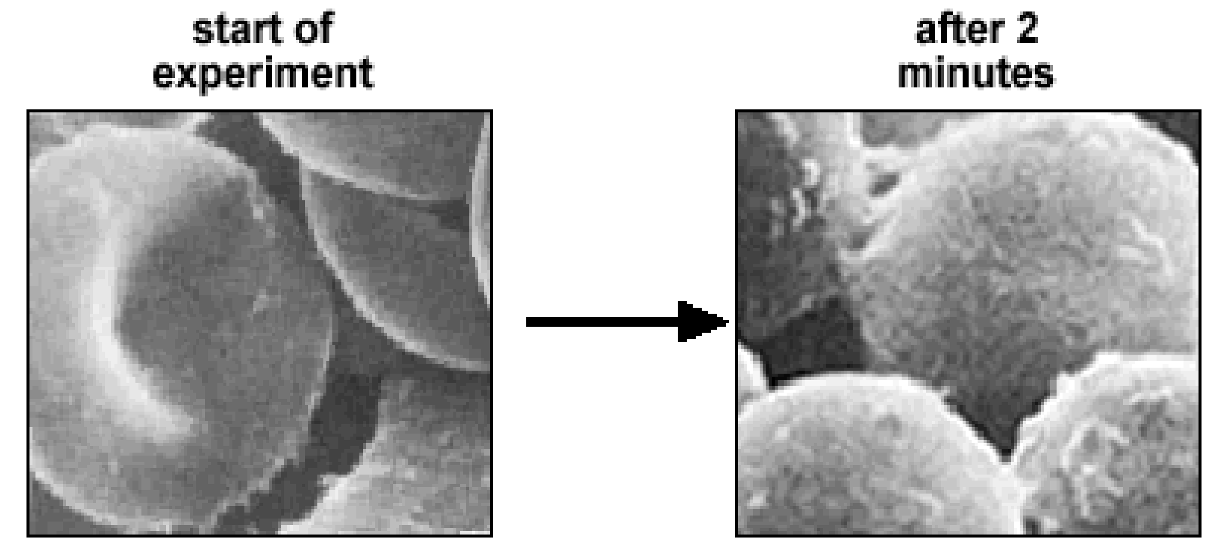
(b) **Hypotonic solution:** When two solutions are being compared, then the solution with lower osmotic pressure is termed as hypertonic.

(c) **Isotonic solutions:** Two solutions having same osmotic pressures at same temperature. (This implies $C_1 = C_2$).

Hypertonic solution

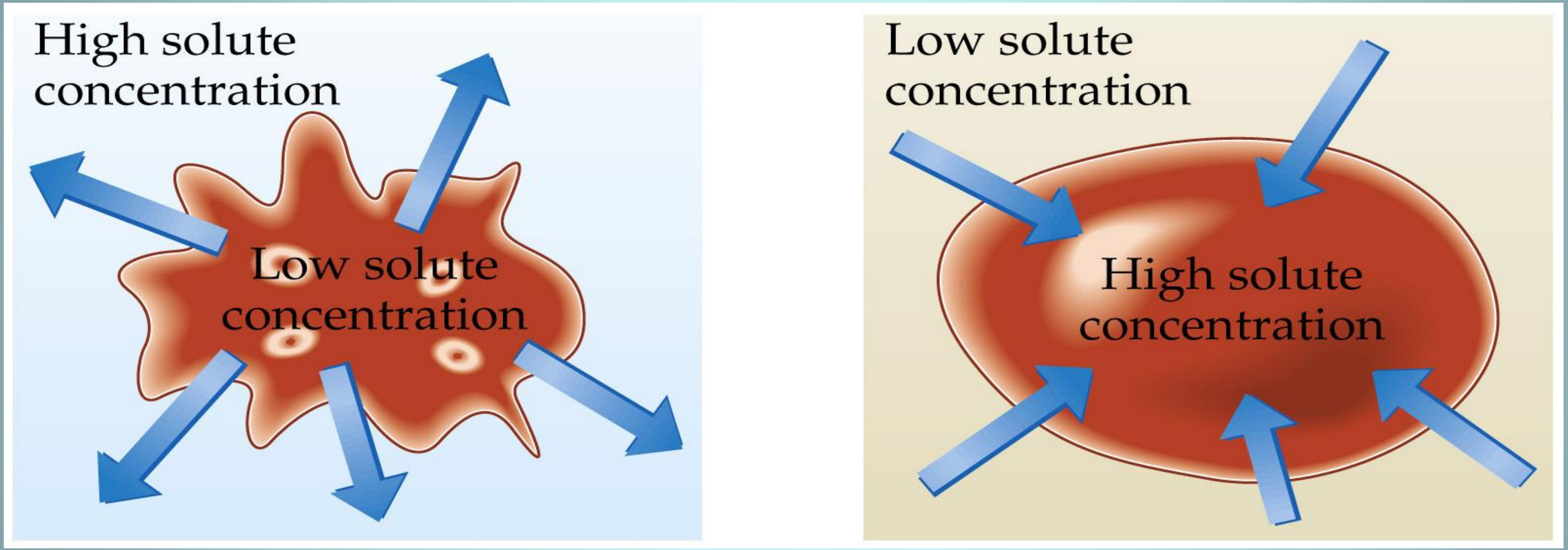


Hypotonic solution



start of experiment

after 2 minutes


High solute concentration
Low solute concentration
Low solute concentration
High solute concentration

Note:-Osmotic pressures can be determined quite accurately, hence it is used in the determination molecular weights of large proteins and similar substances.

Reverse Osmosis: If a pressure greater than the osmotic pressure is applied on the concentrated solution, the solvent starts to flow from concentrated solution to dilute solution (or pure solvent). This is reverse osmosis. One of its chief uses is desalination of sea water to get pure drinking water.

Q. Calculate osmotic pressure of 5% solution of cane sugar (sucrose) at 15ºC.

Solution: m = mol. mass of sucrose ($C_{12}H_{22}O_{11}$) = 342

$w = 5g$ V =- 100 mL = 0.1 litre
$S = 0.082,$ $T = (15 + 273) = 288$ K

Applying the equation $PV = \frac{w}{m} ST,$

$$P = \frac{5}{342} \times \frac{1}{0.1} = 0.082 \times 288 = 3.453]$$

Q 2. Consider a vertical tube of corss-sectional area of 1cm^2. The bottom of the tube is closed with a semipermeable membrane and 1 g glucose is placed in the tube. The closed end of the tube is immersed in pure water. What will be the height of the liquid level in the tube at equilibrium? The density of solution may be taken as 1g/cm^2. What is the osmotic pressure at equilibrium at 25ºC? Assume negligible depth of immersion of tube.

Solution: Let height in tube = h cm

$V = (h \times 1)\ \text{cm}^3$ ∵ Cross-sectional area = 1cm^2

$\pi V = \text{nRT}$

$$\pi \times \left(\frac{\text{h} \times 1}{1000}\right) = \frac{1}{180} \times 0.0821 \times 298$$

$$\pi = \frac{134.92}{h}\ \text{atm}$$

$$\pi = h \times d \times \text{g}$$

$$\frac{134.92}{h} = \frac{h \times 1}{100} \times \frac{9.8}{101.325}$$

1 atm = 101.325 KP$_a$

$$\text{h} = 375\ \text{cm} = 3.75\ \text{m}$$

$\pi = h \times d \times \text{g} = 3.75 \times 1 \times 9.8$ = 36.7 KP$_a$ [**Ans.** 3.75 m; 36.7 KP$_a$]

Q3. A 5% soltuion of cane sugar is isotonic with 0.877% soltuion of urea. Calculate the molecular mass of urea if molecular mass of cansugar is 342.

Solution: Let the molecular mass of urea be m_2

Molarity of sugar = $\frac{w_1}{m_1 \times V_1} = \frac{5}{342 \times 0.1}$

Molarity of urea = $\frac{w_2}{m_2 \times V_2} = \frac{0.877}{m_2 \times 0.1}$

For isotonic solutions,

$$\frac{w_1}{m_1 \times V_1} = \frac{w_2}{m_2 \times V_2} \Rightarrow \frac{5}{342 \times 0.1} = \frac{0.877}{m_2 \times 0.1}$$

$$m_2 = \frac{0.877 \times 342}{5} = 59.987$$

Vapour pressure lowering, boiling point elevation, freezing point depression and osmotic pressure are colligative properties which depend upon the fraction of solute and solvent particles in solution and not upon the chemical nature of the solute.
If solute molecules dissociates/dissociates in solution, there are more/less particles in solution and therefore, lowering of vapour pressure shows an increase/decrease effect.

$$NaCl_{(s)} \rightleftharpoons Na^{+}_{(aq)} + Cl^{-}_{(aq)}$$

$$nAB \rightleftharpoons (AB)_n$$

$$2C_6H_5COOH \rightleftharpoons (C_6H_5COOH)_2$$

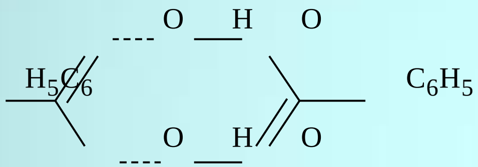
In 1886, Van’t Hoff, Jacobus Henricus (Dutch chemist, 1859,-1911) introduced a factor ‘i’ known as Van’t Hoff factor to express the extent to association or dissociation of a solute in solution.

1. **The extent of dissociation and colligative property.** A solute dissociates completely or partially in solution makes available more particles than would otherwise be present in solution and therefore, a colligative property shows an increased effect. For example, molecular masses obtained of strong acids, bases and salts are much less than their normal values. As an example, one particle of potassium chloride on dissociation in water gives two particles, K^+ and Cl^- and therefore, the molecular mass obtained by a colligative property is half of its normal molecular mass.

$$\underset{1\ \text{mol}}{K^+Cl^-_{(s)}} + nH_2O \longrightarrow \underset{1\text{mol}}{K^+_{(aq)}} + \underset{1\ \text{mol}}{Cl^-_{(aq)}}$$

2. **The extent of association and colligative property:** A solute that associates in solution provides less particles that would otherwise be present in solution and therefore, the colligative property shows the decreased effect. For example, benzoic acid in benzene is found to have molecular mass which is just twice its normalmolecular mass.

It is found that compounds which are capable of forming hydrogen bonds, e.g., phenols, carboxylic aids, alcohols: because of association show decreased effect of colligative property.



A dimer of benzoic acid

$$i = \frac{\text{number of solute particles actually present in solution}}{\text{number of solute particles dissolved}}$$

$$= \frac{\text{Observed colligative property}}{\text{normal colligative property}} = \frac{\text{observed molality}}{\text{normal molality}} = \frac{\text{normal molecular weight of solute}}{\text{observed molecular weight of solute}}$$

The Van’t Hoff factor for a solute can be calculated by the following modified equations:

(i) $\frac{P_A^0 - P_A}{P_A^0} = i X_B$ (ii) $\Delta T_f = iK_f m$ (iii) $\Delta T_b = iK_b m$ (iv) $\pi = iCRT$

where C is molarity of the solution.

Note: For non-electrolytes; $i = 1$

For electrolytes; $i > 1$ (If solute particles undergo Dissociation in the solution)

$i < 1$ (If solute particles undergo Association in the solution)

Application of Van’t Hoff Factor:

i) Calculation of Degree of Dissociation of solute particles:

$$A_n \rightleftharpoons nA$$

No. of moles dissolved	1 mol	0
No. of moles after dissociation	$1 - \alpha$	$n\alpha$ Total
number of moles present in solution	$= (1 - \alpha) + n\alpha$	

Van’t Hoff factor, $i = \dfrac{\text{Moles of solute actually present in solution}}{\text{Moles of solute dissolved}}$

$$= \frac{(1-\alpha)+n\alpha}{1} = 1+(n-1)\alpha \qquad \text{or} \qquad \alpha = \frac{i-1}{n-1}$$

ii) **Calculation of Degree of Association of solute particles:** Let n moles of the solute, A, associate to form $(A)_n$. If α is the degree of association.

	nA	$\rightleftharpoons A_n$
No. of moles dissolved	1 mol	0
No. of moles after dissociation	$1-\alpha$	α/n

Total number of moles present in solution $= (1-\alpha) + \alpha/n$

$$i = \left[1-\alpha\left(1-\frac{1}{n}\right)\right] \quad \text{Hence} \quad \alpha = \frac{i-1}{\frac{1}{n}-1} = (i-1)\times\frac{n}{1-n}$$

Illustration 14. A solution is prepared by dissolving 26.3g of $CdSO_4$ in 1000g water. The depression in freezing point of solution was found to be 0.284K. Calculate the Van't Hoff factor. The cryoscopic constant of water is 1.86K kg solvent mol^{-1}- solute.

Solution: Molecular mass $CdSO_4 = 112.4 + 32 + 4 \times 16 = 208.4$ g/mol

$$\text{Molality } CdSO_4 = \frac{\text{Mass } CdSO_4}{\text{Molecular mass } CdSO_4 \times \text{Mass solvent in kg}}$$

$$= \frac{26.3\text{g}}{(208.4\text{g/mol}) \times \left(\frac{1000}{1000}\text{kg}\right)} = 0.216\text{m}$$

$$\Delta T_f = iK_f m \quad \text{or} \quad i = \frac{\Delta T_f}{K_f m} = \frac{0.284\text{K}}{1.86\text{K/m} \times 0.126\text{m}} = 1.21$$

Illustration 15. Three particles of a solute, A, associate in benzene to form species A_3. Calculate the freezing point of 0.25 molal solution. The degree of association of solute A is found to be 0.80. the freezing point of benzene and its cryoscopic constant are 5.5°C and 5.12 Km^{-1} respectively.

Solution: $3A \longrightarrow A_3$

	$3A$	A_3
No. of moles dissolved	3	0
No. of moles after dissociation	$m(1-\alpha)$	$m\alpha/3$

Total moles present after dissociation

$$= m(1-\alpha) + m\frac{\alpha}{3} = m\left(1-\alpha+\frac{\alpha}{3}\right) = m\left(1-\frac{2\alpha}{3}\right) = 0.25m\left[\frac{3-2\times0.8}{3}\right] = 0.177m$$

$$\Delta T_f = K_f m \quad \text{or} \quad T_f^0 - T_f = 5.12\ Km^{-1} \times 0.117\ m = 0.6$$

$$T_f = T_f^0 - 0.6°C = 5.5°C - 0.6°C = 4.9°C$$

Practice Problem

1. A pentimolal solution of potassium chloride freezes at -0.68°C. If K_f for H_2O is 1.86, the degree of dissociation of KCl is -
(A) 75% (B) 83% (C) 65% (D) 92%

2. The depressions in freezing point of 1 M urea, 1 M glucose and 1 M NaCl are in the ratio :
(A) 1 : 2 : 3 (B) 3 : 2 : 2 (C) 1 : 1 : 2 (D) none of these

2. An electrolyte A gives 3 ions and B is a non-electrolyte. If 0.1 M solution of B produces an osmotic pressure P, then 0.05 M solution of A will produce an osmotic pressure, assuming that the electrolyte is completely ionised.
(A) 1.5 P (B) P (C) 0.5 P (D) 0.75 P

4. Which is the correct relation between osmotic pressure of 0.1 M NaCl solution and 0.1 M Na_2SO_4 solution ?
(A) the osmotic pressure of Na_2SO_4 is less than NaCl solution
(B) the osmotic pressure of Na_2SO_4 is more than NaCl solution
(C) both have same osmotic pressures
(D) none of the above

5. Which one of the following pairs of solutions will be expected to be isotonic under the same temperature?
(A) 0.1 M urea and 0.1 M NaCl (B) 0.1 M urea and 0.2 M $MgCl_2$
(C) 0.1 M NaCl and 0.1 M Na_2SO_4 (D) 0.1 M $Ca(NO_3)_2$ and 0.1 M Na_2SO_4

Q.6 The van't Hoff factor of a 0.005 M aqueous solution of KCl is 1.95. The degree of ionisation of KCl is-
(A) 0.95 (B) 0.97 (C) 0.94 (D) 0.96

Q.7 What is the freezing point of a solution containing 8.1 g HBr in 100 g water, assuming the acid to be 90% ionised.? [K_f for water = 1.86 K kg mol^{-1}]

(A) 0.85ºC (B) -3.53ºC (C) 0ºC (D) -0.35ºC

8. The molal freezing point constant for water is 1.86 K kg mol^{-1}. Therefore, the freezing point of 0.1 M NaCl solution in water is expected to be :

(A) –1.86ºC (B) –0.186ºC (C) –0.372ºC (D) +372ºC

9. Select correct statement :

(A) b. p. of 1 molal NaCl solution is twice that of 1 molal sucrose solution
(B) b. p. elevation of 1 molal glucose solution is half of the 1 molal KCl solution
(C) b.p. is a colligative property
(D) all of the above

10. Two solution of KNO_3 and CH_3COOH are prepared separately molarity of both in 0.1 M and osmotic pressure are P_1 & P_2. The correct relationship between the osmotic pressure is -

(A) $P_2 > P_1$ (B) $P_1 > P_2$ (C) $P_1 = P_2$ (D) $\frac{P_1}{P_1+P_2} + \frac{P_2}{P_1+P_2}$

Q.11A 5.8% wt/vol. NaCl solution will exert an osmotic pressure closest to which one of the following -

(A) 5.8% (wt/vol) sucrose solution (B) 5.8% (wt/vol) glucose solution
(C) 2 molal sucrose solution (D) 1 molal glucose solution

Q.12 How many grams of NaBr must be added to270 gm of water to lower the vapour pressure by 3.125 mm Hg at temperature at which vapour pressure of water is 50 mm Hg. Assume 100% ionisation of NaBr

(A) 51.5 gm (B) 103 gm (C) 75 gm (D) 37.5 gm

Q.13 Sea water is found to contain NaCl & $MgCl_2$. If NaCl is 80% ionised and $MgCl_2$ is 50% ionised then van't Hoff factor is -

(A) 1.3 (B) 5.0 (C) 3.3 (D) 3.8

Q.14 The f.p of a 0.08 molal solution of $NaHSO_4$ is –0.372°C. The dissociation constant for the reaction,

$HSO_4^{-} \longrightarrow H^{+} + SO_4^{2-}$; is - [$K_f$ for water = 1.86°C]

(A) 2×10^{-4} (B) 4×10^{-4} (C) 2×10^{-2} (D) 4×10^{-2}

Q.15 If the observed and normal osmotic pressures of a 1% NaCl solution are 5.75 and 3.00 atm, the degree of dissociation of NaCl is –

(A) 0.9 (B) 1.0 (C) 0.57 (D) 0.3

Q.16 0.01 M solution of KCl and $BaCl_2$ are prepared in water. The freezing point of KCl is found to be –2°C. What freezing point would you expect for $BaCl_2$ solution – (A) –5°C

(B) –4°C (C) –3°C (D) –2°C

Q.17 The elevation in boiling point of a solution of 10 g of a binary electrolyte (molecular mass 100) in 100 of water is ΔT_b. The value of K_b for water is –

(A) $\frac{\Delta T_b}{2}$ (B) 10 (C) $10\Delta T_B$ (D) $\frac{\Delta T_b}{10}$

Q.18 Van’t Hoff factors are x, y, z in the case of association, dissociation and no change respectively. Increasing order is -

(A) $x < y < z$ (B) $x = y = z$ (C) $y < x < z$ (D) $x < z < y$

Q.19 1 mole each of following solutes are taken in 5 moles water,

(i) NaCl (ii) K_2SO_4 (iii) Na_3PO_4 (iv) glucose

Assuming 100% ionisation of the electrolyte, relative decrease in V. P. will be in order

(A) i < ii < iii < iv (B) iv < iii < ii < i (C) iv < i < ii < iii (D) equal

Q.20 A 0.002 molar solution of NaCl having degree of dissociation of 90% at 27°C has osmotic pressure equal to -

(A) 0.94 bar (B) 9.4 bar (C) 0.094 bar (D) 9.4×10^{-4} bar

Q.21 At 20°C, the vapour pressure of 0.1 M solution of urea is 0.0311 mm less than that of water and the vapour pressure of 0.1 M solution of KCl is 0.0574 mm less than that of water. The apparent degree of dissociation of KCl at this dilution is -

(A) 92.1% (B) 84.6% (C) 68.4% (D) 54.1%

22. The freezing point of a solution of 20.5 g NH_4Br in 100 g of water is –6.2ºC. The freezing point of a solution of 3.42 g cane-sugar in 100 g of water is –0.185ºC. The degree of ionisation of salt is -
(A) 80% (B) 30% (C) 60% (D) 40%

23. A 1.2% solution (wt./ volume) of NaCl is isotonic with 7.2% solution (wt. /volume) of glucose. Degree of ionisation and van't Hoff factor of NaCl is -

(A) α = 95%, i = 1.95
(B) α = 90%, i = 1.90
(C) α = 85%, i = 1.85
(D) α = 75%, i = 1.75

Q.24 1 g of monobasic acid in 100 g of water lowers the freezing point by 0.168º. If 0.2 g of same acid requires 15.1 mL of N/10 alkali for complete neutralization, degree of dissociation of acid will be -
[K_f for H_2O is 1.86 K mol^{-1} kg]
(A) 16.8% (B) 22.4% (C) 19.6% (D) 26.2%

Practice Problem

1. (B)
2. (C)
3. (A)
4. (B)
5. (D)
6. (A)
7. (B)
8. (C)
9. (B)
10. (D)
11. (C)
12. (A)
13. (C)
14. (D)
15. (A)
16. (C)
17. (A)
18. (D)
19. (C)
20. (C)
21. (B)
22. (C)
23. (A)
24. (C)

BOOST YOUR LEARNING

Q 1. Which one of the following salts would have the same value of the van't Hoff factor as that of $K_3[Fe(CN_6)]$?.

(A) $Al_2(SO_4)_3$ (B) NaCl (C) Na_2SO_4 (D) $Al(NO_3)_3$

Q 2. The vapour pressure of benzene at a certain temperature is 640 mm of Hg. A non -volatile and non- electrolytic solid, weighing 2.175g, is added to 39.08g of benzene. The vapour pressure of thesolution is 600mm of Hg. What is the molecular mass of the solid substance ?.

(A) 49.50 (B) 59.6 (C) 65 (D) 79.8

Q 3. A 5 % solution of cane sugar (mol. mass = 342) is isotonic with 1 % solution of a substance X . The molecular mass of X is :

(A) 34.2 (B) 171.2 (C) 68.4 (D) 136.8

Q 4. The degree of dissociation 'α' of a weak electrolyte is:

(A) $\frac{i-1}{n+1}$ (B) $\frac{i-1}{n-1}$ (C) $\frac{n-1}{i-1}$ (D) $\frac{n+1}{i-1}$

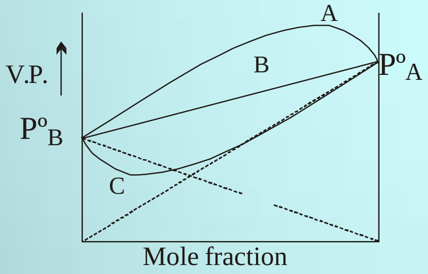
Q 5. The molal boiling point constant for water is 0.513 K kg mol^{-1} . When 0.1 mole of sugar is dissolved in 200 g of water , the solution boils under a pressure of 1 atm at :

(A) 100.513 °C (B) 100.0513 °C (C) 100.256 °C (D) 101.025 °C

Q 6. The correct expression relating molality (m) , molarity (M) , density (D) and molar mass (M_2) of solute is :

(A) $m = \frac{M}{d + M M_2}$ (B) $m = \frac{M}{d - M M_2}$ (C) $m = \frac{d + M M_2}{M}$ (D) $m = \frac{d - M M_2}{M}$

Q 7. Match the following graph



A (i) (+) deviation B (ii) ideal C (iii) (-) deviation

(A) A (i) , B (ii) , C (iii)

(B) A (iii) , B (ii) , C (i)

(C) A (ii) , B (iii) , C (i)

(D) none of these

Q 8. Human blood gives rise to an osmotic pressure of approximately 7.65 atm at body temperature, 37^0C. Hence , molarity of an glucose solution to be, to have the same osmotic pressure as blood is :

(A) 0.30 M (B) 0.20M (C) 0.10 M (D) 0.50 M

Q 9. At a given temperature, total vapour pressure in Torr of a mixture of volatile components A and B is given by $p = 120 - 75\ X_B$ hence, vapour pressure of pure A and B respectively (in Torr) are:

(A) 120, 75 (B) 120, 195 (C) 120, 45 (D) 75, 45

Q 10. Total vapour pressure of mixture of 1 mole volatile component A (p^o_A = 100 mg Hg) and 3 moles of volatile component B (p^o_B = 60 mm Hg) is 75 mm . For such case:

(A) there is positive deviation from Raoult’s law

(B) boiling point has been lowered

(C) force of attraction between A and B is smaller than that between A and A or between B and B

(D) all the above statements are correct

Q 11. Vapour pressure of pure water is 40 mm . If a non-volatile solute is added to it , vapour pressure falls by 4 mm . Hence, molality of solution is :

(A) 6.173 molal (B) 3.0864 molal (C) 1.543 molal (D) 0.772 molal

Q 12. The vapour pressure of a pure liquid A is 40 mm Hg at 310 K. The vapour pressure of this liquid in a solution with liquid B is 32 mm Hg. Mole fraction of A in the solution, if it obeys Raoult's law, is :

(A) 0.8 (B) 0.5 (C) 0.2 (D) 0.4

Q 13. The total concentration of dissolved particles inside red blood cells is approximately 0.30 M and the membrane surrounding the cells is semipermeable. What would be the osmotic pressure (in atmosphere) inside the cells become if the cells were removed from the blood plasma and placed in pure water at 298 K?

(A) 7.34 atm (B) 1.78 atm (C) 2.34 atm (D) 0.74 atm

Q 14. Which one of the following pairs of solutions will be expected to be isotonic under the same temperature ?

(A) 0.1 M urea and 0.1 M NaCl
(B) 0.1 M urea and 0.2 M $MgCl_2$
(C) 0.1 M NaCl and 0.1 M Na_2SO_4
(D) 0.1 M $Ca(NO_3)_2$ and 0.1 M Na_2SO_4

1. D **2.** C **3.** C **4.** B **5.** C **6.** B **7.** A

8. A **9.** C **10.** D **11.** A **12.** A **13.** A **14.** D

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