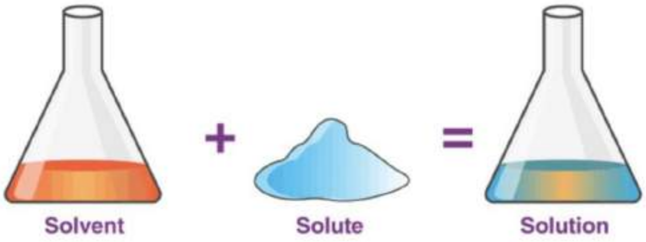
Chapter 2

Solutions

Solutions, Mixtures & Types of Solutions

What is a Solution?

- A solution is a homogeneous mixture of two or more components in which the particle size is smaller than 1 nm.
- Common examples of solutions are sugar in water and salt in water solutions, soda water, etc. In a solution, all the components appear as a single phase. There is particle homogeneity i.e. particles are evenly distributed. This is why a whole bottle of soft drink has the same taste throughout.



Solute and Solvent

- **Solvent:** The substance which is present in the largest quantity in a solution; is generally referred to as a solvent.
  Example: In the solution of salt in water, since water is present in larger quantity, thus, water is called the solvent. It is the solvent that decides the phase of a solution.
- **Solute:** The substance which is present in lesser quantity in a solution is generally called the solute.
  In other words, one or more components present in a solution other than the solvent are is called the solute.
  Example: In the solution of salt in water, salt is called the solute. The solute may be more than one.

Note: Physical state of solvent and solution is same.

Different Types of Solutions

1. Binary Solution

Solutions which contain only two components are called a binary solution. For example, a solution of salt in water is a type of binary solution, as it contains only two components.

Binary Solution = Solute + Solvent

Similarly, it is called **ternary** and **quaternary** if it is composed of **three** and **four components**, respectively.

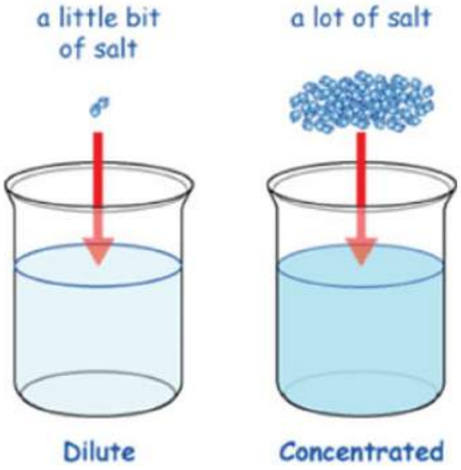
Thus; a solution may be regarded as a single-phase containing more than one component.

2. Dilute Solution

A solution in which relatively a small amount of solute is dissolved in a large amount of solvent is called a dilute solution.

3. Concentrated Solution

A solution in which relatively a large amount of the solute is present is called a concentrated solution.

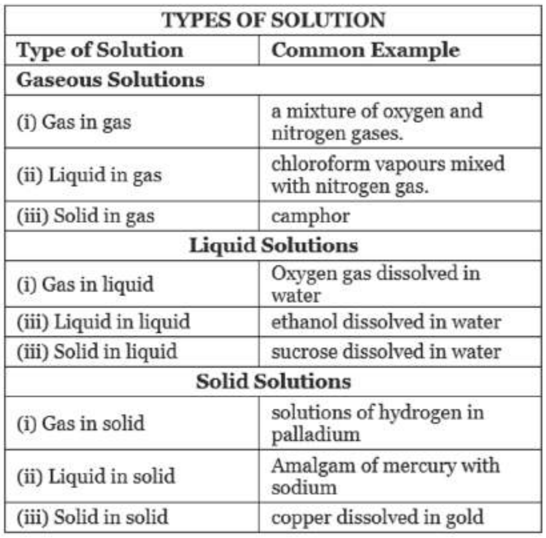


Properties of a Solution

- A solution consists of a single-phase i.e. it is a monophasic system.
- A solution is a uniform throughout, such as uniform properties such as density, refractive index, etc.
- The components of a solution cannot be easily separated by physical methods.
- The composition of a solution is not definite but can vary within certain limits.

- Certain properties of solution such as density, viscosity, surface tension, boiling point, freezing point etc. vary with the composition of the solution.

Table: Types of Solution



TYPES OF SOLUTION	
Type of Solution	**Common Example**
Gaseous Solutions	
(i) Gas in gas	a mixture of oxygen and nitrogen gases.
(ii) Liquid in gas	chloroform vapours mixed with nitrogen gas.
(iii) Solid in gas	camphor
Liquid Solutions	
(i) Gas in liquid	Oxygen gas dissolved in water
(iii) Liquid in liquid	ethanol dissolved in water
(iii) Solid in liquid	sucrose dissolved in water
Solid Solutions	
(i) Gas in solid	solutions of hydrogen in palladium
(ii) Liquid in solid	Amalgam of mercury with sodium
(iii) Solid in solid	copper dissolved in gold

In a solution, components may be solid, liquid or gas.

Gaseous, Liquid & Solid Solutions

1. Gaseous Solution

Solutions in which solvent is present is a gaseous state is called Gaseous solution. Gaseous solutions can be divided into following three types on the basis of phases of solute and solvent;

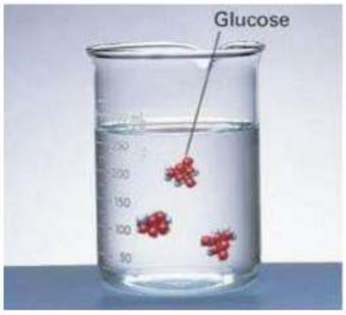
1. **Gas - Gas Solution:** Solutions in which solute and solvent both are gases; are called Gas-gas Solutions.
   Example: solution (mixture) of nitrogen and oxygen, solution (mixture) of carbon dioxide and nitrogen, solution (mixture) of carbon dioxide and oxygen, etc.
2. **Liquid Gas Solution:** Solutions, in which solute is in a liquid state and solvent is in a gaseous state, are called Liquid-Gas Solution.
   Example: solution (mixture) of chloroform in nitrogen gas.
3. **Solid Gas Solution:** Solutions, in which solute is in solid-state and solvent is in a gaseous state, are called Solid-Gas Solutions.
   Example: Solution (mixture) of camphor in nitrogen gas.

2. Liquid Solution

Solutions, in which solvent is present in a liquid state, are called Liquid solutions.

Liquid solutions can be classified into the following three types:

1. **Gas-Liquid Solution:** Solutions having solute in gaseous state and solvent in the liquid state are called Gas-Liquid Solutions.
   Example: Solution (mixture) of oxygen in water, a mixture of carbon dioxide in water. Coca-cola, a beverage, is an example of a gas-liquid solution, as it has carbon dioxide dissolved in water.
2. **Liquid - Liquid Solution:** Solutions, in which solute and solvent both are present in a liquid state, are called liquid liquid solutions.
   Example: Vinegar solution, vinegar is the mixture of ethanoic acid and water. Solution of ethanol in water, etc.
3. **Solid-Liquid Solution:** Solutions, in which solutes present in solid-state and solvent is in a liquid state, are called solid-liquid solutions.
   Example: Solution of salt in water, solution of glucose in water, etc.



Glucose in water

3. Solid Solution

Solutions having solvent in the solid-state, are called solid solutions.

The solid solution can be divided into the following three categories:

1. **Gas-Solid Solution:** Solutions having solvent in solid-state and solute in the gaseous state are called gas-solid solutions.
   Example: solution of hydrogen in palladium.

2. **Liquid-Solid Solution:** Solutions having solvent in solid-state and solute in the liquid state are called liquid-solid solutions.
   Example: an amalgam of mercury with sodium.
3. **Solid-solid solution:** Solutions having solvent and solute both in the solid-state are called solid-solid solutions.
   Example: Solution of gold and copper.

What are Mixtures?

- When two or more chemically non-reacting substances are mixed, they form mixtures. A mixture may be heterogeneous or homogeneous.
- A heterogeneous mixture consists of distinct phases and the observed properties are just the sum of the properties of individual phases. However, a homogeneous mixture consists of a single-phase which has properties that may differ drastically from those of the individual components.
- A homogeneous mixture whose composition can·be varied within certain limits is termed a true solution.
- The constituents of a solution cannot be separated by filtration, settling or centrifugal action. All solutions are characterised by
  (i) Homogeneity
  (ii) Absence of settling
  (iii) The molecular or ionic state of sub-division of the components.
  When the solution is composed of only two chemical substances, it is termed a binary solution.
- Similarly, it is called ternary and quaternary if it is composed of three and four. components, respectively. thus; a solution may be regarded as a single phase containing more than one component.

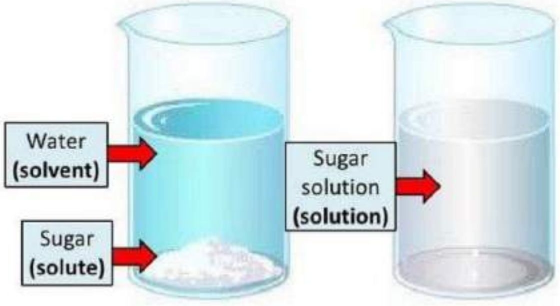
Example

- A mixture of salt and sugar.
- A mixture of oxygen and nitrogen.
- A mixture of sugar in water.

Homogeneous and Heterogeneous Mixture

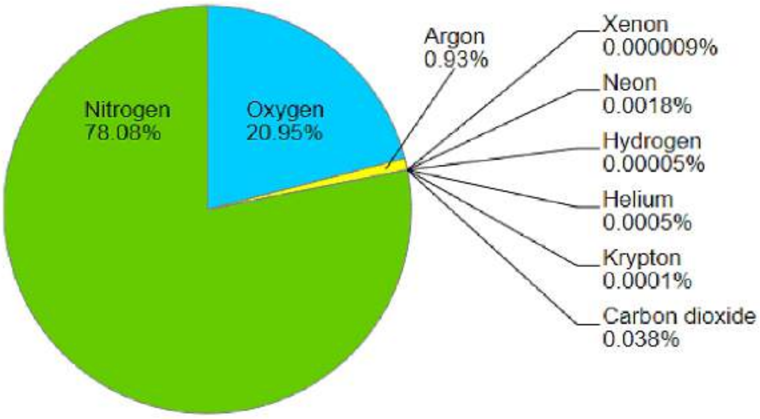
Homogeneous Mixture: A mixture of two or more components having no distinguish phase is called a homogeneous mixture.
The homogeneous mixture is generally referred to as a solution.
Example: When two spoons of salt are mixed in a glass of water, the mixture so

obtained has no distinguish phase and this is called a solution.



Solution

Air is a mixture of different gases with no distinguish phase, thus, the air is often referred to as the solution.



In a homogeneous mixture,

1. i.e. solution, the composition, and properties of the solution are uniform throughout.
2. **Heterogeneous Mixture:** A mixture of two or more components with distinguish phase is called a heterogeneous mixture.
   Example: A mixture of mustard oil and water, in this mixture phases of water and mustard oil, can be seen and distinguished clearly, and hence called heterogeneous mixture.

Heterogeneous Mixture: Oil and Water

Raoult's Law

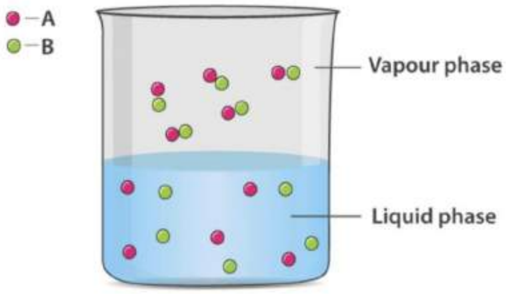
Who discovers Raoult's Law?

- Raoult's law has been named after François-Marie Raoult, a French chemist who while conducting an experiment found out that when substances were mixed in a solution, the vapour pressure of the solution decreased simultaneously.
- Raoult's law was established in the year 1887 and is also considered the law of thermodynamics.

What is Raoult's Law?

Raoult's law states that:
A solvent's partial vapour pressure in a solution (or mixture) is equal or identical to the vapour pressure of the pure solvent multiplied by its mole fraction in the solution.

Mathematically, Raoult's law equation is written as:
$P_{solution} = X_{solvent} P^0_{solvent}$
Where,
$P_{solution}$ = vapour pressure of the solution
$X_{solvent}$ = mole fraction of the solvent
$P^0_{solvent}$ = vapour pressure of the pure solvent



Let's understand this by looking at the example below:

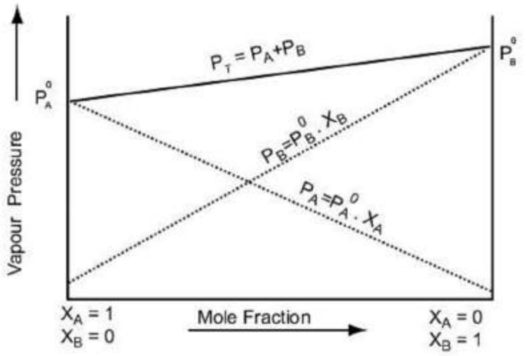
Let two volatile liquids A and B dissolve each other to form an ideal solution. Then the vapours above the solution will contain the vapours of A and B. Applying Dalton's law of partial pressure the total vapour pressure of the solution will be

$P_{solution} = P_A + P_B$

Where,

P_A and P_B are the partial vapour pressures of A and B.

Solution being dilute (Condition for ideality) Raoult's law can be applied.



Vapour Pressure Diagram for Ideal Solution

Raoult's law for binary solutions state that

The vapour pressure of any volatile constituent of a binary solution at any given temperature is equal to the product of the vapour pressure of pure constituent and its mole fraction

$P_A = P^o_A X_A$

$P_B = P^o_B X_B$

Where:

- P^o_A and P^o_B are vapour pressures of pure A and B respectively

- x_A and x_B are mole fraction of A and B in liquid solution respectively

Hence, *P* (Solution) *or* $P_s = P_A{}^0 X_A + P_B{}^0 X_B$
Also, $P_s = P^0{}_A(1\text{-}X_B) + P^0{}_B X_B$
$\Rightarrow P_s = P^0{}_A + (P^0{}_B - P^0{}_A) X_B$
This equation is of the form y = mx + c. The value of m (slope) may be (+ve) or (–ve) depending upon whether $P^0{}_B > P^0{}_A$ (m = + ve) or $P^0{}_B < P^0{}_A$ (m = –ve).
Hence a plot of a graph of P_s versus X_B will be a straight line with an intercept on the y-axis equal to p_A and slope equal to $(P^0{}_B - P^0{}_A)$

Total Pressure of a Solution will be:

- P (Solution) = PA + PB = $x_A P^0{}_A + x_B P^0{}_B$

$$P\text{ (Solution)} = \frac{n_A.P_A^0}{n_A + n_B} + \frac{n_B.P_B^0}{n_A + n_B}$$

$$P\text{ (Solution)} = \frac{n_A.P_A^0 + n_B.P_B^0}{n_A + n_B}$$

Vapour Composition

- Vapour composition means to find out the mole fraction of A and B in vapour i.e y_A and y_B.
- Dalton's law of particle pressure is used to calculate the vapour composition, as we know, Partial pressure = mole fraction × total pressure
  $\Rightarrow p_A = y_A \times p_S$
  or $y_A = P_A/P_S$
  Similarly for B
  $\Rightarrow y_B = P_A/P_S$

where y_A and y_B are mole fraction of 'A' and 'B' in the vapour phase and $y_A + y_B = 1$

SPECIAL NOTE:

x_A and x_B are mole fraction of 'A' and 'B' in the solution phase and $x_A + x_B = 1$
y_A and y_B are mole fraction of 'A' and 'B' in the vapour phase and $y_A + y_B = 1$

Raoult's Law as a special case of Henry's law

- At given temperature liquids vaporize. At equilibrium, the pressure exerted by the vapour of the liquid over the liquid phase is referred to as vapour pressure.
- According to Raoult's law, the vapour pressure of a volatile component in a given solution can be defined by $p_i = p_i^{\circ} x_i$
- In an answer of a gas in a fluid one of the segments is volatile to the point that it exists as a gas and solvency is given by Henry's law which expresses that $p = K_H x$
- Comparing both the equations we get that partial pressure of the volatile component or gas is directly proportional to its mole fraction in solution. Proportionality constant K_H differs from p_i°
- Therefore, Raoult's law turns into a unique instance of Henry's law in which K_H get to be equivalent to p_i°

Limitations of Raoult's Law

There are a few limitations to Raoult's law:

1. Raoult's law is apt for describing ideal solutions. However, ideal solutions are hard to find and they are rare. Different chemical components have to be chemically identical equally.
2. Since many of the liquids that are in the mixture do not have the same uniformity in terms of attractive forces these type of solutions tends to deviate away from the law.

There is either a negative or a positive deviation. The negative deviation occurs when the vapour pressure is lower than expected from Raoult's law. An example of negative deviation is a mixture of chloroform and acetone or a solution of water and hydrochloric acid.

Alternatively, positive deviation takes place when the cohesion between similar molecules is greater or that it exceeds adhesion between unlike or dissimilar molecules. Both components of the mixture can easily escape from the solution. An example of positive deviation includes the mixtures of benzene and methanol or ethanol and chloroform.

Example 1. The vapour pressure 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 40g of methanol. Calculate the total vapour pressure of the solution.

Solution.

Number of moles of ethanol = 60/40 = 1.5

Number of moles of methanol = 40/32 = 1.25
$X_A = 1.25/1.25 + 1.3 = 0.4545$ and $X_B = 1 - 0.4545 = 0.545$
Let A = CH_3OH, B = C_2H_5OH
Total pressure of the solution
$P_T = X_AP^0{}_A + X_BP^0B$
$= 0.4545 \times 88.7 + 0.545 \times 44.5 = 40.31 + 24.27$
$= 64.58$ mm Hg

Example 2. The composition of vapour over a binary ideal solution is determined by the composition of the liquid. If X_A and Y_A are the mole fraction of A in the liquid and vapour, respectively find the value of X_A for which $Y_A - X_A$ has a minimum. What is the value of the pressure at this composition?

Solution.

$$y_A = \frac{x_A P_A^0}{P_B^0 + \left(P_A^0 - P_B^0\right)x_A}$$

Subtracting x_A from both sides, we get

$$y_A - x_A = \frac{x_A P_A^0}{P_B^0 + \left(P_A^0 - P_B^0\right)x_A} - x_A$$

Now differentiating w.r.t. x_A, we get

$$\frac{d(y_A - x_A)}{dx_A} = \frac{P_A^0}{\left(P_A^0 - P_B^0\right)x_A + P_B^0} - \frac{x_A P_A^0\left(P_A^0 - P_B^0\right)}{\left\{P_B^0 + \left(P_A^0 - P_B^0\right)x_A\right\}^2} - 1$$

The value of x_A at which $y_A - x_A$ has a minimum value can be obtained by putting the above derivative equal to zero. Thus we have

$$\frac{P_A^0}{P_B^0 + \left(P_A^0 - P_B^0\right)x_A} - \frac{x_A P_A^0\left(P_A^0 - P_B^0\right)}{\left\{P_B^0 + \left(P_A^0 - P_B^0\right)x_A\right\}^2} - 1 = 0$$

Solving for x_A, we get

$$x_A = \frac{\sqrt{P_A^0 P_B^0} - P_B^0}{P_A^0 - P_B^0}$$

hence

$$P = \sqrt{P_A^0 P_B^0}$$

Example 3. A very small amount of non-volatile solute (that does not dissociate) is dissolved in 56.8 cm^3 of benzene (density 0.889 g cm^{-3}). At room temperature, the vapour pressure of this solution is 99.88 mm Hg while that of benzene is 100mm Hg. Find the molality of this solution. If the freezing temperature of this

solution is 0.73 degrees lower than that of benzene. What is the value of the molal freezing point depression constant of benzene?

Solution.

As $\frac{P^0 - P_s}{P_s} = \frac{n_1}{n_2} = \frac{w_1 \times m_2}{m_1 \times w_2}$

$$\Rightarrow \frac{P^0 - P_s}{P_s} = \left(\frac{1000 \times w_1}{m_1 \times w_2}\right) \times \frac{m_2}{1000} = m \times \frac{m_2}{1000}$$

$$\begin{pmatrix} m & = \text{molality} \\ m_2 & = \text{molecular wt of solvent} \end{pmatrix}$$

$$\therefore \frac{100 - 98.88}{98.88} = m \times \frac{78}{1000}$$

$$\therefore m = \frac{1.12 \times 1000}{78 \times 98.88} = 0.1452$$

Also,

$\Delta T_f = K_f \times$ molality f

$\therefore 0.73 = K \times 0.1452$

$f_K = 5.028$ K. molality

Example 4. What is the composition of the vapour which is in equilibrium at 30°C with a benzene-toluene solution with a mole fraction of benzene of 0.400? ($P^o_B = 119$ torr and $P_T{}^o = 37.0$ torr)

Solution.

Total pressure of the solution is given by

$P_T = X_B P^0_B + X_T P^0_T$

$= 0.4 \times 119 + 0.6 \times 37$

$= 47.6 + 22.2$

$= 69.8$ torr

Applying Dalton's law for mole fraction in the vapour phase.

$Y_B = P_B/P_T = 47.6/62.4$

$= 0.763$

$Y_T = 1 - 0.763$

$= 0.237$

Colligative Properties: Relative Lowering of Vapour Pressure

What are Colligative Properties?

- A dilute solution is one in which the amount of the solute is very small in comparison to the amount of the solvent.
- The dilute solutions show more or less ideal behaviour as the heat and volume changes, accompanying the mixing of solute and solvent, are negligible for all practical purposes. Dilute solutions obey Raoult's law.
- The properties of dilute solutions which depend only on the number of particles of solute present in the solution and not on their identity are called **colligative properties** (denoting depending upon collection).
- We shall assume here that the solute is **non-volatile**, so it does not contribute to the vapour. We shall also assume that the solute does not dissolve in the solid solvent, that is, the pure solid solvent separates when the solution is frozen, the latter assumption is quite drastic, although it is true for many mixtures, it can be avoided.

Colligative properties are the properties of only dilute solution which are supposed to behave as ideal solutions.

Different Types of Colligative Properties of Solution

The various colligative properties are:

- Lowering of vapour pressure
- Elevation of boiling point
- Depression of freezing point
- Osmotic pressure

Relative Lowering of Vapour Pressure

- It has been known for a long time that when a non-volatile solute is dissolved in a liquid, the vapour pressure of the solution becomes lower than the vapour pressure of the pure solvent.
- In **1886, the French chemist, Francois Raoult**, after a series of experiments on a number of solvents including water, benzene and ether, succeeded in establishing a relationship between the lowering of the vapour pressure of a solution and the mole fraction of the non-volatile solute.

- Let us consider a solution obtained by dissolving n moles of a non-volatile solute in N moles of a volatile solvent. Then mole fraction of the solvent, $X_1 = N/(n + N)$ and mole fraction of the solute, $X_2 = n/(N + n)$. Since the solute is non-volatile, it would have a negligible vapour pressure. The vapour pressure of the solution is, therefore merely the vapour pressure of the solvent.

According to Raoult's law, the vapour pressure of a solvent (P_1) in an ideal solution is given by the expression:
$P_1 = X_1 P^o 1$ (1)
where $P^o 1$ is the vapour pressure of the pure solvent. Since $X_1 + X_2 = 1$, Eq. 1 may be written as
$P_1 = (1 - X_2) P^o 1$ (2)
or $P_1/P^o 1 = 1 - X_2$
or $P_1 - P^o 1/P^o 1 = X_2$ (3)
The expression on the left-hand side of Equation (3) is usually called the relative lowering of vapour pressure. Equation (3) may thus be stated as:

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.

This is one of the statements of **Raoult's law.**
Since mole fraction of the solute, X_2 is given by $n / (N + n)$, Equation (3) may be expressed as $P^o 1 - P_1/P^o 1 = n/N + n$ ....(4)
It is evident from Equation (4) that the lowering of the vapour pressure of a solution depends upon the number of moles (and hence on the number of molecules) of the solute and not upon the nature of the solute dissolved in a given amount of the solvent. Hence, lowering vapour pressure is a colligative property.

Determination of Molar Masses from Lowering of Vapour Pressure

- It is possible to calculate molar masses of non-volatile non-electrolytic solutes by measuring the vapour pressures of their dilute solutions.
- Suppose, a given mass, w gram, of a solute of molar mass m, dissolved in W gram of solvent of molar mass M lowers the vapour pressure from $P^\circ 1$ to P_1.

Then, by Equation (4)

$$\frac{P_1^0 - P_1}{P_1^0} = \frac{n}{N+n} = \frac{w/m}{W/M + w/m} \quad ....(5)$$

$$\frac{P_1^\circ - P_1}{P_1^\circ} = \frac{n}{N} = \frac{w/m}{W/M} = \frac{wM}{Wm} \quad ....(6)$$

$$\text{or, } m = \frac{wM}{W\ (P_1^\circ - P_1)/P_1^\circ}$$

Measurement of Lowering of Vapour Pressure

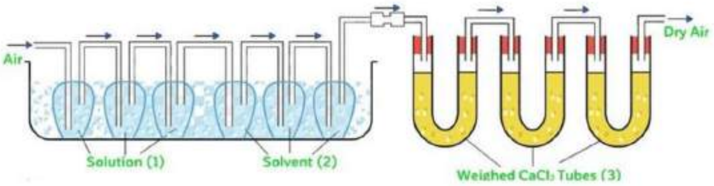
1. **Barometric Method:**
   The individual vapour pressure of a liquid was calculated by Raoult and then the same process was followed to calculate the vapour pressure of the solution as well. He poured the liquid or the solution into a Torricellian vacuum of a barometer tube and calculated the depression of the mercury level. This method was later found to be neither practicable nor accurate as the lowering of vapour pressure is almost negligible.
2. **Manometric Method:**
   The vapour pressure of a liquid or solution can be fairly measured with the help of a manometer. Let us assume a bulb is charged with the liquid or solution. The air in the connecting tube of the instrument is then removed with a vacuum pump. With the stopcock being closed, the pressure inside is only due to the vapour evaporating from the solution or liquid. This method can be applied to aqueous solutions. The manometric liquid used can be either mercury or n-butyl phthalate which has a low density and low volatility.
3. **Ostwald and Walker's Dynamic Method (Gas Saturation Method):**
   When air is passed through any gas, the gas diffuses into the air due to the principle of diffusion till the pressure of the gas in the air is equal to that of the gas outside. Therefore as air is passed through the solution, it absorbs the vapours of the solvent till the pressure of the solvent vapours in the air is P (vapour pressure of the solvent in the solution).
   Mass of vapour absorbed or loss in weight of solution = PVm/RT
   Where, P = pressure of the solvent vapours,
   V = volume available for vapours in the solution bulb,
   T = temperature of the bulb and
   m = molecular weight of the solvent.
   As the air passes through the solvent, the pressure difference of the vapours in the air and outside is P^{o} - P. So the air absorbs this amount of vapours and gets saturated.

Loss in weight of solvent bulb = $(P^\circ - P)Vm/RT$
As the sum of the losses of weight in the two containers is equal to the gain in weight of $CaCl_2$,
The gain in weight of $CaCl_2$ filled tubes =

$$= \frac{P^\circ Vm}{RT}$$

$$\frac{\text{Loss in wt. of solvent}}{\text{Gain in wt. of } CaCl_2} = \frac{P^\circ - P}{P^\circ}.$$

Method: In this method, a stream of dry air is passed successively through
(i) a solution
(ii) the pure solvent (water) and
(iii) a reagent (anhydrous $CaCl_2$) that can absorb the vapours of the solvent. The complete assembly is shown in the figure, given below:



Ostwald - Walker Experiment

- The first three bulbs contain a weighed amount of the solution under examination and the next three bulbs contain a weighed amount of the pure solvent.
- A weighed amount of $CaCl_2$ is taken in the set of U - tubes at the end. All the bulbs are at the same temperature and the volume available for the vapours in the solution and solvent bulbs are the same temperatures and the volume available for the vapours in the solution and solvent bulbs are the same.

It is designed in order to calculate the relative lowering of vapour pressure of a solvent due to a non - volatile solute.

Practice Question: The density of a 0.438 M solution of potassium chromate at 298 K is 1.063 g cm^{-3}. Calculate the vapour pressure of water above this solution. Given: P° (water) = 23.79 mm Hg.
Solution.

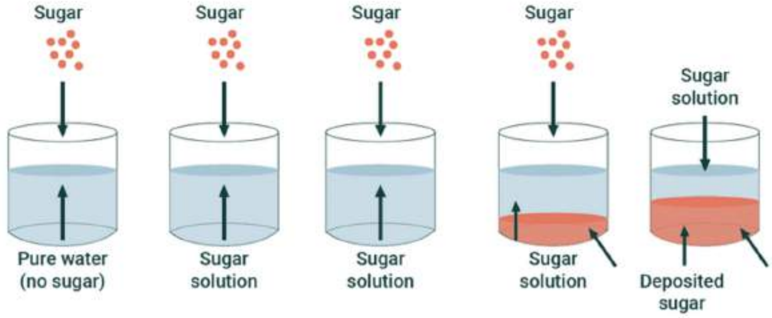
A solution of 0.438 M means 0.438 mol of K_2CrO_4 is present in 1L of the solution.
Now,
Mass of K_2CrO_4 dissolved per litre of the solution = $0.438 \times 194 = 84.972$ g
Mass of 1L of solution = $1000 \times 1.063 = 1063$ g
Amount of water in 1L of solution = $978.028/18 = 54.255$ mol
Assuming K_2CrO_4 to be completely dissociated in the solution, we will have;
Amount of total solute species in the solution = $3 \times 0.438 = 1.314$ mol.
Mole fraction of water solution = $54.335/(54.335 + 1.314) = 0.976$
Finally, Vapour pressure of water above solution = $0.976 \times 23.79 = 23.22$ mm Hg

Solubility: Solid in a Liquid, Gas in a Liquid & Liquid in a Liquid

What is Solubility?

The maximum amount of solute that can dissolve in a known quantity of solvent at a certain temperature is its solubility.

A solution is a homogeneous mixture of one or more solutes in a solvent. Sugar cubes added to a cup of tea or coffee is a common example of a solution. The property which helps sugar molecules to dissolve is known as solubility. Hence, the term solubility can be defined as a property of a substance (solute) to dissolve in a given solvent. A solute is any substance that can be either solid or liquid or gas dissolved in a solvent.



On this basis, the factors affecting solubility vary on the state of the solute:

- Liquids in Liquids
- Solids in Liquids
- Gases in Liquids

The maximum amount of solute which can be dissolved in a specified amount of solvent at a given temperature is called **the solubility of a substance (solute).**

Solubility of a Solid in a Liquid

Conditions for a solute to dissolve in a solvent

- Solute and solvent both should be polar or non-polar.
- The intermolecular attractions of both the solute and solvent should be similar.

DISSOLUTION

Dissolution means to dissolve.
When a solid is added to a solvent (liquid); the concentration of solution increases because of dissolving of some of the solute. This process is called dissolution.

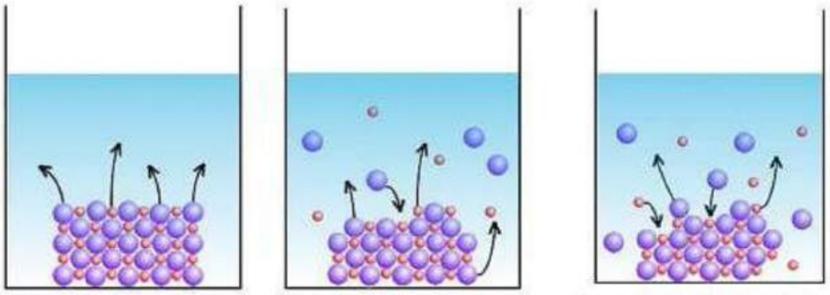
CRYSTALLIZATION

In the process of dissolution, some of the particles of solute collide with the solid particles of solute and separated out of the solution, which is called crystallization.

A stage is reached when the two processes occur at the same rate. Under such conditions, a number of solute particles going into the solution will be equal to the solute particles separating out and a state of dynamic equilibrium is reached.

Solution equilibrium

Rate of dissolving = rate of crystallization



Salt is initially put into the water and begins dissolving.

Salt continues to dissolve; however, dissolved ions will also precipitate. Because the salt dissolves faster than its ions precipitate, the net movement is towards dissolution.

Eventually, the rate of dissolution will equal the rate of precipitation. The solution will be in equilibrium, but the ions wil continue to dissolve and precipitate.

DYNAMIC EQUILIBRIUM

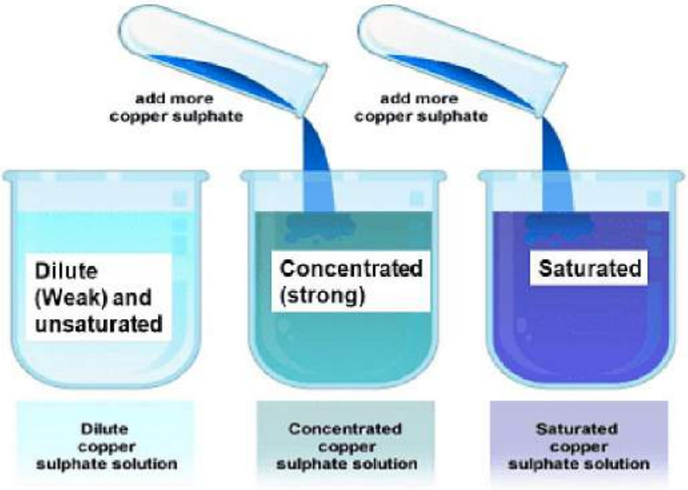
In the process of dissolution and crystallization, the stage in which the rate of both of the process started and keeps on occurring at the same rate is called the **dynamic equilibrium.**

In the condition of dynamic equilibrium number of solid particles mixing in the solution becomes equal to the solute particles separating out from the solution. The state of dynamic equilibrium can be shown by using the following equation: **Solute + Solvent ⇆ Solution**
A similar process occurs when a gas is dissolved in liquid.

SATURATED SOLUTION

At the stage of dynamic equilibrium the concentration of solute remains constant in solution under given temperature and pressure, is called saturated solution.

The solution in which no more solute can be dissolved under the given conditions, i.e. temperature and pressure are called a saturated solution.



UNSATURATED SOLUTION

The solution in which more solute can be dissolved under the given conditions, i.e. temperature and pressure, is called unsaturated solution.

FACTORS AFFECTING SOLUBILITY

1. **Nature of Solute and Solvent**
   Like Dissolves Like Every solid does not dissolve in every liquid. Only polar solute (solid) dissolves in polar liquid (solvent) and non-polar solute (solid) dissolved in non-polar liquid(solvent).
   If intermolecular attractions of solute and solvent are similar, then that solute (solid) dissolve in that very solvent.
   Example: Sugar and common salt readily dissolve in water while naphthalene and anthracene do not. Naphthalene and anthracene dissolve in benzene while common salt and sugar do not.
2. **Effect of Temperature:**
   Apart from the nature of solute and solvent, temperature also affects solid solubility considerably.
   If the dissolution process is endothermic ($\Delta H > 0$), then the solubility should increase with an increase in temperature in accordance with **Le Chatelier's Principle.**
   If the dissolution process is exothermic ($\Delta H < 0$) the solid solubility should decrease.
3. **Effect of Pressure:**
   Solid solubility hardly gets affected by changes in pressure. This is due to the fact that solids and liquids are highly incompressible and practically do not get affected by changes in pressure.

Solubility of Gases in Liquids

Gas solubility in liquids deals with the concept of gas dissolving in a solvent. Let us first define solubility.
For any substance, solubility is the maximum amount of solute that can be dissolved in a given solvent at a particular temperature.

Now our concern is gas solubility in liquids. The gas solubility in liquids is greatly affected by temperature and pressure as well as the nature of the solute and the solvent.
The **common examples** are carbonated beverages, i.e., soft drinks, household cleaners containing aqueous solutions of ammonia, a formalin-an aqueous solution of formaldehyde, etc.

Vapour Solutions & Types of Solutions

TYPE OF SOLUTIONS

Solutions can have continuously variable compositions, and they are homogeneous on a scale beyond the size of individual molecules. This definition can be used to cover a wide variety of systems, including ordinary solution such as alcohol in water or $HClO_4$ in benzene and even solution of large proteins in aqueous salt solutions. It is also useful sometimes to consider some colloidal suspensions undergoing Brownian motion as solutions, and there are solid solutions where one solid is uniformly dissolved in another.

SOME EXAMPLES OF SOLUTIONS

Solute	**Solvent**	**Name of Type**	**Heat of Solution per Mole of Solute (kJ)**
$O_{2(g)}$	$N_{2(g)}$	Gaseous	0
Toluene	Benzene	Ideal	-0.1
Acetone	Chloroform	Non ideal	5
$NaCl_{(s)}$	$H_2O_{(\ell)}$	Ionic	-3.9
$H_2SO_4(\ell)$	$H_2O_{(\ell)}$	Ionic	95.3

Positive values are heat released

Most solutions can be described as having a majority called a solvent and one or more minority ingredients called solutes. The solvent is usually a liquid, whereas solutes can be solids, liquids, or gases. Solutions can be distinguished from compounds by the kind of interaction between ingredients. Compounds form as a result of interactions between relatively permanent partners, while the interactions in solutions involve continuously variable sets of solute and solvent molecules, and this interaction is widely distributed among a large and solvent molecule. Above table gives some examples of solutions and for each we want to be able to understand why the solute dissolves in the solvent.

$O_{2(g)}$ in $N_{2(g)}$: This first example is; of course, of one gas dissolved in another all gases dissolve in each other in all proportions. The reason for this is that solute and solvent do not interact. This is illustrated in fig. which shows that

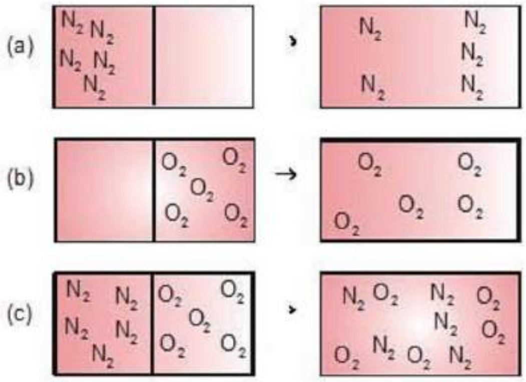


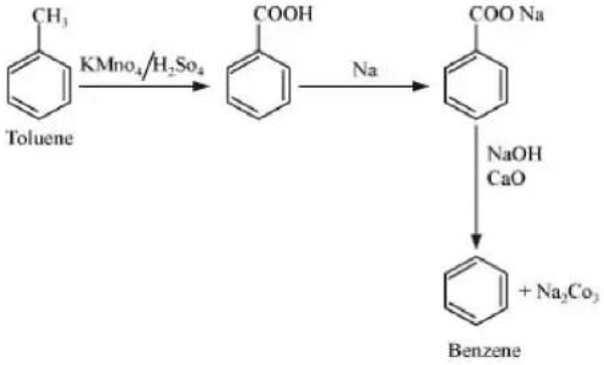
Fig: The expansion of gas as illustrated by a solution of N_2 and O_2 (diagrammatic). The expansions of (a) N_2 and of (b) O_2 are shown to be equivalent to forming (c) a solution of N_2 and O_2.

The process of two gases dissolving in each other is equivalent to the expansion of each gas into the larger volume without any interaction with the other. As we can see from this figure and as we also know from our daily experience, this mixing takes place spontaneously. In a gas, the high thermal energy that the molecules posses keeps them always on the move. This motion allows them to distribute themselves between the two bulbs in an arrangement with the greatest probability of occurring.

That distribution results in equal O_2 or N_2 partial pressures in each bulb with the N_2 and O_2 completely mixed. It is important to note that the energy of the system has not changed, only the way in which the molecules are distributed; that is, the entropy, S of the system has changed. On the molecular level, entropy is a measure of randomness; a maximum in entropy corresponds to the most probable distribution on a statistical basis.

While the mixing of ideal gases is controlled by entropy, the mixing of molecules that interact with each other can surely be controlled by energy. In the mixing process the molecular interactions can either cause the energy to increases or decrease. Chemical changes that are very exothermic show a large decrease in energy and enthalpy; as a result, they are spontaneous. However, most solutes dissolve in solvents because mixing increase the system's entropy ($\Delta S > 0$); that it is more probable for the solutes to dissolve in the solvents then for them to remain separate as pure substances.

Toluene in Benzene:



These two similar liquids readily dissolve in each other. At first glance we might think this solution shows the same pattern of mixing as do two ideal gases, but this cannot be correct since the molecules in a liquid interact with each other very strongly. The key to this solution is that the molecules of the two liquids have similar electronic structures and similar sizes. As a result, the benzene - benzene, benzene - toluene and toluene - toluene interactions are very similar. A toluene molecule, as an approximation, does not know if it is surrounded by other toluene molecule or by benzene molecules.
As we might expect, there is a very negligible heat of solution. These two liquids completely dissolve one in the other and are an ideal solution. These two liquids completely dissolve one in what is called an ideal solution. The entropy gained by mixing toluene with benzene is the same as that gained by mixing two ideal gases. Solvent and solute molecules have no specific interaction with each other that do not have with molecules of their own kind. As a result the molecules distribute randomly in the solution and the change in entropy upon mixing is the same as that for two ideal gases.

Acetone in Chloroform: These two liquids are not very similar; the attraction of acetone and chloroform molecules for each other is quite different from the attraction of the like molecules for each other. When acetone and chloroform are mixed heat is given off so they do not form an ideal solution.
Even so, they are completely miscible. In some cases when the molecules in two liquids have quite different interactions, they may not be completely miscible. For example water and acetone are completely miscible, but water and chloroform are not. The property of liquids used to characterize solvent - solute

interactions is called polarity. Polarity measures the small separation of positive and negative charges in molecules. Water is considered to be the most polar of the common solvents, as attested by the fact that it is the best solvent for ionic solutes. Acetone has an intermediate value of polarity, and chloroform is much less polar than acetone. Molecules interact very differently with molecules of widely different degrees of polarity than they do with others of their own kind. This difference in interaction leads to immiscibility.

$NaCl(s)$ in $H_2O(\ell)$:

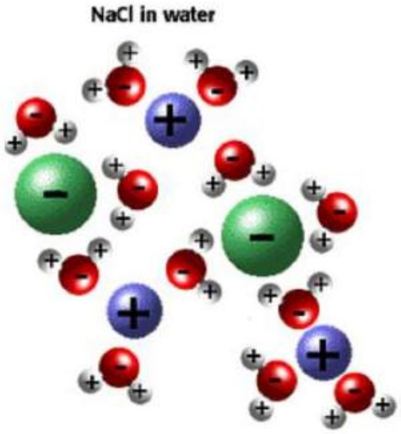


Fig: NaCl in H_2O

The compound NaCl has the high melting temperature characteristic of most ionic solids. It consist of Na and Cl^- ions. When NaCl dissolves in water, these ions interact with the water molecules and separate. The interaction with water is particularly large for positively charged ions, and the Na is surrounded by six closely bound water molecules, Ions surrounded by closely bound water molecules are said to be hydrated. For salts such as $CaCl_2$ of $AlCl_3$, the water molecules interact even more strongly with their cations and they give off heat when they dissolve.

For NaCl the energy required to separate the Na and Cl - ions is nearly balanced by the energy of interaction between the water and the ions. Salts such as $NaNO_3$ or NH_4NO_3 make their solutions colder when they dissolve to produce hydrated Na, NH_4, and NO_3- ions. The entropy of solution for an ionic solid would never be expected to be as high as its entropy of vaporization; nevertheless, salts such as NaCl and $NaNO_3$ dissolve in water because there is a grater probability of finding them in the form of separated and hydrated ions than packed neatly in a solid. Again entropy is the controlling factor.

$H_2SO_4(\ell)$ in $H_2O(\ell)$: Almost every chemist knows that H_2SO_4 gives off a large amount of heat when it dissolves in water. While pure H_2SO_4 does not contain ions, as indicted by that fact that it is a liquid at room temperature, in dilute aqueous solutions it completely ionizes into H and SO_4^{2-}. Its high heat of solution arises largely from the heat of hydration of H. Other proton - yielding solutes like HCl(g) and $HClO_4(\ell)$ also have large, positive heats of solution so they readily dissolve in water.

LIQUID SOLUTION

Concept of Vapour Pressure: When a pure liquid is kept in closed vessel (in which no air is present) the liquid evaporates to give the vapours. After sometime a dynamic equilibrium is established between liquid and vapours. The pressure that the vapours exert at equilibrium on the walls of the container or on the surface of the liquid is called the vapour pressure of the liquid at that temperature, Figure (a).

Case 1: What would happen to the vapour pressure of the liquid if we take a bigger container, Figure (b) or a wider container, Figure (c).

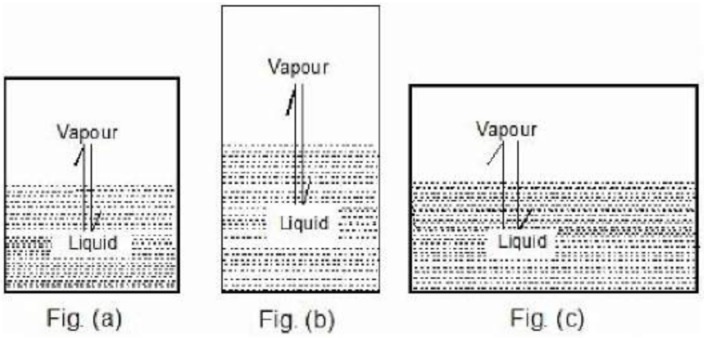
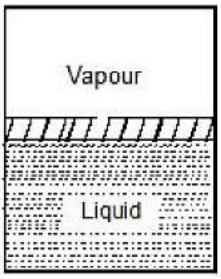


Fig. (a) Fig. (b) Fig. (c)

Key concept:

When the liquid is in equilibrium with vapours, Liquid $\rightleftharpoons$ Vapours, the K_p of the system is $K_p = P_v$, where P_v is the vapour pressure. We know that Kp for a given chemical equilibrium is a constant and only depends on temperature. There fore the vapour pressure of the liquid is a constant and does not depend on the nature of the vessel used and that it only depends on temperature.

Case 2: Take a vessel with the same liquid as in case 1 and cover it with a glass plate (of negligible weight) having a hole in it. Would the vapour pressure be the same now?

Key concept:

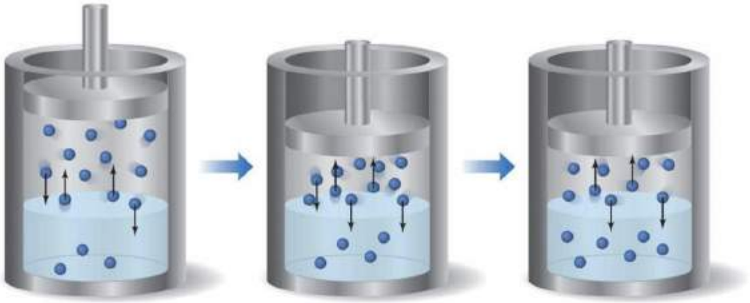
Well, the liquid system is the same and the temperature is also same. There fore the vapour pressure should be same. The vapour pressure of a liquid is independent of the surface area exposed on top of the liquid surface provided the surface area exposed should not be zero.

Henry's Law: Effect of Pressure on Solubility of Gases in Liquids

Henry's Law

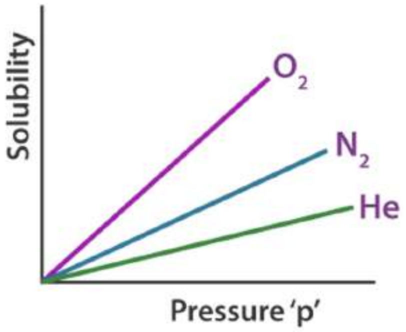
Henry's Law gives a quantitative relation between pressure and gas solubility in a liquid. It states that:
The solubility of a gas in a liquid is directly proportional to the partial pressure of the gas present above the surface of liquid or solution.

The solubility is taken as the mass of the gas dissolved per unit volume of the liquid. Thus, if m is the mass of the gas dissolved per unit volume of the solvent and P is the pressure of the gas in equilibrium with the solution, then
$m \propto p$
$m = Kp$
where K is the proportionality constant.
When $P = 1$, $m = K$, i. e., the solubility of the gas at unit pressure is equal to constant K.



Factors Affecting the Henry's Law Constant

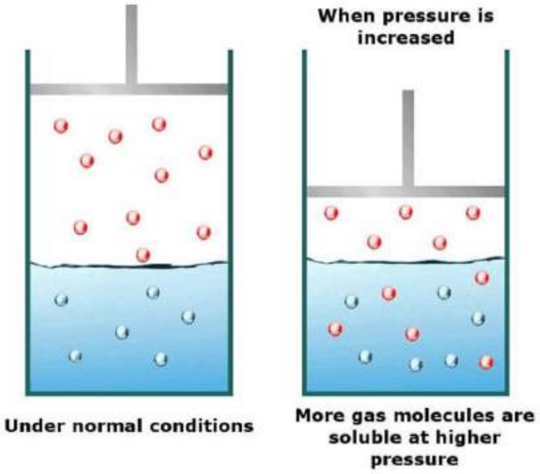
1. The nature of the gas
2. Nature of solvent
3. Temperature
4. The units of pressure



Therefore, different gases have different Henry's laws constant in different solvents, as illustrated graphically above.

Effect of Pressure on Solubility of Gases in Liquids

1. Solubility of a gas in liquid increases with an increase in pressure and vice versa. That is the solubility of a gas in liquid decreases with a decrease in pressure.



2. The solubility of a gas in liquid decreases with an increase in Henry's Law constant (K_H), at a given pressure.

This means at a given pressure higher the value of K_H (Henry's Law constant), the lower is the solubility of the gas in a liquid and vice versa.

Example 1. If N_2 gas is bubbled through water at 293 K, how many millimoles of N_2 gas would dissolve in 1 litre of water? Assume that N_2 exerts a partial pressure of 0.987 bar. Given that Henry's law constant for N_2 at 293 K is 76.48 kbar.

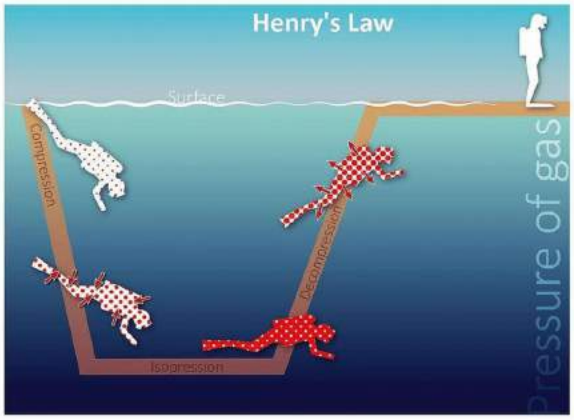
Solution.

The solubility of gas is related to the mole fraction in aqueous solution.
The mole fraction of the gas in the solution is calculated by applying Henry's law. **Thus:**
x (Nitrogen) = p(nitrogen)/K_H = 0.987 bar/76.480 = 1.29×10^{-5}
As 1 litre of water contains 55.5 mol of it, therefore if n represents number of moles of N_2 in solution,
x (Nitrogen) = n mol/n mol + 55.5 mol = n/55.5 = 1.29×10^{-5}
(n in denominator is neglected as it is $<<$ 55.5)
Thus n = $1.29 \times 10^{-5} \times 55.5$ mol = 7.16×10^{-4} mol

Application of Henry's Law

1. **Pepsi and other Carbonated Drinks:** Since the solubility of a gas in liquid increases with an increase in pressure, hence increasing the solubility of CO_2 in soft drinks and soda water, the bottle is sealed under high pressure.
2. Scuba divers have to face the problems of bends. When they dive and go deeper in water, pressure gradually increases resulting in an increase in the solubility of atmospheric gases in the blood. Bends is a medical condition which blocks the blood capillaries due to the formation of bubbles of nitrogen in the blood. Bends is very painful and dangerous to live.

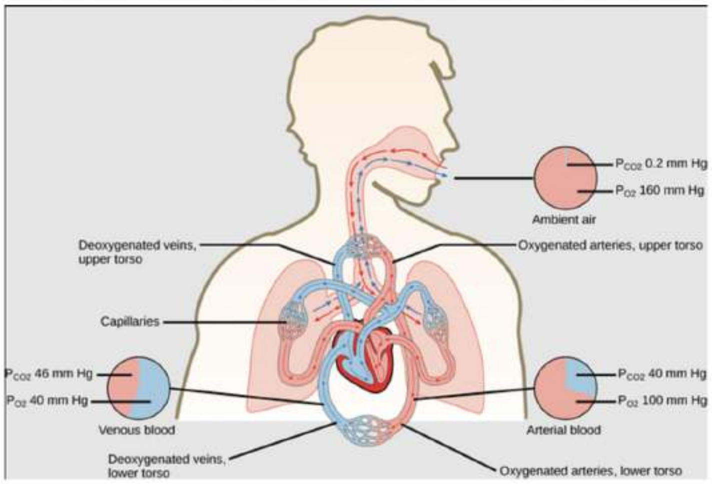
   When scuba divers come towards the surface of the water they have to face bends. Hence scuba diver uses a tank filled with air diluted with helium (11.7% helium, 56.2% nitrogen and 32.1% oxygen) to avoid bends as well as toxic effects of high concentration of nitrogen in the blood because of increase in pressure underwater and decreasing pressure towards the water surface.



3. People, who live at high altitudes and climbers (mountaineers) have to face a problem called anoxia. Anoxia is also a medical condition.

The partial pressure of oxygen in the atmosphere decreases with high altitude. A decrease in partial pressure of oxygen leads to a low concentration of oxygen in blood and tissues. Because of low concentration of oxygen people feel short of breath and become weak and unable to think clearly To avoid the condition of anoxia, mountaineers use oxygen cylinder while climbing to high altitude.

4. **Respiration and the Oxygenation of Blood:** In the lungs, where oxygen is present in the air with high partial pressure, haemoglobin combines with oxygen to form oxyhaemoglobin. In tissues where the partial pressure of oxygen is low, oxyhaemoglobin releases oxygen for utilization in cellular activities.



Respiration and the Oxygenation of Blood

Limitations of Henry's Law

Henry's law holds good if the following conditions are fulfilled:

- The pressure is not too high,
- The temperature is not very low,
- The gas does not chemically combine with the solvent.

Example.2. Calculate the concentration of CO_2 in a soft drink that is bottled at partial pressure of CO_2 of 4 atm' over the liquid at 25° C. The Henry' Law constant for CO_2 in water at 25 °C is 3.1×10^{-2} mol/litre-atm.

Solution.
According to Henry's Law:
$S = KP$
$3.1 \times 10^{-2} \times 4 = 0.12$ mol litre^{-1}

The natural waters contain dissolved; O_2 which is vital for the existence of aquatic life in the sea, rivers and lakes.

There are many gases that readily dissolve in water, while there are gases that do not dissolve in water under normal conditions. **Oxygen is only sparingly soluble in water while HCl or ammonia readily dissolves in water.** The solubility of a gas in a liquid is expressed in terms of the absorption coefficient. It is defined as the volume of the gas in mL that can be dissolved by 1 mL of a liquid solvent at the temperature of the experiment at one atmospheric pressure. The volume of the gas is measured at STP. Thus, if v is the volume of the gas dissolved, reduced to STP, V is the volume of the solvent and P is the pressure of the gas in atmospheres, then the absorption coefficient, a, is given by $\alpha = v/VP$

FACTORS AFFECTING SOLUBILITY

1. **Effect of Pressure:**

   It has been found that the gas solubility in liquids increases with an increase in pressure. To have a better understanding of the effect of pressure on gas solubility let us consider a system of a gas solution in a solvent in a closed container in a state of dynamic equilibrium. Now the solution is in equilibrium and hence the rate of gaseous molecules entering the solution is equal to the rate of gaseous molecules leaving the solution.

   Now suppose we increase the pressure of the system by compressing the gas molecules present in the solution. As a result of an increase in pressure, the gases molecules will now be concentrated in a smaller volume. This will result in an increase in the number of gas molecules per unit volume available above the solution. Since the number of gas molecules presents above the solution has increased, the rate with which the gas molecules will be entering the solution will also increase. The end result is an increase in the number of gas molecules in the solution until a new equilibrium point is attained. Thus the solubility of gases increases with an increase in the pressure of a gas above the solution.

2. **Effect of Temperature:**
   Gas solubility in liquids is found to decrease with an increase in temperature. The gas molecules in a liquid are dissolved by the process of dissolution. During this process, heat is evolved. According to Le Chatelier's Principle which states that when the equilibrium of a system is disturbed, the system readjusts itself in such a way that the effect that has caused the change in equilibrium is countered. So, as we know that dissolution is an exothermic process, the solubility should decrease with an increase in temperature to validate Le Chatelier's Principle.
3. **Nature of the gas and solvent:**
   Generally, the gases which can be easily liquefied are more soluble in common solvents.
   Example: CO_2 is more soluble in water than oxygen or hydrogen. The gases which react with the solvent possess higher solubility. HCl and NH_3 are highly soluble in water. Oxygen, nitrogen and carbon dioxide are much more soluble in ethyl alcohol than in water. at the same temperature and pressure.

Solubility of Liquids In Liquids

Water is known as a universal solvent as it dissolves almost every solute except for a few. Certain factors can influence the solubility of a substance.
Solubility is the new bond formation between the solute molecules and solvent molecules. In terms of quantity, solubility is the maximum concentration of solute that dissolves in a known concentration of solvent at a given temperature. Based on the concentration of solute dissolves in a solvent, solutes are categorized into highly soluble, sparingly soluble or insoluble. If a concentration of 0.1 g or more of a solute can be dissolved in a 100ml solvent, it is said to be soluble. While a concentration below 0.1 g is dissolved in the solvent it is said to be sparingly soluble. Thus, it is said that solubility is a quantitative expression and expressed by the unit gram/litre (g/L).

Based on solubility, different types of solution can be obtained. A saturated solution is a solution where a given amount of solute is completely soluble in a solvent at a given temperature. On the other hand, a supersaturated solution is one where solute starts salting out or precipitate after a particular concentration is dissolved at the same temperature.

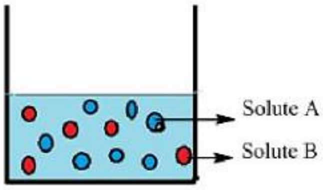
Factors Affecting Solubility

The solubility of a substance depends on the physical and chemical properties of that substance. In addition to this, there are a few conditions that can manipulate it. Temperature, pressure and the type of bond and forces between the particles are few among them.

1. **Temperature:**
   By changing the temperature we can increase the soluble property of a solute. Generally, water dissolves solutes at 20° C or 100° C. Sparingly soluble solid or liquid substances can be dissolved completely by increasing the temperature. But in the case of gaseous substance, temperature inversely influences solubility i.e. as the temperature increases gases expand and escapes from their solvent.
2. **Forces and Bonds:**
   Like dissolves in like. The type of intermolecular forces and bonds vary among each molecule. The chances of solubility between two unlike substances are more challengeable than the like substances. For example, water is a polar solvent where a polar solute like ethanol is easily soluble.
3. **Pressure:**
   Gaseous substances are much influenced by solids and liquids by pressure. When the partial pressure of gas increases, the chance of its solubility is also increased. A soda bottle is an example of where CO_2 is bottled under high pressure.

Expressing Concentration of Solution: Mole Fraction

Mole fraction



Mole fraction can be defined as the ratio of number of moles of the component in the solution to the total number of moles of all components in the solution.

- It is denoted by the alphabet x and subscript written on the right hand side of x denotes the component of which mole fraction is being calculated.
- Mathematically, Mole fraction of a component

$$= \frac{\text{Number of moles of the component}}{\text{Total number of moles of all components}}$$

- Let us consider a binary mixture of A and B. Let the number of moles of A and B bee n_A and n_B respectively, then

$$\text{Mole fraction of A} = x_A = \frac{n_A}{n_A + n_B}$$

$$\text{Mole fraction of B} = x_B = \frac{n_B}{n_A + n_B}$$

- For solution where number of components = i

$$\text{Mole fraction} = x_i = \frac{n_i}{n_1 + n_2 + \ldots\ldots + n_i} = \frac{n_i}{\sum n_i}$$

- In a given solution sum of the mole fractions of all the components is unity.
  Mathematically, $x_1 + x_2 + x + x_i = 1$

Problem 1. Calculate the mole fraction of benzene in solution containing 30% by mass in carbon tetrachloride.

Solution.

Total mass of the solution = 100 g
Mass of benzene = 30 g.
∴ Mass of carbon tetrachloride = (100 - 30) g = 70 g
Molar mass of benzene (C_6H_6) = (6 × 12 + 6 × 1) g mol^{-1} = 78 g mol^{-1}
∴ Number of moles of C_6H_6 =30/78 mol
= 0.3846 mol
Molar mass of carbon tetrachloride (CCl_4) = 1 × 12 + 4 × 355 = 154 g mol^{-1}
∴ Number of moles of CCl_4 = 70/154 mol = 0.4545 mol
Mole fraction of C_6H_6

$$= \frac{\text{Number of moles of } C_6H_6}{\text{Number of moles of } C_6H_6 + \text{Number of moles of } CCl_4} \times 100\%$$

$$= \frac{0.3846}{0.3846 + 0.4545} = 0.458$$

Problem 2. A tank is charged with a mixture of 1.0×10^3 mol of oxygen and 4.5×10^3 mol of helium. Calculate the mole fraction of each gas in the mixture.

Solution.

The given parameters are
$N_{He} = 4.5 \times 10^3$ mol and $N_{O2} = 1.0 \times 10^3$ mol
Mole fraction can be calculated as
$X_{He} = 4.5 \times 10^3 \text{ mol} / 4.5 \times 10^3 \text{ mol} + 1.0 \times 10^3 \text{ mol}$
$X_{He} = 4.5 \text{ mol} / 5.5 \text{ mol}$
$X_{He} = 0.82$
$X_{O2} = 2.0 \times 10^3 \text{ mol} / 4.5 \times 10^3 \text{ mol} + 1.0 \times 10^3 \text{ mol}$
$X_{O2} = 1.0 \times 10^3 / 5.5 \times 10^3$
$X_{O2} = 0.18$

Problem 3. Determine the mole fraction of methanol CH_3OH and water in a solution prepared by dissolving 4.5 g of alcohol in 40 g of H_2O. M of H_2O is 18 and M of CH_3OH is 32.

Solution.

Moles of $CH_3OH = 4.5 / 32 = 0.14$ mole
Moles of $H_2O = 40 / 18 = 2.2$ moles
Therefore, according to the equation
mole fraction of $CH_3OH = 0.14 / 2.2 + 0.14$
$= 0.061$

Problem 4. What is the mole fraction of carbon tetrachloride (CCl4) in solution if 3.47 moles of CCl4 is dissolved in 8.54 moles of benzene (C_6H_6)?

Solution.

$$\text{Mole Fraction } CCl_4 (\chi_{CCl_4}) = \frac{\text{moles of } CCl_4}{\text{total moles}}$$

$$\chi_{CCl_4} = \frac{3.47 \text{ moles } CCl_4}{3.47 \text{ moles } CCl_4 + 8.54 \text{ moles } C_6H_6}$$

$\chi_{CCl_4} = 0.289$

Problem 5. What is the mole fraction of formaldehyde (CH_2O) in solution if 25.7 grams of CH_2O is dissolved in 3.25 moles of carbon tetrachloride (CCl_4)?

Solution.
The grams of acetone will need to be converted into moles in order to solve for mole fraction.

$$25.7\ grams\ CH_2O \times \frac{1\ mole\ CH_2O}{30.03\ grams\ CH_2O} = 0.856\ moles\ CH_2O$$

$$Mole\ Fraction\ CH_2O(\chi_{CH_2O}) = \frac{moles\ of\ CH_2O}{total\ moles}$$

$$\chi_{CH_2O} = \frac{0.856\ moles\ CH_2O}{0.856\ moles\ CH_2O + 3.25\ moles\ CCl_4}$$

$$\chi_{CH_2O} = 0.208$$

Problem 6. 0.100 mole of NaCl is dissolved into 100.0 grams of pure H_2O. What is the mole fraction of NaCl?

Solution.
100.0 g / 18.0 g mol^{-1} = 5.56 mol of H_2O
Add that to the 0.100 mol of NaCl = 5.56 + 0.100 = 5.66 mol total
Mole fraction of NaCl = 0.100 mol / 5.66 mol = 0.018

The mole fraction of the H_2O:

5.56 mol / 5.66 mol = 0.982

Problem 7. A solution is prepared by mixing 25.0 g of water, H_2O, and 25.0 g of ethanol, C_2H_5OH. Determine the mole fractions of each substance.

Solution.
(1) Determine the moles of each substance:
H2O ⇒ 25.0 g / 18.0 g/mol = 1.34 mol
C_2H_5OH ⇒ 25.0 g / 46.07 g/mol = 0.543 mol
(2) Determine mole fractions:
H_2O ⇒ 1.34 mol / (1.34 mol + 0.543 mol) = 0.71
C_2H_5OH ⇒ 0.543 mol / (1.34 mol + 0.543 mol) = 0.29

Problem 8. A solution contains 10.0 g pentane, 10.0 g hexane and 10.0 g benzene. What is the mole fraction of hexane?

Solution.
(1) You need to determine the moles of pentane, hexane and benzene:
to do this, you need the molecular weights. Here are the formulas:
pentane: C_5H_{12}
hexane: C_6H_{14}
benzene: C_6H_6
(2) When you have the moles of each, add them together.
(3) Then, divide the moles of hexane by the total.

Problem 9. The molality of an aqueous solution of sugar ($C_{12}H_{22}O_{11}$) is 1.62m. Calculate the mole fractions of sugar and water.

Solution.
(1) Molality is moles solute / kg of solvent. There fore we know our solution is:
1.62 mol $C_{12}H_{22}O_{11}$
1.00 kg = 1000 g of water
(2) Calculate the moles of water present:
1000 g / 18.0152 g/mol = 55.50868 mol
(3) Determine the mole fraction of the sugar:
1.62 mol / (1.62 mol + 55.50868 mol) = 0.028357 = 0.0284 (to three sf)
(4) You can calculate the mole fraction of the water by subtraction.

Problem 10. How many grams of water must be used to dissolve 100.0 grams of sucrose ($C_{12}H_{22}O_{11}$) to prepare a 0.020 mole fraction of sucrose in the solution?

Solution.
(1) Determine moles of sucrose:
100.0 g / 342.2948 g/mol = 0.292145835 mol
(2) Determine moles of water required to make the solution 0.020 mole fraction of sucrose:
$0.020 = 0.292 / (0.292 + x)$
$(0.020)(0.292 + x) = 0.292$
$0.00584 + 0.02x = 0.292$
$0.02x = 0.28616$
x = 14.308 mol of H_2O
Comment: you can also do this:
0.292 is to 0.02 as x is to 0.98

(3) Determine grams of water:
14.308 mol × 18.015 g/mol = 258.0 g

Problem 11. Surprisingly, water (in the form of ice) is slightly soluble in liquid nitrogen. At -196 °C, (the boiling point of liquid nitrogen) the mole fraction of water in a saturated solution is 1.00×10^{-5}. Compute the mass of water that can dissolve in 1.00 kg of boiling liquid nitrogen.

Solution.
(1) Use the definition of mole fraction to set up the following:
χ_{water} = moles water / (moles water + moles nitrogen)
$1.00 \times 10^{-5} = x / (x + 71.3944041)$
I'm going to carry some guard digits until the end of the calculation.
(2) Some algebra:
$(1.00 \times 10^{-5}) (x) + 7.139440411 \times 10^{-4} = x$
$0.99999x = 7.139440411 \times 10^{-4}$
$x = 7.139511806 \times 10^{-4}$ mol of H_2O
(3) Calculate grams of water from moles of water:
$7.139511806 \times 10^{-4}$ mol × 18.0152 g/mol = 1.2862×10^{-2} g
1.29×10^{-2} g (to three sf)

Problem 12. What is the mole fraction of cinnamic acid in a mixture that is 50.0% weight urea in cinnamic acid (urea = 60.06 g/mol; cinnamic acid = 148.16 g/mol)

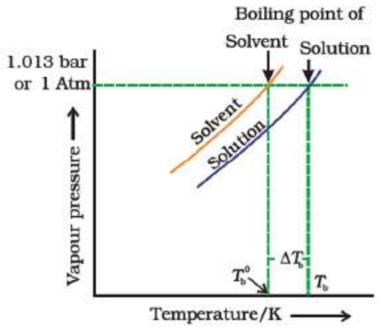
Solution.
(1) Let us assume 100.0 g of this mixture are present.
Therefore:
50.0 g is urea
50.0 g is cinnamic
(2) Convert grams to moles:
urea: 50.0 g / 60.06 g/mol = 0.8325 mol
cinnamic acid: 50.0 g / 148.16 g/mol = 0.3375 mol
(3) Determine mole fraction of cinnamic acid:
0.3375 mol / 1.1700 mol = 0.2885

Colligative Properties: Elevation in Boiling Point & Depression in Freezing Point

What is Boiling Point Elevation?

- Boiling point elevation refers to the increase in the boiling point of a solvent upon the addition of a solute.

- When a non-volatile solute is added to a solvent, the resulting solution has a higher boiling point than that of the pure solvent. For example, the boiling point of a solution of sodium chloride (salt) and water is greater than that of pure water.
- Boiling point elevation is a colligative property of matter, i.e. it is dependent on the solute-to-solvent ratio but not on the solute's identity. This implies that the elevation in the boiling point of a solution depends on the amount of solute added to it.
- The greater the concentration of solute in the solution, the greater the boiling point elevation.



Why Does Boiling Point Elevation Occur?

- Since the addition of a non-volatile solute causes a decrease in the vapour pressure of a solution, the boiling point of a solution is elevated as compared to the solvent i.e it must be heated to a higher temperature to make its vapour pressure equal to atmospheric pressure. Thus the solution boils at a higher temperature than the pure solvent.
- If T_b° is the boiling point of the solvent and T_b is the boiling point of the solution.

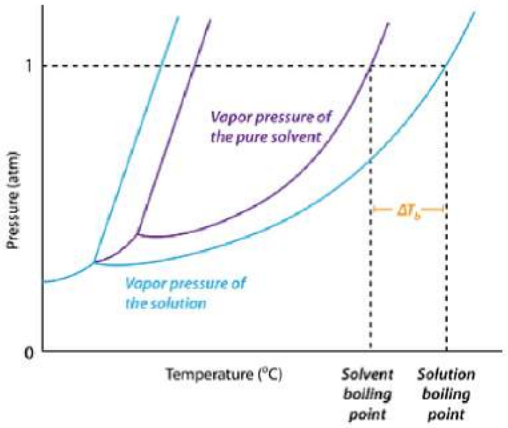


Fig: Elevation in boiling point

We can see from the figure that the solution needs to be heated to a higher temperature to make it boil.

The difference between the boiling points of the solution and the solvent is known as the elevation in boiling point (ΔT_b).

Elevation of boiling point, (ΔT_b) = Boiling point of the solution - Boiling point of pure solvent
Elevation of boiling point, (ΔT_b) = $T_b - T_b^{\circ}$
Experimentally, it is observed that elevation in boiling point is directly proportional to molal concentration of solute dissolved indefinite amount of the solvent.
$\Delta T_b \propto$ molality
$\Delta T_b = K_b \times$ molality (1)
$\Delta T_b = K_b \times m$
Where K_b is proportionality constant and is known as the molal boiling point elevation constant or the ebullioscopic constant. It has the units of degree kg mol^{-1} or K kg mol^{-1}.
Molality can be written as:

Molality (m) = Number of moles of solute/Mass of solvent in kg

$$m = \frac{\frac{w}{M}}{\frac{W\ (in\ Kg)}{1000}} = \frac{w \times 1000}{MW\ (in\ kg)}$$

w = mass of solute in grams
M = molecular wt of solute
W = mass of solvent in gram.

$$\Delta T_b = K_b \times \frac{\frac{w}{M}}{\frac{W\ (in\ Kg)}{1000}} = \frac{w \times 1000}{MW\ (in\ kg)}$$

Significance of K_b

Now if, m = 1 then,
$\Delta T_b = K_b$. Thus, the molal elevation constant K_b is defined as the elevation of the boiling point when the molality of the solution is one i.e. when 1 mole of the solute is dissolved in 1 kg of the solvent, the elevation of boiling point is equal of K_b.

Example 1. A 5 percent aqueous solution by mass of a non-volatile solute boils at 100.15°C. Calculate the molar mass of the solute. $K_b = 0.52$ K kg mol $^{-1}$.

Solution.

The normal boiling point of water is 100°C.
The elevation in boiling point is 0.15°C.
A 5 percent solution means that in a 100 g solution 5 g of the solute is present.
This implies that the solvent is 95 g.
If the molar mass of the solute is M, then the molality of the solute in the solution is,

$$\frac{5/M}{95} \times 1000, \triangle T_b = K_b\, m$$

$$0.15 = 0.52 \times \frac{5/M}{95} \times 1000$$

M = 182.4 g/mol

Example 2. A solution of 12.5 g urea in 170 g of water gave a boiling point elevation of 0.63 K. Calculate the molar mass of urea, taking $K_b = 0.52$ K/m.

Solution.

Given: Mass of urea, $w_2 = 12.5$ g
Mass of water, $w_1 = 170$ g = 0.17 kg
Evaluation of boiling point, $\Delta T_b = 0.63$ K
Molar mass of urea, M =?
$K_b = 0.52$ K m^{-1}
Molar mass of the solute (urea) is given by:

$$M = \frac{K_b \times W_2}{W_1 \times \triangle T_b} = \frac{0.52 \times 12.5}{0.17 \times 0.63} g/mol$$

= 60.7 g mol $^{-1}$

Example 3. Calculate the molecular mass of a substance 1.0 g of which on being dissolved in 100 g of solvent gave an elevation of 0.307 K in the boiling point. (Molal elevation constant (K_b) = 1.84 K/m).

Solution.

We know that, ΔT_b =, where n_2 is the no. of moles of solute; w_1 is the mass of the solvent in kg.
n_2 = Mass of solute/Molar mass of the solute = 1.0 g/M and w_1 = 100 g = 0.1 kg
Substituting these values, we get,

$$0.307\ k = \frac{1.84\ K\ kg\ mol^{-1}}{0.1kg} \times \frac{1.0g}{M}$$

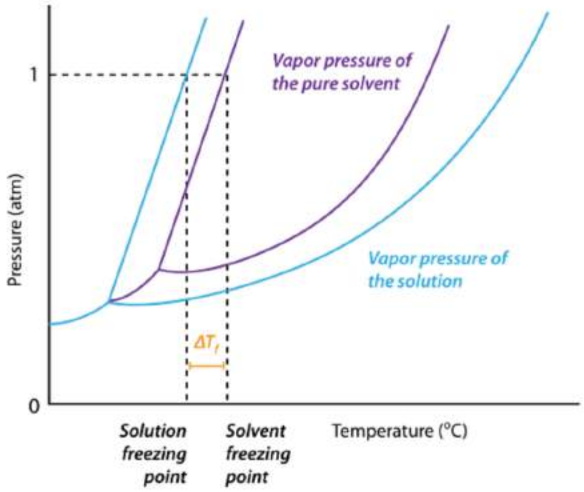
$$So,\ M = \frac{1.84\ K\ kg\ mol^{-1} \times 1.0\ g}{0.1kg \times 0.307\ K} = \frac{1.84 \times 1.0}{0.1 \times 0.307}\ g/mol$$

$= 59.9$ g/mol

What is Freezing Point Depression?

The freezing point of a substance is the temperature at which it's liquid and the solid phases have the same vapour pressure.

It is a colligative property of solutions that is generally proportional to the molality of the added solute. The depression in the freezing point of a solution can be described by the following formula: $\mathbf{\Delta T_f = iK_f \times m}$
Where ΔTf is the freezing point depression,
i is the Van't Hoff factor,
K_f is the cryoscopic constant, and
m is the molality.

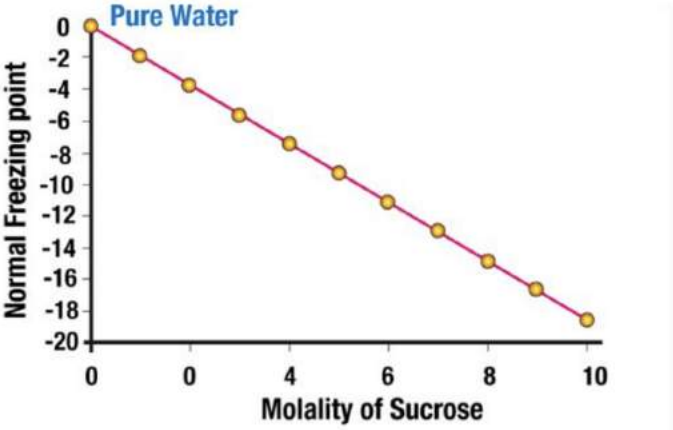


Why does the Freezing Point Depression Occur?

The reason for the depression of the freezing point of a solvent upon the addition of a solute is explained below:

1. At the freezing point of a solvent, there exists an equilibrium between the liquid state and the solid-state of the solvent.
2. This implies that the vapour pressures of both the liquid and the solid phase are equal.

3. Upon the addition of a solute that is non-volatile, the vapour pressure of the solution is found to be lower than the vapour pressure of the pure solvent.
4. This causes the solid and the solution to reach equilibrium at lower temperatures.



If the difference between the freezing point of the solvent and the solution is represented as ΔT_f,
Depression of Freezing point, (ΔT_f) = Freezing point of the solution - Freezing point of pure solvent
Depression of Freezing point, (ΔT_f) = $T_f - T_f^\circ$
Experimentally, it is observed that Depression in the Freezing point is directly proportional to the molal concentration of solute dissolved indefinite amount of the solvent.
$\Delta T_f \propto$ molality
$\Delta T_f = K_f \times$ molality .....(1)
$\Delta T_f = K_f \times m$
Where K_f is proportionality constant and is known as the molal Depression point constant or the Cryoscopic constant. It has the units of degree kg mol^{-1} or K kg mol^{-1}.

Molality can be written as

Molality (m) = Number of moles of Solute/Mass of Solvent in Kg

$$m = \frac{\frac{w}{M}}{\frac{W\,(in\,Kg)}{1000}} = \frac{w \times 1000}{M \times W\,(in\,kg)}$$

w = mass of solute in grams
M = molecular wt of solute

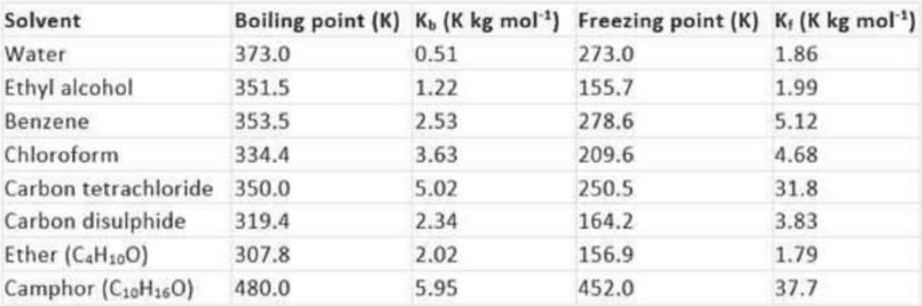
W = mass of solvent in gram.

$$\Delta T_f = K_f \times \frac{\frac{w}{M}}{\frac{W\ (in\ Kg)}{1000}} = \frac{w \times 1000}{M \times W\ (in\ kg)}$$

Significance of K_f:

$\Delta T_f = K_f m$. So, if m = 1 i.e. one mole of solute is dissolved in one kg of the solvent, then, $\Delta T_f = K_f$.
Thus,
The molal freezing point depression constant is equal to the depression in the freezing point produced when one mole of solute is dissolved in 1 kg of the solvent.

The values of molal elevation constant (K_b) for some common solvents are given in Table.



Solvent	Boiling point (K)	K_b (K kg mol^{-1})	Freezing point (K)	K_f (K kg mol^{-1})
Water	373.0	0.51	273.0	1.86
Ethyl alcohol	351.5	1.22	155.7	1.99
Benzene	353.5	2.53	278.6	5.12
Chloroform	334.4	3.63	209.6	4.68
Carbon tetrachloride	350.0	5.02	250.5	31.8
Carbon disulphide	319.4	2.34	164.2	3.83
Ether ($C_4H_{10}O$)	307.8	2.02	156.9	1.79
Camphor ($C_{10}H_{16}O$)	480.0	5.95	452.0	37.7

K_b and K_f can be obtained from the following relationships:

$$K_b = \frac{RT_b^2 M_{solvent}}{1000 \times \Delta_{fus}H}$$

and

$$K_f = \frac{RT_f^2 M_{solvent}}{1000 \times \Delta_{fus}H}$$

Where, T_b = boiling point of the solvent,
T_f = freezing point of the solvent,
$M_{solvent}$ = molar mass of the solvent,
$\Delta_{vap}H$ = enthalpy of vaporization and
$\Delta_{fus}H$ = enthalpy of fusion.

Key concept: Camphor is commonly used in determining the molecular mass of a solute because of its very high cryoscopic constant (K_f).

Example 1. An aqueous solution of a non-volatile solute boils at 100.17°C. At what temperature would it freeze? ($K_b = 0.52$ K kg mol $^{-1}$ and $K_f = 1.88$ K kg mol $^{-1}$).

Solution.
$\Delta T_b = 0.17°C$
$m = \Delta T_b/K_b = 0.17/0.52$
$= 0.327$ molal,
$\Delta T_f = K_f \times$ molality
$\Delta T_f = 1.86 \times 0.327 = 0.608$
Freezing point of the solution is - 0.608°C.

Example 2. 1.4 g of (acetone dissolved) in 100 g of benzene gave a solution which freezes at 277.12 K. Pure benzene freezes at 278.4. 2.8 g of a solid (A) dissolved in 100 g of benzene gave a solution which froze at 277.76 K. Calculate the molecular weight of (A).

Solution.
For acetone solute + Benzene solvent mixture:
$\Delta T = K'_f \times 1000 \times w/M \times W$
$(278.40 - 277.12) = 1000 \times K_f \times 1.4/100 \times 58$
or $1.28 = 1000 \times K_f \times 1.4/100 \times 58$ ...(i)
For solute (A) + Benzene mixture (Let M be the molecular Weight of A)
$(278.40 - 277.76) = 1000 \times K_f \times 2.8/100 \times M$ ...(ii)
By Eqs. (i) and (ii)
M = 232g

Example 3. Ethylene glycol ($HOH_2C - CH_2OH$) is used as an antifreeze for water to be used in car radiators in cold places. How much ethylene glycol should be added to 1 kg of water to prevent it from freezing at -10°C? Molal depression constant of water is 1.86 K kg mol^{-1}.

Solution.
Mass of water (solvent), $w_1 = 1$ kg
$\Delta T_f = 10°C$ $K_f = 1.86$ K kg mol^{-1}
Mass of ethylene glycol required, $w_2 =?$
Molar mass of ethylene glycol = (12 + 3 +16) × 2 g/mol = 62 g/mol
We know, $\Delta T_f = K_f(w_2/62)/w_1$ or $10 = 1.86 \times w_2/62 \text{ x } 1$
This gives, $w_2 = 10 \times 62 \times 1/1.86 = 333.3$ g

Example 4. Normal freezing point of a solvent is 150°C. A 0.5 molal solution of

urea in the above solvent causes a freezing point depression of two degrees. Calculate the molal depression constant

Solution.
We know, $\Delta T_f = K_f m$
So, $K_f = \Delta T_f/m = 2\ \text{deg}/0.5\ \text{mol Kg}^{-1} = 4\ \text{deg. kg mol}^{-1}$

Example 5. A solution of urea in water freezes at 0.400°C. What will be the boiling point of the same solution if the depression and elevation constants for water are 1.86 deg kg mol^{-1} and 0.512 deg kg mol^{-1} respectively? Solution: We have the relationships:

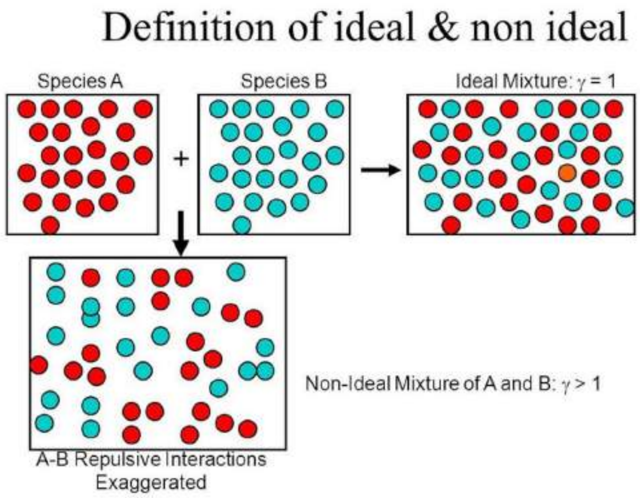
Solution.
$\Delta T_b = K_b n_2/w_1$ ...(i)
And $\Delta T_f = K_f n_2/w_1$ ...(ii)
Where n_2 is the number of moles of the solute, and w_1 is the mass of solvent in kg.
Dividing equation (i) by equation (ii),
$\Delta T_b/\Delta T_f = K_b/K_f$
or,

$$\Delta T_b = \frac{\Delta T_f \times K_b}{K_f} = \frac{0.4 \times 0.512}{1.86}\ ^\circ C$$

$= 0.11^\circ C$
Then, Boiling point of the urea solution = 100°C + 0.11°C = 100.11°C.

Ideal & Non-Ideal Solutions

Raoult's Law states that the mole fraction of the solute component is directly proportional to its partial pressure.
On the basis of Raoult's Law, liquid-liquid solutions are classified into two types of solutions, they are:
- Ideal Solutions
- Non-ideal Solutions



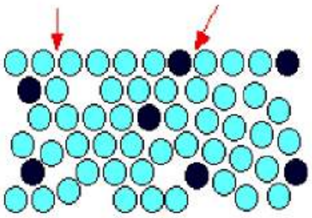
What is an Ideal Solution?

An ideal solution is a mixture in which the molecules of different species are distinguishable, however, unlike the ideal gas, the molecules in ideal solution exert forces on one another. When those forces are the same for all molecules independent of species then a solution is said to be ideal.

Characteristics of Ideal Solution

- The solutions which obey Raoult's Law at every range of concentration and at all temperatures are called Ideal Solutions.
- We can obtain ideal solutions by mixing two ideal components that are, a solute and a solvent having similar molecular size and structure.
  Example: consider two liquids A and B, and mix them. The formed solution will experience several intermolecular forces of attractions inside it, which will be:
  - A – A intermolecular forces of attraction
  - B – B intermolecular forces of attraction
  - A – B intermolecular forces of attraction

- The solution is said to be an ideal solution, only when the intermolecular forces of attraction between A – A, B – B and A – B are nearly equal.



In an ideal solution, the forces between the solvent molecules . . .

. . . are exactly the same as those between solvent and solute.

That means that it takes the same amount of energy for solvent molecules to break away from the surface in either case.

The molecular structure is the same in the case of ideal solutions

- They follow Raoult's Law, which means partial pressure of components A and B in a solution will be $P_A = P_A^0 x_A$ and $P_B = P_B^0 x_B$ where P_A^0 and P_B^0 are respective vapour pressure in pure form and x_A and x_B are respective mole fractions of components A and B.
- The enthalpy of mixing of two components should be zero, that is, $\Delta_{mix} H = 0$. This signifies that no heat is released or absorbed during mixing of two pure components to form ideal solution.
- The volume of mixing of two components should be zero that is, $\Delta_{mix} V = 0$. This means that the total volume of solution is equal to the sum of the volume of solute and solution. Adding further, it also signifies that there is no occurrence of contraction or expansion of volume while mixing of two components.
- The solute-solute interaction and solvent-solvent interaction is nearly equal to solute-solvent interaction

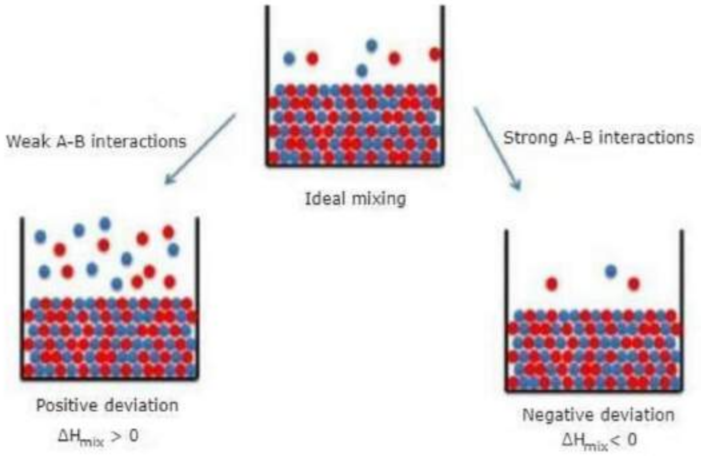
Note: Perfectly ideal solutions are rare in nature, only some solutions show some ideal behaviour.

Examples of Ideal Solutions

- n-hexane and n-heptane
- Bromoethane and Chloroethane
- Benzene and Toluene
- CCl_4 and $SiCl_4$
- Chlorobenzene and Bromobenzene
- Ethyl Bromide and Ethyl Iodide
- n-Butyl Chloride and n-Butyl Bromide

What is a Non-Ideal Solution?

The solutions which don't obey Raoult's law at every range of concentration and at all temperatures are called Non-Ideal Solutions. Non-ideal solutions deviate from ideal solutions and are also known as Non-Ideal Solutions.



Types of Non-Ideal Solutions

Characteristics of Non-Ideal Solution

- The solute-solute and solvent-solvent interaction is different from that of solute-solvent interaction
- The enthalpy of mixing that is, Δmix H $\neq 0$, which means that heat might have released if the enthalpy of mixing is negative (Δmix H < 0) or the heat might have observed if the enthalpy of mixing is positive (Δmix H > 0).
- The volume of mixing that is, Δmix V $\neq 0$, which depicts that there will be some expansion or contraction in dissolution of liquids

Types of Non-Ideal Solution

- Non-ideal solutions showing positive deviation from Raoult's Law
- Non-ideal solutions showing negative deviation from Raoult's Law

Positive Deviation from Raoult's Law

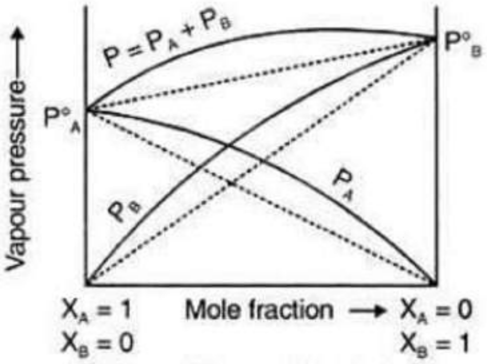
Positive Deviation from Raoult's Law occurs when the vapour pressure of the component is greater than what is expected in Raoult's Law.

Example: consider two components A and B to form non-ideal solutions.

Let the vapour pressure, pure vapour pressure and mole fraction of component A be P_A, $P_A{}^0$ and x_A respectively and that of component B be P_B , $P_B{}^0$ and x_B respectively.

These liquids will show positive deviation when Raoult's Law when

- $P_A > P_A^0 x_A$ and $P_B > P^0_B x_B$, as the total vapour pressure ($P_A^0 x_A + P^0_B x_B$) is greater than what it should be according to Raoult's Law.
- The solute-solvent forces of attraction is weaker than solute-solute and solvent-solvent interaction that is, A – B < A – A or B – B
- The enthalpy of mixing is positive that is, $\Delta_{mix} H > 0$ because the heat absorbed to form new molecular interaction is less than the heat released on breaking of original molecular interaction
- The volume of mixing is positive that is, $\Delta_{mix} V > 0$ as the volume expands on dissolution of components A and B



P-X graph for non-ideal solution showing +ve deviation

Examples: Following are examples of solutions showing positive deviation from Raoult's Law

- Acetone and Carbon disulphide
- Acetone and Benzene
- Carbon Tetrachloride and Toluene or Chloroform
- Methyl Alcohol and Water
- Acetone and Ethanol
- Ethanol and Water

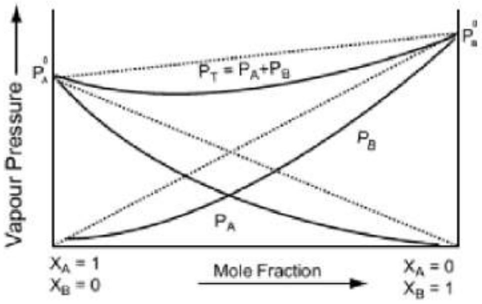
Negative Deviation from Raoult's Law

Negative Deviation occurs when the total vapour pressure is less than what it should be according to Raoult's Law. Considering the same A and B components to form a non-ideal solution, it will show negative deviation from Raoult's Law only when:

- $P_A < P_A{}^0\, x_A$ and $P_B < P^0{}_B\, x_B$ as the total vapour pressure ($P_A{}^0\, x_A + P^0{}_B\, x_B$) is less than what it should be with respect to Raoult's Law
- The solute-solvent interaction is stronger than solute-solute and solvent-solvent interaction that is, A – B > A – A or B – B
- The enthalpy of mixing is negative that is, $\Delta_{\text{mix}} H < 0$ because more heat is released when new molecular interactions are formed
- The volume of mixing is negative that is, $\Delta_{\text{mix}} V < 0$ as the volume decreases on dissolution of components A and B

Examples: Following are examples of solutions showing negative deviation from Raoult's Law

- Chloroform and Benzene
- Chloroform and Diether
- Acetone and Aniline
- Nitric Acid (HNO3) and water
- Acetic Acid and pyridine
- Hydrochloric Acid (HCl) and water



- **Image 5: Graph between vapour pressure and mole fraction**

Ideal solutions	**Non-Ideal solutions**	
	Positive deviation from Raoult's law	**Negative delation from Raoult's law**
1. Obey Raoult's law at every range of concentration	Do not obey Raoult's law.	Do not obey Raoult's law.
2. $\Delta H_{min} = 0$; neither beat is evolved nor absorbed during dissolution.	$\Delta H_{min} = 0$ Endothermic dissolution; heat is absorbed.	$\Delta H_{min} = 0$ Exothermic dissolution; heat is evolved.
3. $\Delta V_{min} = 0$; total volume of solution is equal to sum of volumes of the components.	$\Delta H_{min} = 0$ Volume is increased after dissolution	$\Delta H_{min} = 0$ Volume is decreased after dissolution
4. $P = P_A + P_B = P^o{}_A X_A + P^o{}_B X_B$ i.e, $P_A = P^o{}_A X_A$; $P_B = P^o{}_B X_B$	$P_A > P^o{}_A X_A$; $P_B > P^o{}_B X_B$ $\therefore P_A + P_B > P^o{}_A X_A + P^o{}_B X_B$	$P_A < P^o{}_A X_A$; $P_B < P^o{}_B X_B$ $\therefore P_A + P_B < P^o{}_A X_A + P^o{}_B X_B$
5. A — A, A — B, B - B interactions should be same, and B' are identical in shape, size and character.	A - B attractive force should be weaker than V — A and B B attractive forces. 'A: and B' have different shape, size and character.	A — B attractive force should be greater than A — A and B — B attractive forces. 'A' and B' have different shape, size and character.
6. Escaping tendency of VT and S ¹ should be same m pure liquids and in the solution.	'A' and: B' escape easily showing higher vapour pressure them the expected value.	Escaping tendency of both components **'A'** and 'B' is lowered showing lower vapour pressure than expected ideally
Examples; dilute solutions: benzene - toluene: n-hexane + n-ltplane. chlorobenzene bromobenzene; ethyl bromide + ethyl iodide; n - butyl chloride + n-butyl bromide.	**Examples:** acetone - ethanol acetone - CS,; water + methanol, water + ethanol; CCL_4, + toluene; $CCL_4 + CHC_3$,: acetone + benzene; $CCL_4 + CH_3OH$; cyclohexane - ethanol	**Examples:** acetone - aniline; acetone - chloroform; CH3OH - CH3COOH $H_2O + HNO_3$ chloroform + diethyl ether, water - HCL, acetic acid + pyndine: chloroform - benzene.

What are Azeotropes?

Azeotropes are defined as a mixture of two liquids which has a constant composition in the liquid and vapour phase at all temperatures.

- Azeotropes can't be separated by fractional distillation, as the composition of the vapour phase remains the same after boiling.
- Because of uniform composition azeotropes are also known as Constant Boiling Mixtures.

Each azeotrope has a characteristic **boiling point.**
The boiling point of an azeotrope is either less than the boiling point temperatures of any of its constituents (a positive azeotrope), or greater than the boiling point of any of its constituents (a negative azeotrope).

Types of Azeotropes

- Maximum Boiling Azeotrope
- Minimum Boiling Azeotrope

1. Maximum Boiling Azeotrope

Maximum Boiling Azeotrope is formed when we mix two non-ideal solutions at some specific composition, showing a large negative deviation from Raoult's law.
Examples:

- Nitric Acid (HNO_3) (68%) and water (32%) form maximum boiling azeotrope at a boiling temperature of 393.5 K
- Hydrochloric Acid (HCl) (20.24%) and water form maximum boiling azeotrope at a boiling temperature of 373 K

2. Minimum Boiling Azeotrope

Minimum Boiling Azeotrope is formed when we mix two non-ideal solutions at some specific composition, which shows a large positive deviation from Raoult's Law.

Example: Ethanol (95.5%) and water (4.5%) form minimum boiling azeotrope at a boiling temperature of 351.5 K

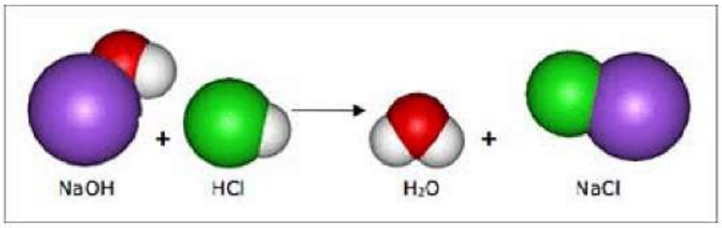
Maximum Boiling Azeotrope	Minimum Boiling Azeotrope
The boiling point of this azeotrope is lower than the boiling points of its constituents.	The boiling point of this azeotrope is higher than the boiling points of its constituents.
This solution exhibits large positive deviation from Raoult's law and large vapour pressure difference of components.	The maximum boiling azeotrope occurs if the solution exhibits negative deviation from ideality
Example: Ethanol boils at 78.4°C, water boils at 100°C, but the azeotrope boils at 78.2°C, which is lower than either of its constituents.	**Example:** Hydrogen chloride boils at -84°C and water at 100°C, but the azeotrope boils at 110°C, which is higher than either of its constituents.

Solved Examples: Solutions - 2

Example 50. Calculate normality of the mixture obtained by mixing 100ml of 0.1N HCl and 50ml of 0.25N NaOH solution.

(a) 0.0467 N
(b) 0.0367 N
(c) 0.0267 N
(d) 0.0167 N

Ans. (d)
Solution.



Molal eq. of HCl = 100 × 0.1 = 10
Molal eq. of NaOH = 50 × 0.25 = 12.5
HCl and NaOH neutralize each other with equal eq.
Eq. of NaOH left = 12.5 - 10 = 2.5
Volume of new solution = 100 + 50 = 150 ml.

$$N_{NaOH}\ left = \frac{2.5}{150} = 0.0167\ N$$

Hence normality of the mixture obtained is **0.0167 N**

Example 51. 300 ml 0.1 M HCl and 200 ml of 0.03M H_2SO_4 are mixed. Calculate the normality of the resulting mixture-
(a) 0.084 N
(b) 0.84 N
(c) 2.04 N
(d) 2.84 N

Ans. (a)

Solution.
For HCl For H_2SO_4
$V_1 = 300$ ml $V_2 = 200$ ml
$N_1 = M \times$ Basicity $N_2 = M \times$ Basicity
$= 0.1 \times 1 = 0.1 = 0.03 \times 2 = 0.06$
Normality of the mixture

$$N = \frac{V_1N_1 \ + \ V_2N_2}{V_1 + V_2}$$
$$= \frac{300 \times 0.1 \times 200 \times 0.06}{500}$$
$$= \frac{30 + 12}{500}$$
= **0.084 N**

Example 52. In what ratio should a 6.5 N HNO_3 be diluted with water to get 3.5 N HNO_3?
(a) 6 : 7
(b) 7 : 6
(c) 5 : 6
(d) 6 : 5

Ans. (b)
Solution.
$N_1V_1 = N_2V_2$
$6.5\ V_1 = 3.5\ (V_1\ x)$
$6.5\ V_1 = 3.5\ V_1\ 3.5\ x$
$3\ V_1 = 3.5\ x$
$\frac{V_1}{x} = \frac{3.5}{3} = \frac{7}{6}$

Example 53. Calculate the amount of each in the following solutions -
(i) 150 ml of N/7 H_2SO_4
(ii) 250 ml of 0.2M $NaHCO_3$
(iii) 400 ml of N/10 Na_2CO_3
(iv) 1052 g of 1 m KOH.
(a) 52g, 2.12g, 4.2g, 1.05g
(b) 1.05g, 4.2g, 2.12g, 52g
(c) 1.05g, 2.12g, 52g, 4.2g
(d) 4.2g, 2.12g, 1.05g, 52g

Ans. (b)
Solution.
(i) Eq. wt. of H_2SO_4
$$= \frac{Mol.\ wt.}{Basicity} = \frac{98}{2} = 49$$
Amount of H_2SO_4 per litre (strength) = Normality × Eq. wt. = × 49 = 7 g/litre

Amount in 150 ml

$$= \frac{7 \times 150}{1000} = 1.05g$$

(ii) Molecular wt. of

$NaHCO_3$ = 23 1 12 48 = 84

Amount of $NaHCO_3$ required to produce 1000 c.c. of one molar solution = 84 g

Amount present per litre in 0.2 M solution = 84 × 0.2 = 16.8 g

Amount present in 250 c.c.

$$= \frac{16.8 \times 250}{1000}$$

= 4.2 g

(iii) Equivalent weight of

$$Na_2CO_3 = \frac{\text{Mol.wt}}{\text{No. of positive valencies}}$$

= 53

Amount of Na_2CO_3 = Normality × Eq. wt. = × 53 = 5.3 g/litre

Amount present in 400 c.c.

$$= \frac{5.3 \times 400}{1000}$$

= 2.12 g

(iv) We know that 1 molal solution of a substance contains 1000 g of solvent.

Wt. of KOH in 1052 g of 1 m KOH solution = 1052 - 1000 = 52 g

Example 54. How many kilograms of wet NaOH containing 12% water are required to prepare 60 litres of 0.50 N solution ?

(a) 1.36 kg
(b) 1.50 kg
(c) 2.40 gm
(d) 3.16 kg

Ans. (a)

Solution.

One litre of 0.50 N NaOH contains = 0.50 × 40g = 20 g = 0.020 kg

60 litres of 0.50 N NaOH contain

= 0.020 × 60 kg = 1.20 kg NaOH

Since the given NaOH contains 12% water, the amount of pure NaOH in 100 kg of the given NaOH = 100 - 12 = 88 kg

Thus 88 kg of pure NaOH is present in 100 kg wet NaOH

1.20 kg of pure NaOH is present in

$$= \frac{100}{88} \times 1.20$$

= 1.36 kg wet NaOH

Example 55. Calculate the vapour pressure of a solution at 100^{0}C containing 3g of cane sugar in 33g of water. (At wt. C = 12 , H = 1 , O = 16)
(a) 760 mm
(b) 756.90 mm
(c) 758.30 mm
(d) None

Ans. (b)
Solution.
Vapour pressure of pure water (solvent) at 1000C, $p^\circ = 760$ mm.
Vapour pressure of solution, p =?
Wt. of solvent, W = 33g
Wt. of solute, w = 3g
Mol. wt. of water (H_2O), M = 18
Mol. wt. of sugar ($C_{12}H_{22}O_{11}$),
$m = (12 \times 12) + (22 \times 1) + (11 \times 16) = 342$
According to Raoult's law,

$$\frac{p^\circ - p}{p^\circ} = \frac{wM}{Wm}$$

$$p = p^o - \frac{w \times M}{m \times W} \times p^o$$

$$p = 760 - \frac{3 \times 18}{342 \times 33} \times 760$$

($p^{\underline{o}}$ for H_2O = 760 mm)
= 760 - 3.19 = 756.90 mm

Example 56. Osmotic pressure of a sugar solution at 24°C is 2.5 atmospheres. Determine the concentration of the solution in gm mole per litre.
(a) 0.0821 moles/litre
(b) 1.082 moles/litre
(c) 0.1025 moles/litre
(d) 0.0827 moles/litre

Ans. (c)
Solution.
Here it is given that
p = 2.5 atm, T = 24 273 = 297K, S = 0.0821 lit. atm. deg^{-1} mol^{-1}, C =?
We know that p = CST
or

$$C = \frac{\pi}{ST} = \frac{2.5}{0.0821 \times 297}$$

= 0.1025 moles/litre

Example 57. Twenty grams of a substance were dissolved in 500 ml. of water and the osmotic pressure of the solution was found to be 600 mm of mercury at 15ºC. Determine the molecular weight of the substance-

(a) 1120
(b) 1198
(c) 1200
(d) None of these

Ans. (c)
Solution.
Here it is given that
w = 20 gm; V = 500 ml.
= 500/1000 = 0.5 litre
p = 600 mm = 600/760 atm;
T = 15 273 = 288^0A
m =?
According to Van't Hoff equation,
pV = nST pV
$= \frac{w}{m} ST$
$m = \frac{wST}{\pi V} = \frac{20 \times 0.0821 \times 288 \times 760}{600 \times 0.5}$
= 1198

Example 58. Blood plasma has the following composition (milli-equivalents per litre). Calculate its osmotic pressure at 37^0C.
Na = 138 , Ca^2 = 5.2, K = 4.5, Mg^2 = 2.0 , Cl^- = 105, HCO_3^- = 25, PO_4^{3-}= 2.2 , SO_4^{2-}= 0.5,
Proteins = 16, Others = 1.0
(a) 7.47 atm
(b) 7.30 atm
(c) 7.29 atm
(d) 7.40 atm

Ans. (a)
Solution.
Since for calculating osmotic pressure we require millimoles/litre therefore
Na^+= 138 Ca^{2+} = 5.2/2 = 2.6, K = 4.5,
Mg^{2+} = 2.0/2 = 1.0, Cl^- = 105,
HCO_3^- = 24,PO_4^{3-}= 2.2/3 = 0.73,
SO_4^{2-}= 0.5/2 = 0.25 , Proteins = 16,

others = 1.0
Total = 294.18 millimoles/litre = 294.18/1000
= 0.294 moles/litre
Now since p = CST
= 0.294 × 0.0821 × .310 = 7.47 atm

Example 59. 0.15g of a substance dissolved in 15g of solvent boiled at a temperature higher by 0.216^0C than that of the pure solvent. Calculate the molecular weight of the substance. Molal elevation constant for the solvent is 2.16^0C.
(a) 216
(b) 100
(c) 178
(d) None of these

Ans. (b)
Solution.
Here it is given that
w = 0.15 g, $DT_b = 0.216^0$C
W = 15g $K_b = 2.16^0$C
m =?
Substituting values in the expression,

$$m = \frac{1000 \times K_b \times w}{\Delta T_b \times W}$$

$$m = \frac{1000 \times 2.16 \times 0.15}{0.216 \times 15}$$

= 100

Example 60. A solution of 0.450 gm of urea (mol. wt 60) in 22.5 g of water showed 0.170^0C of elevation in boiling point. Calculate the molal elevation constant of water-
(a) 0.17ºC
(b) 0.45ºC
(c) 0.51ºC
(d) 0.30ºC
Ans. (c)
Solution.

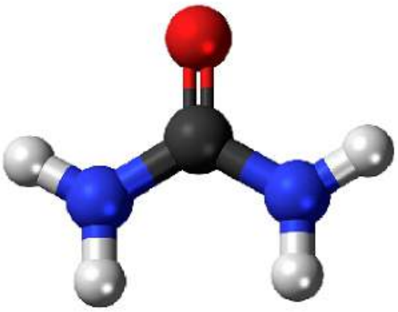


Fig: Structure of urea

Wt. of solute, w = 0.450 g

Wt. of solvent, W = 22.5 g

Mol. wt of solute, m = 60

Molal elevation constant K_b = ?

Boiling point elevation, $DT_b = 0.170^0C$

Substituting these values in the equation

$$K_b = \frac{m \times W \times \Delta T_b}{1000 \times w}$$

$$= \frac{60 \times 22.5 \times 0.170}{1000 \times 0.450}$$

$= 0.51^0C$

Example 61. Calculate the boiling point of a solution containing 0.45g of camphor (mol. wt. 152) dissolved in 35.4g of acetone (b.p. 56.3⁰C); K_b per 100 gm of acetone is 17.2⁰C.

(a) 56.446°C
(b) 52.401°C
(c) 56.146°C
(d) 50.464°C

Ans. (a)

Solution.

Here it is given that

w = 0.45 g, W = 35.4, m = 152,

Kb = 17.2 per 100gm

Now we know that ΔT_b

$$= \frac{100 \times K_b \times w}{m \times W}$$

(Note that this is expression when K_b is given per 100g of the solvent)

Substituting the values in the above expression.

$$\Delta T_b = \frac{100 \times 17.2 \times 0.45}{152 \times 35.4}$$

$= 0.146^0$C
Now we know that
B.P. of solution (T) - B.P. of solvent (T_0) = DT
B.P. of solution (T) = B.P. of solvent(T_0) DT
Hence B.P. of solution = 56.3 0.146
$= 56.446^0$C

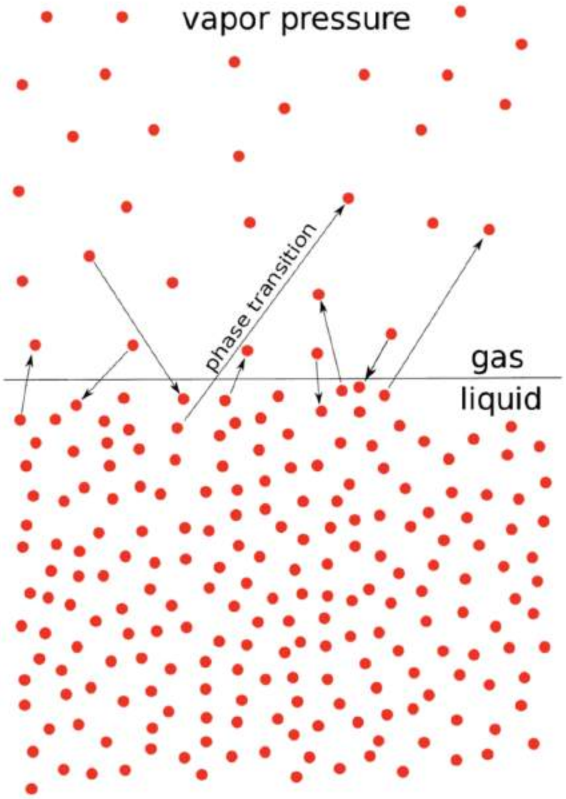
Example 62. The freezing point of 0.2 molal K_2SO_4 is _1.1ºC. Calculate Van't Haff factor and percentage degree of dissociation of K_2SO_4. K_f for water is 1.86º
(a) 97.5
(b) 90.75
(c) 105.5
(d) 85.75

Ans. (a)
Solution.
ΔT_f = freezing point of water -freezing point of solution = 0º C - (1.1º C) = 1.1º
We know that,
$\Delta T_f = i \times K_f \times m$
$1.1 = i \times 1.86 \times 0.2$
$i = \frac{1.1}{1.86 \times 0.2} = 2.95$
But we know
i = 1 (n - 1) a
2.95 = 1 (3 - 1) a = 1 2a
a = 0.975
Van't Haff factor (i) = 2.95
Degree of dissociation = 0.975
Percentage degree of dissociation = **97.5**

Vapour Pressure of Liquid Solutions

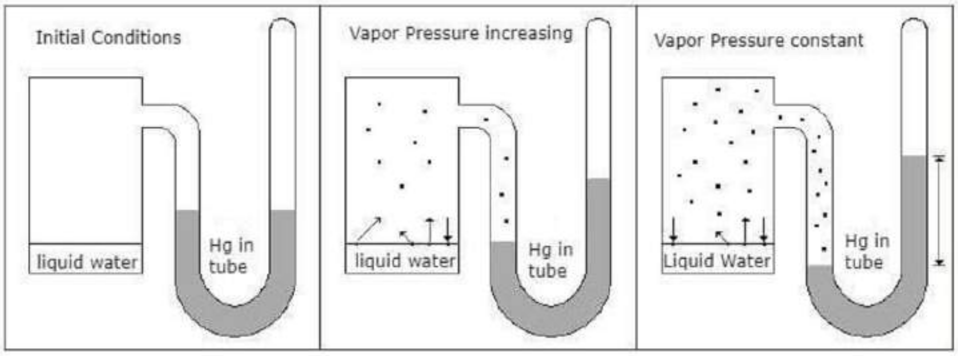
CONCEPT OF VAPOUR PRESSURE

When a pure liquid is kept in a closed vessel (in which no air is present) the liquid evaporates to give the vapours.
The molecules of the liquid which possess high kinetic energy have a tendency to change to vapour state.
After some time a dynamic equilibrium is established between liquid and vapours.



At Equilibrium

rate of evaporation = rate of condensation.
$H_2O\ (\ell) \rightleftharpoons H_2O\ (g)$
The pressure that the vapours exert at equilibrium on the walls of the container or on the surface of the liquid is called the **vapour pressure of the liquid** at that temperature, Figure (a).



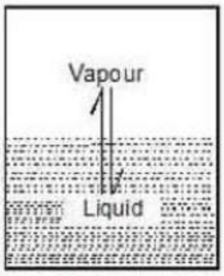


Fig. (a)

Case 1: What would happen to the vapour pressure of the liquid if we take a bigger container, Figure (b) or a wider container, Figure (c).

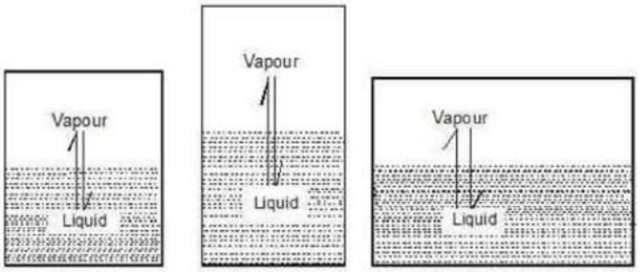
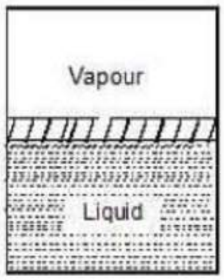


Fig. (a) Fig. (b) Fig. (c)

Key concept: When the liquid is in equilibrium with vapours,
Liquid ⇌ Vapours,
the K_p of the system is $K_p = P_v$,
where P_v is the vapour pressure.

We know that K_p for a given chemical equilibrium is a constant and only depends on temperature. There fore the vapour pressure of the liquid is a constant and does not depend on the nature of the vessel used and that it only depends on temperature.

Case 2: Take a vessel with the same liquid as in case 1 and cover it with a glass plate (of negligible weight) having a hole in it. Would the vapour pressure be the same now?



Key concept: Well, the liquid system is the same and the temperature is also same. Therefore, the vapour pressure should be same. The vapour pressure of a liquid is independent of the surface area exposed on top of the liquid surface provided the surface area exposed should not be zero.

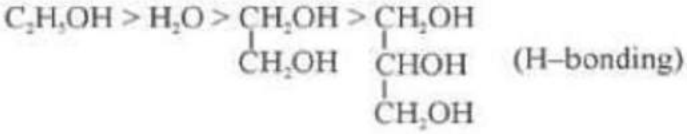
The vapour pressure of liquid depends upon

- Nature of the liquid
- Temperature

(i) Nature of the Liquid: When the intermolecular forces of attractions are stronger then the vapour pressure will be low because less number of molecules can leave the liquid.

Out of C_2H_5OH, CH_3OCH_3, CH_3CHO the one with highest vapour pressure is CH_3OCH_3 and the one with lowest vapour pressure is C_2H_5OH because in C_2H_5OH there is hydrogen bonding leading to strongest intermolecular forces where as in CH_3OCH_3 there is Vander Waals forces leading to weakest intermolecular forces.

Decreasing order of vapour pressure of few liquids is



$$C_2H_5OH > H_2O > \begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array} > \begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \quad \text{(H–bonding)}$$

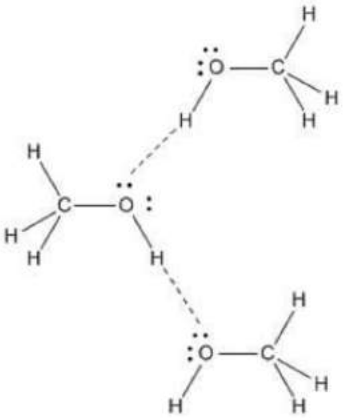
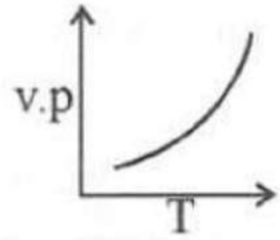


Fig: H-Bonding in Methanol

(ii) Temperature: Higher the temperature, greater would be the vapour pressure.



This is because when temperature is raised, kinetic energy of the molecules increase and therefore the number of molecules leaving surface of liquid, is large.
The **Clausius Clapeyron equation** tells very clearly that as temperature increases the right hand side remains highly and thereby vapour pressure increases.
This equation is,

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_v}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

which tells as to how vapour pressure changes with nature of liquid and temperature when vapour pressure is low then the temperature at which the liquid would boil will be high. In the above equation P_1 and P_2 are vapour pressure of liquid at T_1 and T_2 respectively, ΔHv, heat of vaporization and R is gas constant.

VAPOUR PRESSURE OF LIQUID SOLUTIONS

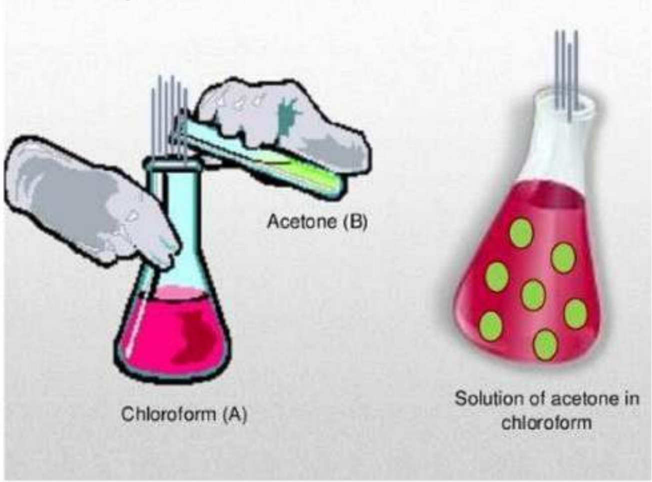


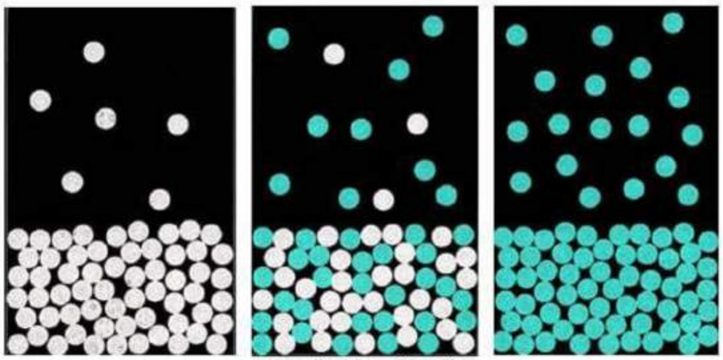
Fig: Example of Liquid in Liquid Solution
Liquid Solution is formed when we dissolve a solid, liquid or gas in a particular liquid solvent.

Vapour Pressure of liquid solutions is defined as the pressure exerted by the vapours on the liquid solvent when kept in equilibrium and a certain temperature.

- It varies with the nature of liquid and temperature of the surroundings.

Some characteristics of the vapour pressure of liquid solutions are as follows:

- The pure liquid has more vapour pressure as compared to liquid's solution.
  Example: take two beaker one filled with water and other with lemon juice and water, you'll find that the beaker filled with water has more vapour pressure
- Vapour pressure is inversely proportional to forces of attraction between molecules of a liquid
- Vapour pressure increases with increase in temperature, as molecules gain kinetic energy and vapourise briskly



Vapor-liquid equilibria for pure tolune

Vapor-liquid equilibria for equal amounts of pure tolune + benzene

Vapor-liquid equilibria for pure benzene

Fig: Vapour pressure equilibrium in different solution

Liquid solution can contain volatile solute and solvent as well. In most cases, the solvent is volatile in nature and the solute left out to be non-volatile.

<u>Vapour pressure can be evaluated in two cases which are:</u>

- Vapour pressure of liquid-liquid solutions that is, solute and solvent both are in liquid phase
- Vapour pressure of solid- liquid solutions that is, solute is in solid state and solvent is in liquid phase

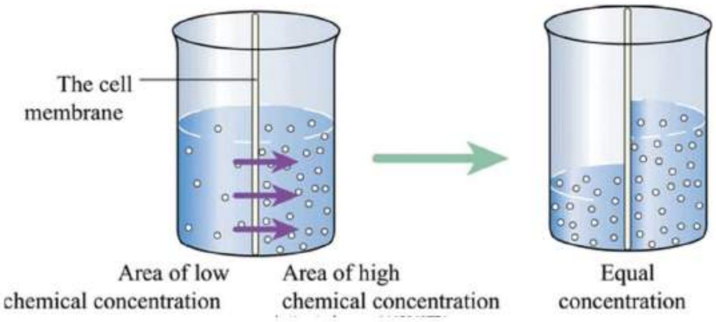
Vapour Pressure of Liquid-Liquid Solutions

To find out vapour pressure of the liquid-liquid solution, we take two volatile liquid solutions and name their liquid component as A and B. When we place the volatile liquid with their components in a closed vessel, we find that equilibrium is established between the liquid phase and vapour phase.
Suppose P_{total} is the overall vapour pressure at an equilibrium state and let P_A and P_B be the partial vapour pressures of components A and B respectively.
Applying Dalton's law of partial pressure the total vapour pressure of the solution will be
$P_{solution} = P_A + P_B$
Where P_A and P_B are the partial vapour pressures of A and B.
Adding further, the mole fraction of respective components is x_A and x_B respectively.
To evaluate vapour pressure of volatile liquids, we use **Raoult's Law**.

Osmosis, Osmotic Pressure, Reverse Osmosis & Water Purification

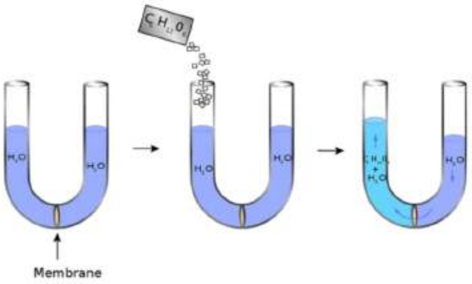
What is Osmosis?

You haven't seen pickles being made at home, have you? That's all there is to osmosis' magic. **How does osmosis work, though?** Do you realise that osmosis is one of the most important factors in the survival of many species? We will learn everything about osmosis and osmotic pressure in this document.
In the process of Osmosis, solvent moves from a region of its higher concentration to a region of its lower concentration through a semi-permeable membrane, which allows the free passage of only solvent molecules.
Osmosis is the phenomenon of solvent flow through a semi-permeable membrane to equalize the solute concentrations on both sides of the membrane.



What is Osmotic Pressure?

Osmotic Pressure can be defined as:
The minimum pressure which should be applied on the solution, so as to prevent the migration of solvent molecules into the solution through a semi-permeable membrane.



The osmotic pressure p of a solution is related to the molar concentration of solute M as: $\pi = MRT$,
Where R is the gas constant and T is the absolute temperature.

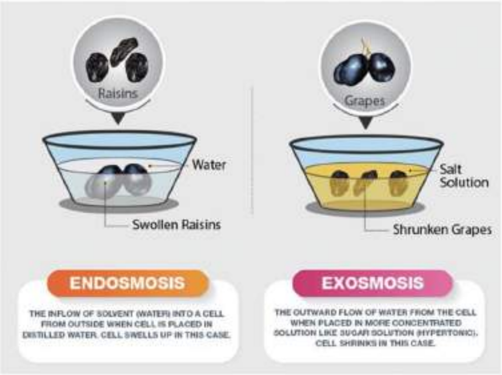
Van't Hoff equation for a dilute solution is similar to the ideal gas equation,
$\pi V = nRT$
Where π = osmotic pressure
R = gas constant

Some typical examples of osmosis and osmotic pressure are:

(i) The climbing of water up a tall tree from the soil.
(ii) Bursting of red-blood cells when placed in water.
(ii) Swelling of dry raisins when placed in water.

TYPES OF OSMOSIS

1. **Exosmosis:** This is the outward flow of water from a cell containing an aqueous solution through a semipermeable membrane, e.g. grape in NaCl solution.
2. **Endosmosis:** This is the inward flow of water into a cell containing an aqueous solution through a semipermeable membrane, e.g. grape in water.



THE INFLOW OF SOLVENT (WATER) INTO A CELL FROM OUTSIDE WHEN CELL IS PLACED IN DISTILLED WATER. CELL SWELLS UP IN THIS CASE.

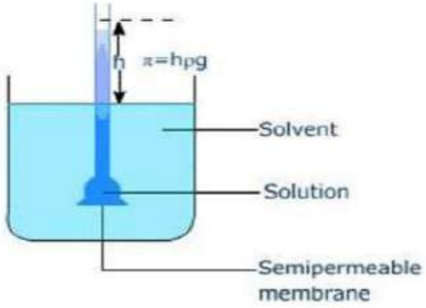
THE OUTWARD FLOW OF WATER FROM THE CELL WHEN PLACED IN MORE CONCENTRATED SOLUTION LIKE SUGAR SOLUTION (HYPERTONIC). CELL SHRINKS IN THIS CASE.

Difference between Endosmosis and Exosmosis

Key concept: The semipermeable membranes allow a selective passage to only the solvent molecules. Cellophane, parchment paper and animal protein membranes are typical semipermeable membranes.

- The most frequently used semipermeable membrane in the laboratory is that of copper ferrocyanide, $Cu_2[Fe(CN)_6]$ because it is very strong and can withstand very high pressure.
- Remember that the semipermeable membrane of $Cu_2[Fe(CN)_6]$ does not work in non-aqueous solution because it gets dissolved in nonaqueous solvents.
- Another synthetic semipermeable membrane is that of calcium phosphate.
- Natural semipermeable membranes are cell walls, pig's bladder, the skin surrounding white of an egg, the membrane surrounding RBCs etc.

The **hydrostatic pressure** set up as a result of osmosis is a measure of the osmotic pressure of the solution.
For instance, if the solution of density d rises to height h, then osmotic pressure is expressed as $\pi = h \times d \times g$, where g is the acceleration due to gravity.



TONICITY

The ability of an extracellular solution to make water move into or out of a cell by osmosis is known as its tonicity.

Three terms—**hypertonic, hypotonic, and isotonic**—are used to describe whether a solution will cause water to move into or out of a cell:

Isotonic Solution

A pair of solutions having the same osmotic pressure are known as isotonic solutions.

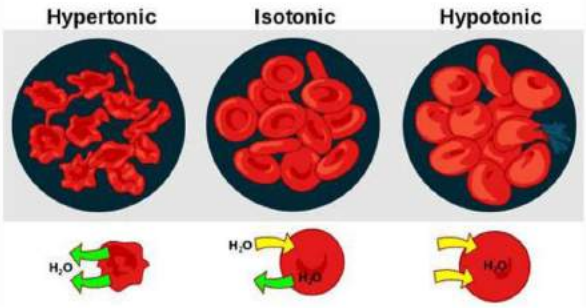
- If two such solutions are separated by a semipermeable membrane, there will be a transference of solvent from one solution to the other.
- Isotonic solutions have the same concentration.
- 0.85% NaCl solutions are found to be isotonic with blood, while 0.9% NaCl solution isotonic with human RBCs.
  For isotonic solution, $\pi_1 = \pi_2$
  Or $C_1 = C_2 \Rightarrow n_1/V_1 = n_2/V_2$
  or $W_1/m_1V_1 = W_2/m_2V_2$

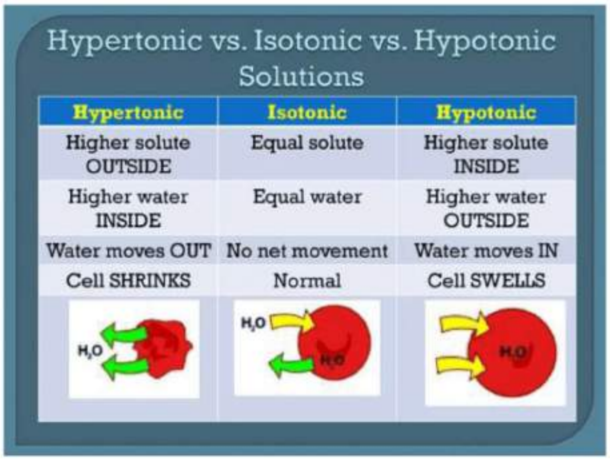
Hypertonic Solution

If a cell is placed in a hypertonic solution, there will be a net flow of water out of the cell, and the cell will lose volume. A solution will be hypertonic to a cell if its solute concentration is higher than that inside the cell, and the solutes cannot cross the membrane.
When placed in hypertonic solutions, the fluid from the plant cells comes out and thus the cells contract in size (plasmolysis). When excess fertilizers (like urea) are applied, plasmolysis takes place and plants dry up (wilt).

Hypotonic Solution

If a cell is placed in a hypotonic solution, there will be a net flow of water into the cell, and the cell will gain volume. If the solute concentration outside the cell is lower than inside the cell, and the solutes cannot cross the membrane, then that solution is hypotonic to the cell. When placed in water or hypotonic solutions, cell swell and burst (haemolysis).



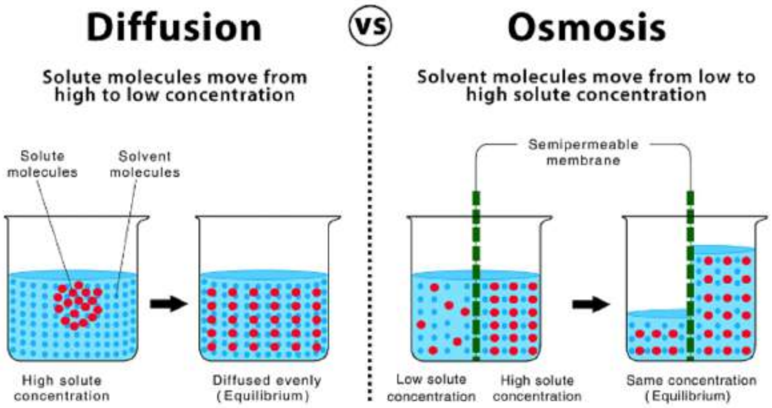


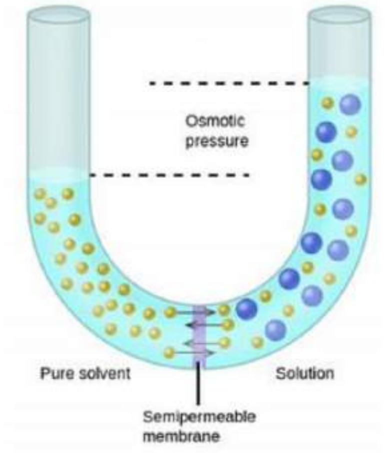
Hypertonic vs. Isotonic vs. Hypotonic Solutions

Hypertonic	Isotonic	Hypotonic
Higher solute OUTSIDE	Equal solute	Higher solute INSIDE
Higher water INSIDE	Equal water	Higher water OUTSIDE
Water moves OUT	No net movement	Water moves IN
Cell SHRINKS	Normal	Cell SWELLS

COMPARISON BETWEEN DIFFUSION AND OSMOSIS

Osmosis	**Diffusion**
It Is limited only to the liquid medium.	Occurs In all mediums - Solid, Liquid and gas.
Requires a semipermeable membrane.	Do not require a semipermeable membrane.
Depends on the number of solute particles dissolved in the solvent.	Depends on the presence of other particles.
Requires water for the movement of particles.	Do not require water for the movement of particles.
Only the solvent molecules can diffuse.	Both the molecules of solute and solvent can diffuse.
The flow of particles occurs only in one direction.	The flow of particles occurs in all the directions.





Difference between Osmotic Pressure and Vapour Pressure

Osmotic pressure	Vapour pressure
It is the minimum pressure which should be applied on the solution so as to prevent the migration of solvent molecules into the solution through a semi-permeable membrane.	It is the maximum pressure exerted by the vapour above the surface of solution in a closed container.

Example 1. Calculate the osmotic pressure and vapour pressure of 0.6% aqueous solution of a non-volatile, non-electrolyte solute, urea (NH_2CONH_2) at 25°C. The vapour pressure of pure water at 25°C is 24 mm Hg. Take densities to be 1 g mL^{-1} and assume ideal behaviour of the solution. Gas constant, R = 0.082 L atm. mol^{-1} K^{-1}.
Key concept: Please refer to difference between osmotic pressure and vapour pressure while solving this illustration.

Solution.
Concentration of urea solution = 0.6%
This means, solution contains 0.6 g of urea per 100 g, and hence 100 mL of the solution,
So,
Mass of urea per litre of solution
$= 0.6/100 \times 100 = 6$ g
Molar mass of urea, M = 60 g/mol
Concentration of urea in solution
$= 6/60$ mol/L $= 0.1$ mol/L

Example 2. At 25˚C, the osmotic pressure of human blood due to the pressure of various solutes in the blood is 7.65 atm. Assuming that molarity and molality are almost same, calculate the freezing point of blood. $K_f = 1.86$ K kg/mol.

Solution.

According to the Van't Hoff equation,

$p = CRT$

$c = 7.65/\ (0.082)(298) = 0.313$ mol/L

Since molarity and molality are same,

$\Delta T_f = K_f m$

$\Delta T_f = 1.86 \times 0.313 = 0.582$

Freezing point of blood is - 0.582˚C.

Example 3. At 27°C, 36 g of glucose per litre has an osmotic pressure of 4.92 atm. If the osmotic pressure of solution is 1.5 atm at the same temperature, what should be its concentration?

Solution.

Given that,

$\pi_1 = 4.92$ atm, $\pi_2 = 1.5$ atm

$$C_1 = \frac{3}{180 \times 1} \quad \left(\because C = \frac{w}{M \times V}\right),\ C_2 = ?$$

$\pi_1 V_1 = n_1 R T_1$

$\pi_2 V_2 = n_2 R T_2$

At same temperature,

$$\frac{\pi_1}{\pi_2} = \frac{n_1}{V_1} \times \frac{V_2}{n_2} = \frac{C_1}{C_2}$$

$$\therefore \quad \frac{4.92}{1.5} = \frac{36}{180 \times C_2}$$

$\therefore C_2 = 0.061$ mol/litre

Example 4. At 25°C, a solution containing 0.2 g of polyisobutylene in 100 mL of benzene developed a rise of 2.5 mm at osmotic equilibrium. Calculate the molecular weight of polyisobutylene if the density of the solution is 0.88 g/mL.

Solution.

Height developed = 2.4mm

Osmotic pressure = h.d.g

$= \frac{2.4}{10} \times 0.88 \times 981$

207.187 dyne cm^{-2}

Now $\pi V = nRT$

207.187×100

$= \frac{0.2}{M} \times 8.314 \times 10^7 \times 298$

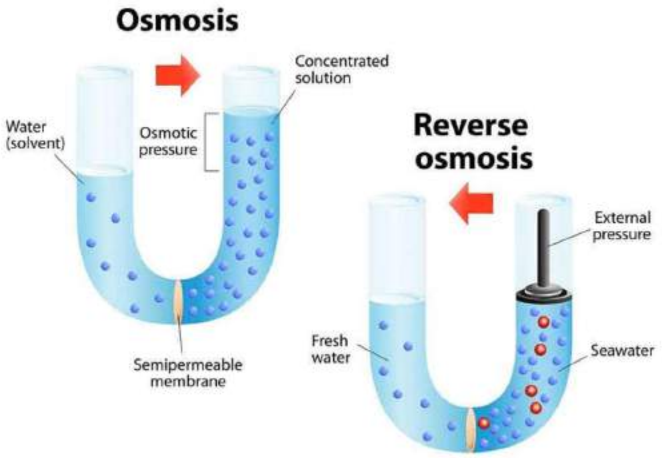
(R in erg; V in mL, using CGS system)

$M = 2.39$

What is Reverse Osmosis (RO)?

RO is a process in which a large pressure is applied to the solution side so as to overcome the osmotic pressure.

This pushes the pure solvent under pressure, out of the solution through the semi-permeable membrane. This process finds a number of practical applications. Some of them are the purification of drinking water, removal of salt from water molecules, removal of effluents from water, etc.



Water Purification

RO is considered one of the most important water purification technologies. The contaminants present in water are removed by pushing water under pressure through a semi-permeable membrane. Pure water is thus squeezed out which is fit for drinking. RO is also used in the desalinization of seawater. RO is a reliable source for obtaining potable water.

- The process eliminates dissolved and suspended impurities, even bacteria.
- The membrane is small enough to allow the solvent molecules to pass but does not allow large ions or molecules to pass through its pores.
- Polymer membranes are used for the desalinization of seawater.
- Cellulose acetate is often used as a semi-permeable membrane. It allows water molecules to pass but is impermeable to impurities.
- It finds application in military, wastewater purification, food industry, landfill leachate purification, etc.

Abnormal Molar Masses

ABNORMAL MOLAR MASS

Molecular masses of the solute can be easily determined with the help of colligative properties; relative lowering in vapour pressure, boiling point elevation, freezing point depression, and osmotic pressure easily. But, we derived the relation between the molecular mass of solute and colligative properties under some assumptions, which are:

- The solution is diluted that is, solvent is available in large amount in order to obey Raoult's Law
- The solute neither went dissociation or association in the solution

So, how do we determine the molecular mass of solute in case the above assumptions are not valid? Basically, the abnormality is due to:

(i) Association of Solute Particles

- Some solute molecules start to associate inside the solution.
- This means now there are less number of solute particles in the solution.
- As colligative properties vary with solute particles in the solution, they will decrease along with the solute particles.
- As colligative properties are inversely proportional to the molecular mass of solute, we get a higher molar mass of the solute.
- **For Example:** Ethanoic acid or acetic acid (CH_3COOH) associate in solution to form a dimer due to hydrogen bonding.

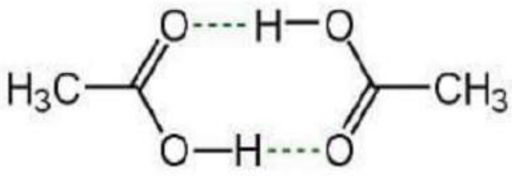
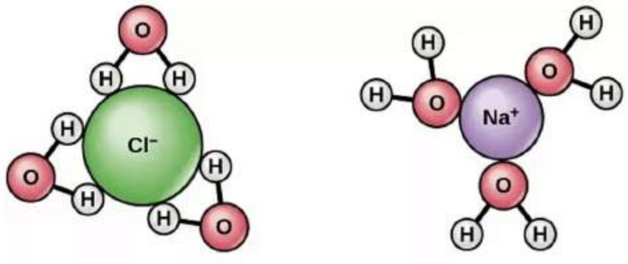


Image 2: Ethanoic Acid dimer due to hydrogen bonding

(ii) Dissociation of Solute Particles

- Some solute molecules, generally electrolytes dissociate into two or more ions/particles when dissolved in a solution.
- This leads to increase in solute particles in the solution, thereby increase in colligative properties of solutions.
- As colligative properties and molecular mass of solute varies inversely, we get a lower molar mass of the solute.



NaCl dissociate into two ions when dissolved in water
Such a molar mass, whose value is higher or lower than its expected value is known as Abnormal Molar Mass. For Example, weak electrolytes dissociate in water to form ions, example Hydrofluoric Acid (HF), dissociate into hydrogen cation and fluorine anion.

VAN'T HOFF FACTOR

To determine colligative properties for solutions which undergo association and dissociation, a Dutch physical chemist Jacobus Henricus van't Hoff in the year 1880 introduced the concept of Van't Hoff Factor i to sort out association and dissociation problem while calculating the molar mass of solute.
The Van't Hoff factor is denoted by 'i' and is obtained when we divide normal mass with an abnormal mass of solute. Mathematically, it is represented in three forms:

i = Normal Molar Mass/Abnormal Molar Mass
i = Observed Colligative property/Calculated Colligative property
i = Total Number of Moles of Particles after Association/Dissociation / Total Number of Moles of Particles before Association / Dissociation
Thus, the value of i depends upon the state of solute in the solution.

Following cases become possible.

- When, **$i = 1$,** then the solute remains unaffected (i.e., normal) in solution.
- When, **$i > 1$,** then the solute undergoes dissociation in solution.
- When, **$i < 1$,** then the solute undergoes association in solution.

Thus, for
Potassium chloride (KCl) in aqueous solution, i is nearly equal to 2.
Barium chloride ($BaCl_2$) in aqueous solution, i is nearly equal to 3.
Benzoic acid (C_6H_5COOH) in benzene, i is nearly equal to 0.5.
Acetic acid (CH_3COOH) in benzene, i is nearly equal to 0.5.

CALCULATION OF I (VAN'T HOFF FACTOR)

First, we write an equation of the solute being associated or dissociated
CASE 1: WHEN SOLUTE UNDERGOES DISSOCIATION WHEN DISSOLVED IN SOLVENT

Degree of dissociation: It is defined as the number of moles dissociated over the initial number of moles taken.

Van't Hoff factor = Total number of particles at equilibrium/Total initial number of particle
Let c moles per litre of an electrolyte A_xB_y be taken and let it dissociated as
$A_xB_y \rightarrow xA^{y+} + yB^{x-}$
$t = 0 \quad C \quad 0 \quad 0$
$c\,(1 - \alpha)\ xc\alpha\ yc\alpha$ At equilibrium
i = concentration or number of moles after dissociation/concentration or number of moles before dissociation
$i = [c - c\alpha + xc\alpha + yc\alpha\,]/c$
or $i = [1 - \alpha + x\alpha + y\alpha\,]/1$
$= \ 1 + [(x + y) - 1]\alpha$
Let $x + y = n$ = number of particles formed after dissociation
$i = 1 + (n - 1)\alpha$

$$\boxed{\frac{i-1}{n-1}=\alpha}$$

Degree of Association may be defined as the number of molecules associated per unit volume over initial concentration

i = Total number of particles or concentration after association/Total number of particles or concentration before association

Let n molecules of an electrolyte A undergo association

then, $nA \rightarrow A_n$

$$\begin{array}{ccl} C & 0 & t = 0 \\ C - C\cdot\alpha & C.\alpha/n & \text{At. equilibrium} \end{array}$$

$$\Rightarrow\ i = \frac{C - C\cdot\alpha + \frac{C\cdot\alpha}{n}}{C}$$

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

$$i = 1 + \left(\frac{1}{n} - 1\right)\alpha$$

$$\boxed{\frac{(i-1)n}{1-n} = \alpha}$$

MODIFIED EQUATIONS FOR COLLIGATIVE PROPERTIES

For solutes which undergo dissociation or association in solutions, the equations for the colligative properties are modified by inserting the van'tHoff's factor in them as follows:

	Colligative property	equation for colligative property	
		when solute remains normal	when the solute undergoes association / dissociation
1.	Relative lowering of vapour pressure	$\frac{P_s^0 - P_s}{P_s^0} = X_{solute}$	$\frac{P_s^0 - P_s}{P_s^0} = iX_{solute}$
2.	Elevation of the boiling point	$\Delta T_b = K_b \times m$	$\Delta T_b = i\,K_b \times m$
3.	Depression of the freezing point	$\Delta T_f = K_f \times m$	$\Delta T_f = i\,K_f \times m$
4.	Osmotic pressure	$\pi = CRT$	$\pi = iCRT$

Example 1. Acetic acid (CH_3COOH) associates in benzene to form double molecules. 1.65 g of acetic acid when dissolved in 100 g of benzene raised the boiling point by 0.36°C. Calculate the Van't Hoff factor and the degree of association of acetic acid in benzene. ($K_b = 2.57$ K kg mol $^{-1}$).

Solution.

	$2CH_3COOH \rightleftharpoons$	$(CH_3COOH)_2$
Initial moles	1.65/60	0
At equilibrium	$\frac{1.65}{60}(1-\alpha)$	$\frac{1.65}{60}\frac{\alpha}{2}$

Total moles at equilibrium

$$= \frac{1.65}{60}\left(1-\frac{\alpha}{2}\right)$$

$\Delta T_b = K_b \times m$,

$$0.36 = 2.57 \times \frac{1.65}{60}\left(1-\frac{\alpha}{2}\right)$$

$\alpha = 0.981$

Van't Hoff factor = no. of moles at equilibrium/Initial no. of moles

$$i = 1 - \frac{\propto}{2} = 0.5$$

Example 2. Derive a relationship between K_b, T_b and ΔH_{vap} for a liquid.

Solution.

Let us consider a pure liquid. At its boiling point, T_b, its vapour pressure P° would be equal to the external pressure.

$P^\circ = P_{ext}$ at temperature T_b.

Now let us consider a non-volatile solute dissolved in the liquid. When the solution reaches temperature T_b, the vapour pressure of the system, would be less than the external pressure. When the solution is heated further and it reaches its boiling T_b, the vapour pressure of the solution would be equal to P_{ext} which is equal to the P° of the pure liquid at its boiling point. Since vapour pressure of a system are the K_p's for the respective equilibrium,

$$\ln\frac{K_{PT_2}}{K_{PT_1}}=\frac{\Delta H}{R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$$

$$\ln\frac{P^{\circ}}{P}=\frac{\Delta H_{vap}}{R}\left[\frac{1}{T_b}-\frac{1}{T_b^{\circ}}\right]=\frac{\Delta H_{vap}}{R}\left[\frac{\Delta T_b}{T_b T_b^{\circ}}\right]$$

Assuming the solution to be highly dilute, T_b would be very close to T_b.

$$\ln\frac{P^{\circ}}{P}=\frac{\Delta H_{vap}}{R}\left[\frac{\Delta T_b}{T_b^2}\right]$$

$$-\ln\frac{P}{P^{\circ}}=\frac{\Delta H_{vap}}{R}\left[\frac{\Delta T_b}{T_b^2}\right]$$

$$-\ln\left[1-\left(\frac{P^{\circ}-P}{P^{\circ}}\right)\right]=\frac{\Delta H_{vap}}{R}\left[\frac{\Delta T_b}{T_b^2}\right]$$

$$-\ln\left[1-X_{solute}\right]=\frac{\Delta H_{vap}}{R}\left[\frac{\Delta T_b}{T_b^2}\right]$$

Since X_{solute} is very small, we can make the approximation that in $(1 - x) = -x$ (when x is very small).

$$X_{solute}=\frac{\Delta H_{vap}}{R}\left[\frac{\Delta T_b}{T_b^2}\right] \text{ or } \frac{n}{n+N}=\frac{\Delta H_{vap}}{R}\left[\frac{\Delta T_b}{T_b^2}\right]$$

Ignoring n in comparison to N in the denominator

$$\frac{n}{N}=\frac{\Delta H_{vap}}{R}\left[\frac{\Delta T_b}{T_b^2}\right]$$

$$\frac{n}{\frac{W_{solvent}}{M_{solvent}}}=\frac{\Delta H_{vap}}{R}\left[\frac{\Delta T_b}{T_b^2}\right] \text{ or } \frac{n}{W_{solvent}}=\frac{\Delta H_{vap}}{M_{solvent}R}\left[\frac{\Delta T_b}{T_b^2}\right]$$

Multiplying by 1000 on both the sides, we get,

$$\frac{n}{W_{solvent}}\times 1000=\frac{\Delta H_{vap}}{M_{solvent}R}\left[\frac{\Delta T_b}{T_b^2}\right]\times 1000$$

$$m = \frac{\Delta H_{vap}}{M_{solvent} R}\left[\frac{K_b m}{T_b^2}\right] \times 1000$$

$$Kb = \frac{RT_b^2 M_{solvent}}{1000\ \Delta H_{vap}}$$

Similarly, $K_f = \frac{RT_b^2 M_{solvent}}{1000\ \Delta H_{fus}}$

Example 3. To 500 cm³ of water, 3.0 × 10⁻³ kg of acetic acid is added. If 23% of acetic acid is dissociated, what will be the depression in freezing point? K_f and density of water are 1.86 K kg⁻¹ mol⁻¹ and 0.997 g cm⁻³ respectively.

Solution. Molality of acetic acid

$$= \frac{3 \times 10^{-3} \times 10^3 \times 1000}{60 \times 0.997 \times 500} = 0.1003$$

Total number of moles per kg of solvent = 0.1003 (1 + 0.23)

$\Delta T_f = K_f m = 1.86 \times 0.1003 \times 1.23 = 0.23o$ C

Example. 4. At 300 K, the vapour pressure of an ideal solution containing one mole of A and 3 moles of B is 500 mm of Hg. At the same temperature, if one mole of B is added to this solution, the vapour pressure of the solution increases by 10 mm of Hg. Calculate the V.P. of A and B in their pure state.

Solution.

$$Intially,\ PM = P_A^0 X_A + P_B^0 X_B$$

$$550 = P_A^0 \frac{1}{1+3} + P_B^0 \frac{3}{1+3}$$

or

$$P_A^0 + 3P_B^0 = 2200 \quad ...(i)$$

When, one mole of B is further added to it,

$$PM = P_A^0 X_A + P_B^0 X_B$$

$$56 = P_A^0 \frac{1}{1+4} + P_B^0 \frac{4}{1+4} P_A^0 + 4P_B^0 = 2800 \quad (ii)$$

Solving equations (i) and (ii), we get

$P°_A = 440$ mm, $P°_B = 600$ mm

Example 5. A decinormal solution of NaCl exerts an osmotic pressure of 4.6 atm. at 300 K. Calculate its degree of dissociation. ($R = 0.082$ L atm. $K^{-1}mol^{-1}$).

Solution.

No. of moles of NaCl per litre of solution = 0.1
Osmotic pressure (p) = 4.6 atm., Temperature (T) = 300 K
Had NaCl not dissociated, then
p normal = CRT = 0.1 × 0.082 × 300 atm. = 2.46 atm.
But, pobs = 4.6 atm.
As per definition,

$$i = \frac{observed\ magnitude\ of\ a\ colligative\ property}{Normal\ magnitude\ of\ a\ colligative\ property}$$

$$= \frac{\pi_{obs}}{\pi_{normal}} = \frac{4.6\ atm}{2.46\ atm} = 1.87$$

For the dissociation of an electrolyte producing n ions,

$$a = \frac{i-1}{n-1} = \frac{1.87-1}{2-1} = \frac{0.87}{1} = 0.87$$

So, Percentage dissociation = 100 × a = 100 × 0.87 = 87%

Example 6. Vapour pressure of C_6H_6 and C_7H_8 mixture at 50°C are given by: P = 179 X_B 92, where X_B is mole fraction of C_6H_6. Calculate (in mm):
(A) Vapour pressure of pure liquids.
(B) Vapour pressure of liquid mixture obtained by mixing 936 g C_6H_6 and 736 g toluene.

(C) If the vapours are removed and condensed into liquid and again brought to the temperature of 50°C, what would be mole fraction of C_6H_6 in vapour state?

Solution.

(A) Given, $P = 179X_B + 92$
For pure, C_6H_6, $X_B = 1$
$P°_B = 179 + 92 = 271$ mm
For pure C_7H_8, $X_B = 0$
$P°_T = 179 \times 0 + 92 = 92$ mm
(B) Now $PM = P°_B X_B + P°_T X_T$

$$= 271 \times \frac{12}{12+8} + 92 \times \frac{8}{12+8}$$

$= 162.6 + 36.8 = 199.4$ mm

Moles of $C_6H_6 = 936/78 = 12$
Moles of $C_7H_8 = 736/92 = 8$
(C) Now mole fraction of C_6H_6 in vapour phase of initial mixture (X'_T)

$$X'_T = \frac{P'_B}{P_M} = \frac{162.6}{199.4} = 0.815$$

Moles fraction of C_7H_8 in vapour phase of initial mixture (X'_L)

$$X'_T = \frac{P'_T}{P_M} = \frac{36.8}{199.4} = 0.185$$

These vapours are taken out and condensed into liquid. The liquid is again brought to 50°C to get again vapour-liquid equilibrium.
Thus, mole fraction of C_6H_6 in vapour phase of initial mixture
= Mole fraction of C_6H_6 in liquid phase on II mixture X'_B
Similarly, mole fraction of C_7H_8 in vapour phase of initial mixture
= Mole fraction of C_7H_8 in liquid phase on II mixture X'_T

$new\ PM = P'_B P'_T$ Therefore,

$$new\ PM = P_B^0 X'_B P_T^0 X'_T$$

$= 271 \times 0.815 + 92 \times 0.185$ mm
$= 220.865 + 17.02 = 237.885$ mm
New mole fraction of C_6H_6 in vapour phase

$$= \frac{New\ P'_B}{New\ P_M} = \frac{220.865}{237.885} = 0.928$$

New mole fraction of C_7H_8 in vapour phase = 0.072.

Example 7. The freezing point depression of an HF (aq) solution with molality 0.10 m is -0.201°C. What will be the Van't Hoff factor? Take the value of Kf to be 1.86°Cm^{-1}

Solution.
$HF\ (aq) \rightarrow H^+ + F^-$
We have $\Delta T_f = -0.201$ C0 , $m = 0.10$ and $K_f = 1.86$ °Cm^{-1}
The freezing point depression is $\Delta T_f = i\ K_f m$
$0.201 = i \times 1.86 \times 0.10$
The value of Van't Hoff factor will be 1.08

Example 8. A millimolar solution of potassium ferricyanide is 70% dissociated at 27°C. Find out the osmotic pressure of the solution.

Solution.

Given, concentration of solution = C = 1/1000 M = 10^{-3}M

$$K_3[Fe(CN)_6] \rightarrow 3K^+ + [Fe(CN)_6]^{-3}$$

initial moles	1	0	0
Moles after dissociation	$1-\alpha$	3α	α

Where α = degree of dissociation = 70% = 70/100 = 0.7

Total moles of after dissociation = (1 – α) + 3α + α = 1+ 3α

$\therefore i = 1 + 3\alpha/1$

$i = 1+3\alpha = 1+(3 \times 0.7) = 3.1$

Since osmotic pressure

$\pi = iCRT$

$\therefore \pi = 3.1 \times 10^{-3} \times 0.0821 \times 300$

$= 0.31 \times 3 \times 0.0821$ atm = 0.07635 atm