SOLUTIONS & COLLIGATIVE PROPERTIES

Solution:

A solution is a ***homogenous mixture*** of two or more chemically non-reacting substances existing in one or more states in which each of them loses their individual identity.

In solutions the component present in relatively small amount is called the **solute** and that present in relatively large amount is called the **solvent**. Thus, we have —

$$\boldsymbol{Solution = Solvent + Solute}$$

In solution, solvent or solute may be **solids**, **liquids** or **gases** and depending upon the nature of solvent, three main types of solutions are possible —

1) **Solid Solution**: Here, **solvent** is **solid**, for example, brass, in which 1 part Zn (solute) and 4 part Cu (solvent),
2) **Liquid Solution**: Here, **solvent** is **liquid**, for example, $NaCl$ solution in water solvent, and
3) **Gaseous Solution**: Here, **solvent** is **gas**, for example, air is a gaseous solution of O_2, CO_2, etc. (solute) and N_2 (Solvent).

The following 9- types of solutions are possible with above three types of solvent —

Type	Solute in Solvent	Examples
Solid Solutions	Solid in solid Liquid in solid Gas in solid	Brass ($1\ Zn + 4\ Cu$) alloy $Hg\ in\ Na$ (Sodium amalgam); H_2O in $CuSO_4.5\ H_2O$ crystals Hydrogen gas in spongy Palladium metal
Liquid Solutions	Solid in liquid Liquid in liquid Gas in liquid	Sugar in water Ethanol in water CO_2 gas in water (soda water: cold drinks)
Gaseous Solutions	Solid in gas Liquid in gas Gas in gas	Smoke (C- particles in air) Moisture (water vapour in air) Air (O_2, CO_2, etc. (solute) and N_2); not perfect solution

Different concentration units: Measures of Compositions—

The concentration of a solution represents the quantity of solute in a given quantity of solvent or solution. The concentrations of solutions are expressed in different units. Generally following units are used —

1) **Molarity (M)**: Moles of the solute per litre of the solution
2) **Normality (N)**: Equivalents of the solute per litre of the solution
3) **Molality (m)**: Moles of the solute per kg of the solvent
   Note: $Mass\ of\ solvent = (Volume\ of\ solution \times Density) - Mass\ of\ solute$
4) **Mole Fraction** (χ): It is the ratio of the number of moles of solute (n_2) or solvent (n_1) to the total number of moles (n) in the solution. Thus —

$$Mole\ fraction\ of\ Solvent, \chi_1 = \frac{n_1}{n_1 + n_2} = \frac{n_1}{n}\left[Mole, n = \frac{w\ (mass\ of\ the\ substance)}{M\ (Molar\ mass\ of\ the\ substance)}\right]$$

$$Mole\ fraction\ of\ Solute, \chi_2 = \frac{n_2}{n_1 + n_2} = \frac{n_2}{n}$$

Such that —

$$\boxed{\chi_1 + \chi_2 = 1}$$

Some other units used to express concentrations are —

[**1**] ***Formality*** **(*F*)**: Gram formula mass of the solute(ionic) per litre of the solution

For example: $1F\ NaCl$ solution $= 1\ g$ formula mass of $NaCl/\ L = 58.5\ g$ of $NaCl/\ L$

Generally, if 'a' gram of a solute of formula mass 'F' dissolved in 'b' mL of solution, then the solution so formed has the strength —

$$Formality = \frac{a}{F} \times \frac{1000}{b}\ (F)$$

$$or\ \ Formality = \frac{Mass\ of\ the\ Substance}{Formula\ Mass\ of\ the\ Substance} \times \frac{1000}{Vol\ of\ Sol\ in\ cc\ (mL)}\ (F)$$

[**2**] ***Parts Per Million*** **(*ppm*)**: It is the parts of the solute present per million parts of the solution, *i.e.* —

$$ppm = \frac{Mass\ of\ the\ Solute}{Mass\ of\ the\ Solution} \times 10^6$$

[**3**] ***Percentage*** **(%)**: Mass or volume or both of solute present per 100 parts so the solution. Percentage (%) concentration may be —

$a)$ $\boldsymbol{Mass\ to\ Mass\ Percentage}\left({}^{M}/_{m}\right) = \frac{Mass\ of\ the\ Solute}{Mass\ of\ the\ Solution} \times 100$

For example, $5\%\ \left({}^{M}/_{m}\right)\ solution\ of\ NaCl = 5g\ NaCl\ in\ 100\ mL\ solution$

$b)$ $\boldsymbol{Mass\ to\ Volume\ Percentage}\left({}^{M}/_{V}\right) = \frac{Mass\ of\ the\ Solute\ in\ g}{Mass\ of\ the\ Solution\ in\ mL} \times 100$

For example, $5\%\ \left({}^{M}/_{V}\right)\ solution\ of\ NaCl = 5g\ NaCl\ in\ 95\ g\ water\ (solvent)$

$c)$ $\boldsymbol{Volume\ to\ Volume\ Percentage}\left({}^{V}/_{V}\right) = \frac{Volume\ of\ Solute\ in\ mL}{Volume\ of\ the\ Solution\ in\ mL} \times 100$

$d)$ $\boldsymbol{Volume\ to\ Mass\ Percentage}\left({}^{V}/_{M}\right) = \frac{Volume\ of\ Solute\ in\ mL}{Mass\ of\ the\ Solution\ in\ g} \times 100$

Problem (1): A solution of 20 % $EtOH$ by mass in water has a density of $0.966\ kg\ dm^{-3}$. Calculate —

a) Mole-fraction,
b) Molality and
c) Molarity of $EtOH$ in the solution.

Note :
$1 \rightarrow$ Solvent
$2 \rightarrow$ Solute

Solution: 20 % $EtOH$ in water ($by\ mass$)

$\Rightarrow 20\ g$ Ethanol ($EtOH$) present in $100\ g$ solution

Therefore, mass of water $= 80\ g$

∴ Moles of water, $n_1 = {}^{80}/_{18} = 4.44\ mol$,

And, moles of ethanol, $n_2 = {}^{20}/_{46} = 0.4348\ mol$,

Now, (a) Mole-fraction of ethanol —

$$\chi_2 = \frac{n_2}{n_1 + n_2}$$

$$= \frac{0.4348}{4.44 + 0.4348} = 0.0897$$

$$\left\| \text{Molality } (m) = \frac{a}{M} \times \frac{1000}{b(\text{in gram})} \right.$$

[Therefore, mole-fraction of water, $\chi_2 = 1 - 0.0897 = 0.9103$]

(b) Molality of the 20 % $EtOH$ solution is —

$$= \frac{20}{46} \times \frac{1000}{80} = 5.435\ m\ (i.e. 5.435\ mol\ kg^{-1})$$

$$\left| D = \frac{m}{V} \right.$$

$$(c)\ Volume\ of\ the\ solution\ (b) = \frac{m}{D} = \frac{100 \times 10^{-3} kg}{0.966\ kg\ dm^{-3}} = \frac{100}{966} L\ [\because L = dm^3]$$

$$\therefore Molarity = \frac{a}{M} \times \frac{1000}{b(in\ mL)} = \frac{a}{M} \times Vol\ of\ solution\ in\ L^{-1}$$

$$= \frac{20}{46} \times \frac{1000}{100/966} = 4.2\ M\ (i.e. 4.2\ mol\ L^{-1})$$

Problem (2): An aqueous 12 % $AgNO_3$ solution has a density of 1.1080 $g\ cm^{-3}$ at 20℃ and 1 atm pressure. Find the mole-fraction, the molar concentration and molality (m) of the solute. (Given relative atomic mass of $Ag = 108$)

Solution: 12 % $AgNO_3$ in water ($by\ mass$)

⇒ 12 g Silver nitrate ($AgNO_3$) present in 100 g solution

Therefore, mass of water present = 88 g

∴ Moles of water, $n_{H_2O} = {}^{88}/_{18} = 4.889\ mol$,

And, moles of $AgNO_3$, $n_{AgNO_3} = {}^{12}/_{170} = 0.0706\ mol$,

Now, mole-fraction of $AgNO_3$ —

$$\chi_{AgNO_3} = \frac{n_{AgNO_3}}{n_{H_2O} + n_{AgNO_3}}$$

$$= \frac{0.0706}{4.889 + 0.0706} = 0.0142$$

[Therefore, mole-fraction of water, $\chi_1 = 1 - 0.0142 = 0.9858$]

Hence —

Molar concentration, $c = mol\ L^{-1}$

$$= \frac{0.0706\ mol}{{100g}/{1.1080\ g\ cm^{-3}}} = 7.822 \times 10^{-4} mol\ cm^{-3}$$

$$= 7.822 \times 10^{2} mol\, m^{-3} [1\ cm = 10^{-2} m; 1m^3 = 1000\ L$$

$$= 7.822 \times 10^{-1} mol\, dm^{-3}$$

Finally —

$$\therefore Molarity = \frac{a}{M} \times \frac{1000}{b(in\ mL)}$$

$$= \frac{12}{170} \times \frac{1000}{88} = 0.8021\ M\ (i.e. 0.8021\ mol\, L^{-1})$$

Solubility of Gases in Liquids:

Expressed by the term **Solubility Coefficient —**

Solubility coefficient is defined as the volume of the gas dissolved by the unit volume of the liquid solvent. It is important to note that the volume of the dissolved is determined at the temperature and pressure at which the measurement of solubility is made.

Following are the ***factors that affect*** the Solubility of a gas in a Liquid **—**

1) ***Nature of the gas and solvent***: Gases which can be liquefied ($e.g. CO_2, NH_3, HCl$, *etc*.) more easily are more soluble in common solvents, Again, chemical similarity between the gas and the solvent results greater solubility (***like dissolves like***).
2) ***Effect of Temperature***: At constant pressure, the solubility of a decrease with the rise in temperature (as ***exothermic process***).
3) ***Effect of Pressure***: Pressure has a remarkable effect on the solubility of gases. The effect of pressure on the solubility of gases is well explained by ***Henry's law***.

Effect of Pressure on Solubility: *Henrys law*

With the increase in pressure, solubility of a gas in liquid also increases and the quantitative effect of pressure of a gas is found by ***Henrys law***, which states that —

"The mass of a gas dissolved per unit volume of a liquid solvent is proportional to the pressure of the gas in equilibrium with the solution at constant temperature."

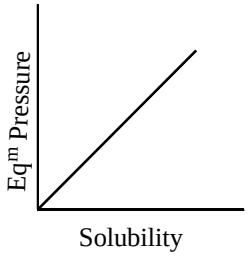
Thus, if 'w' gram of a gas dissolved in 'M' gram of a liquid at pressure 'p', at constant temperature, then according to ***Henrys law*** —

$$\frac{w}{M} \propto p$$

$$or \quad \chi_2 \propto p$$

$$\Rightarrow \chi_2 = k_H' p$$

$$\chi_2 = k_H p \qquad \rightarrow (1)$$



Where: $k_H = {}^{1}/_{k_H'}$ is called the ***Henrys law constant***, whose **magnitude depends on** —

1. The nature of the gas,
2. Solvent and
3. The unit of pressure.

Equation (1) is an equation of straight line passing through origin. Thus, a **plot** of the **solubility** of the gas versus the **equilibriumpressure** at a given temperature gives a straight line passing through origin as shown in the figure. This shows the validity of Henrys law.

***Limitations of Henrys Law*:**

Henrys law is **valid** only for **dilute solution** and especially for **ideal gases**. For real gases, the law holds if—

1. The pressure is low, at high pressure the law becomes less probable, and the proportionality constant shows a considerable variation,
2. The temperature is not too low,
3. The dissolved gas neither reacts with the solvent nor dissociates or associates in the solvent, and
4. The solubility of the gas is low.

Dilute Solution:

Definition: A solution is said to a dilute solution if the number of solute present in the solution is relatively lower than the solvent present in the solution by volume. ($n_1 \gg n_2$)

Binary Solution: A solution having only two components viz. solvent and solute is called a binary solution.

Important: For binary solution we always mean a solution made by non-volatile solute in volatile solvent

Ideal Solution: An ideal solution is defined as the solution in which there is complete uniformity in cohesive forces *i.e.* the solute-solute; solvent-solvent and solute-solvent interactions are identical in an ideal solution. Thus, if there are two components A & B, forming an ideal solution, then the intermolecular forces between $A-A, A-B$ & $B-B$ are essentially equal.

Characteristics of an Ideal Solution —

An ideal solution possesses the following characteristics —

1) There should not be any evolution or absorption of heat during mixing of two pure components, $i.e. \Delta H_{mix} = 0$,
2) There should not be any change in volume during mixing of two pure components, $i.e. \Delta V_{mix} = 0$, and
3) An ideal solution must obey ***Raoults*&*Henrys law*** over the whole range of concentration.

Examples of Ideal Solution —

1) C_2H_4Br &C_2H_4Cl
2) C_6H_{14}&C_7H_{16}
3) C_6H_6&$C_6H_5CH_3$

4) $CCl_4 \& SiCl_4,\ etc.$

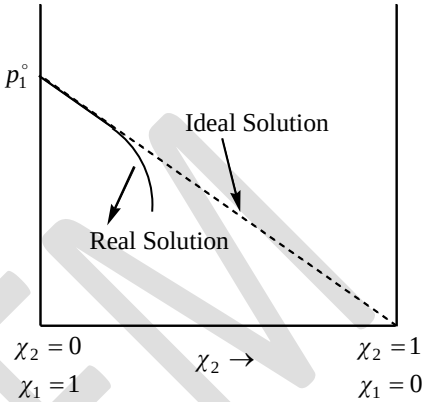
Ideally Dilute Solution: An ideally dilute solution is solution for which —

1) Solvent obeys **Raoults law** and
2) Solute obeys **Henrys law** over the whole range of concentration of the solution

Raoults Law:

[Ideal solution of non-volatile solute in volatile solvent and Raoults law]

We know that the vapour pressure of a pure solvent is always greater than that the vapour pressure of the solution (p), formed by mixing a non-volatile solute.



Thus, if $p_1^0 =$ VP of the pure solvent and

$p =$ VP of the solution of non-volatile solute in volatile solvent, then —

$$p_1^0 > p$$

Thus, the plot of $p_1^0\ vs\ \chi_2$, the mole fraction of the solute in the solution will be a straight line for an ideal solution, as shown in the figure. And, the equation for the ideal solution will be —

$$p = p_1^0 - p_1^0\chi_2 [y = mx + c]$$

$$= (1 - \chi_2)p_1^0 = \chi_1 p_1^0 [\because \chi_1 + \chi_2 = 1]$$

$$Thus, \quad p \propto \chi_1$$

Here, 'χ_1' is the mole-fraction of the solvent.

Thus, the vapour pressure of a solution of a non-volatile solute in a volatile solvent is equal to the product of the vapour pressure of the pure solvent and the mole fraction of the solvent in the solution. This is known as the ***Raoults law***.

Actually, an ***ideal solution*** is the one, which obey Raoults law over the whole range of conc. A ***real solution***behaves ideally when it obeys ***Raoults law*** at low concentration of the solution with $\chi_2 \rightarrow 0$.

Relation between Raoults law and Henrys law:

Raoults law may be regarded as a special case of Henrys law. From Henrys law —

$$p_2 = k_H \chi_2 \qquad \rightarrow (1)$$

p_2 →Pressure of the gas, the solute dissolved

In the case when Henrys law is applicable over the whole range of concentration *i.e.* for an infinitely dilute solution ($\chi_2 \rightarrow 0$, pure solvent) to the liquid solute ($\chi_2 \rightarrow 1$, pure solvent) then p_2 would become the vapour pressure of the pure solvent, hence —

$$p_2^0 = k_H \qquad \rightarrow (2)$$

From equation (1) and (2) —

$$p_2 = p_2^0 \chi_2$$

This expression is identical with the Raoults law, for a volatile solute. All systems, which obey Raoults law, must satisfy Henrys law, but the reverse will only true if Henrys law applies over the whole range of concentration.

Problem (1): $1\ dm^3$ of water under a nitrogen pressure of $1\ atm$ dissolves $2 \times 10^{-5}\ kg$ of nitrogen at $293\ K$. Calculate Henrys law constant.

Solution: From ***Henrys law*** —

$$p = k_H \chi_2$$

Again —

$$\chi_2 = \frac{n_2}{n_1 + n_2}$$

$$= \frac{{}^{2 \times 10^{-5}}/_{28 \times 10^{-3}}}{{}^{1}/_{18 \times 10^{-3}} + {}^{2 \times 10^{-5}}/_{28 \times 10^{-3}}} = 1.29 \times 10^{-5}$$

Here, $p = 1\ atm$

$$\therefore\ k_H = \frac{p}{\chi_2} = \frac{1\ atm}{1.29 \times 10^{-5}} = 7.7 \times 10^4\ atm$$

Problem (2): Calculate the amount of oxygen ($0.20\ atm$) dissolved in $1\ dm^3$ of water at $293\ K$. The Henrys law constant for oxygen is $4.58 \times 10^4\ atm\ \ at\ 293\ K$.

Solution: From Henrys law —

$$\chi_2 = \frac{p}{k_H}$$

$$\Rightarrow \chi_2 = \frac{0.20\ atm}{4.58 \times 10^4\ atm} = 4.37 \times 10^{-6}$$

Now —

$$\chi_2 = \frac{n_2}{n_1 + n_2}$$

$$\Rightarrow 4.37 \times 10^{-6} = \frac{n_2}{1/(18 \times 10^{-3}) + n_2}$$

$$\Rightarrow n_2 = 2.43 \times 10^{-4}$$

$\therefore$ Amount of O_2 dissolved $= 2.43 \times 10^{-4} \times 32 \times 10^{-3}\ kg$

$$= 7.78 \times 10^{-6}\ kg$$

Problem (3): The Henrys law constant for oxygen at $293\ K\ is\ 3.37 \times 10^7\ mm$. Find the solubility of oxygen in $1000\ g$ of water at $293\ K$ and a partial pressure of $190\ mm\ of\ Hg$.

Solution: From Henrys law —

$$\chi_2 = \frac{p}{k_H}$$

$$\Rightarrow \chi_2 = \frac{190\ mm}{3.37 \times 10^7} = 5.75 \times 10^{-6}$$

Again —

$$\chi_2 = \frac{n_2}{n_1 + n_2}$$

$$\Rightarrow 5.75 \times 10^{-6} = \frac{n_2}{1000/18 + n_2}$$

$$\Rightarrow n_2 = 3.194 \times 10^{-4}\ mol/1000\ g\ of\ water$$

$\therefore$ Amount of O_2 dissolved $= 3.194 \times 10^{-4} \times 32\ kg$

$$= 1.03 \times 10^{-2}\ g/1000\ g\ of\ water$$

$$\therefore Solubility\ of\ O_2 = \frac{1.03 \times 10^{-2}}{1000} \times 100$$

$$= 1.03 \times 10^{-3} \frac{g}{1000} g\ of\ water$$

❖ EXPRESSION FOR CHEMICAL POTENTIAL OF THE SOLVENT IN AN IDEAL BINARY SOLUTION :

As the solution of a non-volatile solute is in equilibrium with vapour, the chemical potential of the solvent have the same value as in the solution and in the vapour. Therefore, —

$$\mu_{liq} = \mu_{vap} \qquad \rightarrow (1)$$

Here, μ_{liq} = Chemical potential of the solvent in the solution and
μ_{vap} = Chemical potential in the vapour state

Assuming that the vapour behaves ideally, we have —

$$\mu_{vap} = \mu_{vap}^0 + RT\ \ln p$$

$$\Rightarrow \mu_{liq} = \mu_{vap}^0 + RT\ \ln p,\ \ using\ eq^n(1)$$

Here, p = The vapour pressure of the solvent in the solution, and
μ_{vap}^0 = The chemical potential of the vapour of the solution under standard condition

From ***Raoults law***, we have —

$$p = \chi_1 p_1^0$$

Here, p_1^0 is the vapour pressure of the pure solvent and χ_1 is the mole-fraction of the solvent in the solution. Therefore —

$$\mu_{liq} = \mu_{vap}^0 + RT\ \ln \chi_1 + RT\ \ln p_1^0 \qquad \rightarrow (2)$$

For the pure solvent in equilibrium with its vapour, having vapour pressure p_1^0, the equilibrium condition is —

$$\mu_{liq}^0 = \mu_{vap}^0 + RT\ \ln p_1^0$$

$$\Rightarrow \mu_{vap}^0 = \mu_{liq}^0 - RT\ \ln p_1^0 \qquad \rightarrow (3)$$

From equation (2) and (3), we have —

$$\mu_{liq} = \mu_{liq}^0 + RT\ \ln \chi_1$$

The above equation does not contain any term pertaining the vapour pressure. By omitting the subscript "liquid", it can be written as —

$$\mu_1 = \mu_1^0 + RT \ln \chi_1 \qquad \rightarrow (4)$$

Here, μ_1 is the chemical potential of the solvent in the solution and μ_1^0 is that for the pure solvent in liquid phase. The equation (4) is an expression for the chemical potential of the solvent in the solution.

- ***Chemical Potential of the Solute (non-volatile in volatile solvent) in an Ideal Binary Solution*:**

The expression for the chemical potential of a non-ideal solute in an ideal binary solution can be derived by applying ***Gibbs-Duhem*** equation in the system —

$$n_1 d\mu_1 + n_2 d\mu_2 = 0$$

$$\Rightarrow d\mu_2 = -\frac{n_1}{n_2} d\mu_1$$

$$= -\frac{n_1}{\chi_2} d\mu_1 \qquad \rightarrow (1)$$

Gibbs - Duhem equation is $\sum_{i=1}^{n} n_i d\mu_i = 0$

Solvent, $\chi_1 = \frac{n_1}{n_1 + n_2}$

Solute, $\chi_2 = \frac{n_2}{n_1 + n_2}$

$\therefore \frac{\chi_1}{\chi_2} = \frac{n_1}{n_2}$

Again the chemical potential for a pure solvent in the solution is given by —

$$\mu_1 = \mu_1^0 + RT \ln \chi_1 \qquad \rightarrow (2)$$

Here, μ_1^0 is the chemical potential of the pore solvent in liquid phase, which is a constant quantity for a given solvent.

Now differentiating equation (2) with respect to χ_1 at constant T & P, we get —

$$d\mu_1 = 0 + RT \frac{d\chi_1}{\chi_1}$$

$$i.e.\ d\mu_1 = RT \frac{d\chi_1}{\chi_1} \qquad \rightarrow (3)$$

Substituting equation (3) in equation (1), we have —

$$d\mu_2 = -RT \frac{d\chi_1}{\chi_1} \qquad \rightarrow (4)$$

Since, for a binary solution —

$$\chi_1 + \chi_2 = 1$$

$$\Rightarrow \chi_1 = 1 - \chi_2$$

$$\Rightarrow d\chi_1 = -d\chi_2$$

$$\therefore Equation\ (4) \Rightarrow d\mu_2 = RT \frac{d\chi_2}{\chi_2}$$

Integrating $\mu_2 = RT \ln \chi_2 + I$ (Integrating constant)

When $\chi_2 = 1 i.e.$ for pure solvent, $I = \mu_2^0$ the chemical potential of pure solvent and hence,

$$\mu_2 = \mu_2^0 + RT \ln \chi_2 \qquad \rightarrow (5)$$

Equation (5) is the required expression for the ***chemical potential*** of a ***solute*** in an ideal binary solution. //

❖ *COLLIGATIVE PROPERTIES OF DILUTE SOLUTION* :

: Since the **chemicalpotential** of the **solvent** in the solution is given by the expression —

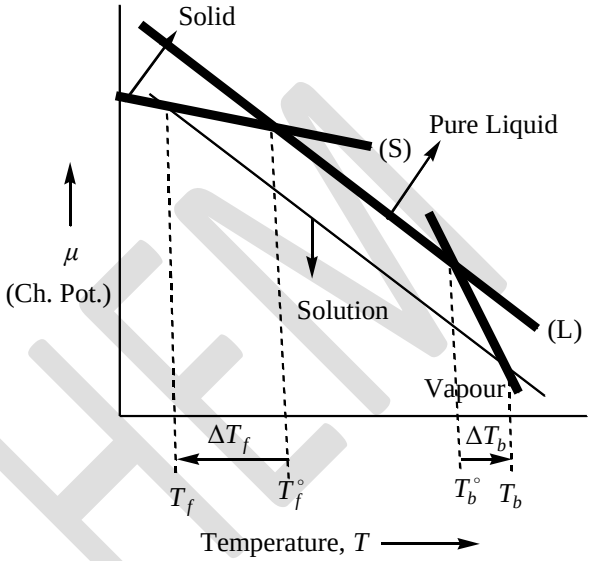
$$\mu_1 = \mu_1^0 + RT \ln \chi_1$$

Where, μ_1^0 = Chemical potential of the pure solvent, and
χ_1 = Mole-fraction of the solvent in the solution

Since, $\chi_1 < 1$

$$\Rightarrow RT \ln \chi_1 = -ve\ quantity\ and\ hence, \mu_1 < \mu_1^0$$

Thus, the ***chemical potential of the solvent in solution is always less than the chemical potential of the pure solvent by an amount*** $\boldsymbol{RT \ln \chi_1}$. Several related properties of the solution have their origin in this lower value of chemical potential. These properties are —



1. Lowering of vapour pressure,
2. Elevation of boiling point,
3. Depression of freezing point, and
4. Osmotic pressure.

Since, all these properties are bound together through their common origin, hence, are called colligative properties (***Latin***: **co** — together & **ligore** — to bind). All these properties have a common characteristic; they do not depend on the **nature of the solute** present but only depends on the **number of solute molecules**. Thus, colligative properties are those properties which depend on the number of solute particles present in the solution.

The plot of $\mu\ vs\ T$ as shown in the **figure** given above, gives an idea about the colligative properties. In the figure **dark-line** represents the pure solvent and the **thick-line** refers to the solvent in the ideal solution. Since, the solute is non-volatile, it does not appear in the vapour phase, and so the curve for the vapour is that of the pure solvent. The solid also containing solvent and so the curve is for pure solid (S). The intersection points of solid and liquid curves are **freezing point**. From the **figure**, it is clear that $T_f < T_f^0$; where T_f is the freezing point of solution and T_f^0 that for pure solvent. Similarly, $T_b^0 > T_b$ *i.e.* **elevation of boiling point**. From the **figure** it is also evident that the magnitude of $\Delta T_f < \Delta T_b$.

The freezing point and boiling point of a solution depends on the equilibrium of the solvent in solution with pure solid solvent or pure solvent vapour. Another equilibrium is also possible to be established between solvent in solution and pure liquid solvent. This is done by increasing the pressure on the solution to rise the 'μ_1' of the solvent in solution to the value of μ_1^0 of the pure solvent. The additional pressure on the solution that is required to establish the equality of the μ_1 of the solvent both in the solution and in pure solvent is called the **osmotic pressure** of the solution.

Lowering of vapour pressure of solvent :

[Raoults law of relative lowering of vapour pressure]

Whenever a non-volatile substance is dissolved in a volatile solvent, the vapour pressure of the solvent is lowered. This lowering of vapour pressure can be explained from ***Raoults law*** of ideal solution.

Considering a solution obtained by dissolving a non-volatile solute in a volatile solvent. If $\chi_1 \& \chi_2$ are the **mole fractions** of the solvent and solute and $p_1^0 \& p$ be the **vapour pressure** of the pure solvent and solvent in solution respectively, than according to ***Raoults law*** —

$$p = p_1^0 \chi_1$$

Since, $\chi_1 < 1, hence\ \ p < p_1^0$

Thus, the vapour pressure of the solution is less than the vapour pressure of the pure solvent. On the other hand, the addition of a non-volatile solute (electrolyte) to the solvent lead to lower the vapour pressure of the pure solvent. If Δp is the lowering of vapour pressure, then —

$$\Delta p = p_1^0 - p$$

$$or \quad p_1^0 - p = p_1^0 - p_1^0 \chi_1$$

$$= p_1^0 (1 - \chi_1)$$

$$= p_1^0 \chi_2$$

$$\Rightarrow \frac{p_1^0 - p}{p_1^0} = \chi_2 \qquad \rightarrow (1)$$

The quantity $(p_1^0 - p)/p_1^0$ is known as the relative lowering of the vapour pressure and is independent of the nature of solute. The equation (1) is called the ***Raoults law of relative lowering of vapour pressure***, and may be **stated** that in dilute solutions, the relative lowering of vapour pressure of the solute is equal to the mole-fraction of the solute (χ_2).

Again, equation (1) can also be written as —

$$\frac{p_1^0 - p}{p_1^0} = \chi_2 = \frac{n_2}{n_1 + n_2}$$

Here, $n_1 \& n_2$ are the number of moles of solvent and solute respectively. For dilute solution, $n_1 \gg n_2$, hence —

$$\frac{p_1^0 - p}{p_1^0} \approx \frac{n_2}{n_1}$$

$$p_1^0 - p = \frac{p_1^0}{n_1} . n_2$$

For a given amount of solvent, at a given temperature $^{p_1^0}/_{n_1} = Constant$

$$\therefore \ (p_1^0 - p) \propto n_2$$

Which means that the lowering of vapour pressure of a solvent is directly proportional to the number of moles of the solute, i.e. the relative lowering of vapour pressure depends only on the

number of moles ($g\text{-}mole$) of the solute in the solution. This indeed is a direct consequence from the ***Raoults law***. The lowering of vapour pressure is thus a colligative property.

Application of Lowering of Vapour Pressure:

Determination of Molar Mass of the Solute from the Lowering of Vapour Pressure:

From the ***Raoults law of Lowering of Vapour Pressure***, we have —

$$\frac{p_1^0 - p}{p_1^0} = \chi_2 = \frac{n_2}{n_1 + n_2} \qquad \rightarrow (1)$$

Where, $p_1^0 =$ vapour pressure of the pure solvent,
$p =$ Vapour pressure of the solvent in the solution,
And $n_1 \& n_2$ are the number of moles of solvent & solute respectively.

If $w_1 \& w_2$ be the masses of the solvent and solute having molar masses $M_1 \& M_2$ respectively, then —

$$n_1 = \frac{w_1}{M_1} \quad and \quad n_2 = \frac{w_2}{M_2}$$

Hence, from equation (1), we have —

$$\frac{p_1^0 - p}{p_1^0} = \frac{{}^{w_2}/_{M_2}}{{}^{w_1}/_{M_1} + {}^{w_2}/_{M_2}} \qquad \rightarrow (2)$$

From equation (2), we can determine the molar mass of the solute (M_2) accurately.

The simplified form of equation (2) can be obtained as —

$$\frac{p_1^0 - p}{p_1^0} = \frac{n_2}{n_1} \quad \because for\ dilute\ Sol^n n_1 \gg n_2 \Rightarrow n_1 + n_2 \approx n_1$$

$$\Rightarrow \frac{p_1^0 - p}{p_1^0} = \frac{{}^{w_2}/_{M_2}}{{}^{w_1}/_{M_1}} = \frac{w_2 M_1}{w_1 M_2}$$

$$\Rightarrow M_2 = \left(\frac{p_1^0}{p_1^0 - p}\right)\frac{w_2}{w_1} M_1 \qquad \rightarrow (3)$$

Using equation (3), we can determine molar mass of the solute easily.

Problem (1): The vapour pressure of water at 293 $K\ is$ 17.540 $mm\ Hg$ and the vapour pressure of a solution containing 0.10824 kg of a non-volatile solute in 1 kg of water at the same temperature is 17.354 $mm\ Hg$. Calculate the molar mass of the solute.

$1 \rightarrow$ Solvent
$2 \rightarrow$ Solute

Solution: Given —

Vapour pressure of pure solvent, water $p_1^0 = 17.540\ mm\ Hg$

Vapour pressure of solution, $p = 17.354\ mm\ Hg$

Mass of the solute, $w_2 = 0.10824\ kg$

Molar mass of the solute, $M_2 = ?$

Mass of the solvent, $w_1 = 1\ kg$

Molar mass of the solvent, $M_1 = 18 \times 10^{-3} kg$

From the ***Raoults law*** of relative lowering of vapour pressure, we have —

$$\frac{p_1^0 - p}{p_1^0} = \chi_2 = \frac{n_2}{n_1 + n_2} = \frac{{}^{w_2}/_{M_2}}{{}^{w_1}/_{M_1} + {}^{w_2}/_{M_2}}$$

$$\Rightarrow M_2 = 0.1819\ kg\ mol^{-1} = 181.9\ g\ mol^{-1}$$

This the accurate value of the molar mass of the solute.

But, if we use the simplified equation —

$$\frac{p_1^0 - p}{p_1^0} = \frac{n_2}{n_1} = \frac{{}^{w_2}/_{M_2}}{{}^{w_2}/_{M_2}}, \quad assuming\ \ n_1 \gg n_2 \Rightarrow n_1 + n_2 \approx n_1$$

Then, $M_2 = 0.1838\ kg\ mol^{-1} = 183.8\ g\ mol^{-1}$

Thus, by using the simplified alternative equation, we have a difference in molar mass by $1.9\ g\ mol^{-1}$. //

Problem (2): The vapour pressure of ethanol at 20℃ is $44.5\ mm$, when $15\ g$ of a non-volatile compound 'A' is dissolved in $500\ g$ of ethanol the vapour pressure is $43.52\ mm$. Calculate the molecular weight of compound 'A'.

Solution: Here —

Vapour pressure of pure solvent, water $p_1^0 = 44.5\ mm$
Vapour pressure of solution, $p = 43.52\ mm$
Mass of the solute, $w_2 = 15\ g$
Molar mass of the solute, $M_2 = ?$
Mass of the solvent, $w_1 = 500\ g$
Molar mass of the solvent, $M_1 = 46\ g\ mol^{-1}$

From the ***Raoults law*** of relative lowering of vapour pressure, we have —

$$\frac{p_1^0 - p}{p_1^0} = \chi_2 = \frac{n_2}{n_1 + n_2} = \frac{{}^{w_2}/_{M_2}}{{}^{w_1}/_{M_1} + {}^{w_2}/_{M_2}}$$

$$\Rightarrow M_2 = 61.34\ g\ mol^{-1}$$

Problem (3): $15g$ of glucose is added to $250g$ of water at 20℃. If the vapour pressure of water at 20℃ is $17.537mm$, calculate —

a) Lowering in vapour pressure, and
b) Relative lowering of vapour pressure at the same temperature.

Solution: From the Raoults law of relative lowering of vapour pressure, we have —

$$\frac{p_1^0 - p}{p_1^0} = \chi_2 = \frac{n_2}{n_1 + n_2}$$

Lowering of vapour pressure is, $\Delta p = p_1^0 - p$

$\therefore$ Lowering of vapour pressure is, $\Delta p = p_1^0 - p = p_1^0 \chi_2$

Here —

$$n_1 = \frac{w_1}{M_1} = \frac{250\ g}{18\ gmol^{-1}} = 13.889\ mol$$

$$n_2 = \frac{w_2}{M_2} = \frac{15\ g}{180\ gmol^{-1}} = 0.083\ mol$$

$$\therefore \quad \chi_2 = \frac{n_2}{n_1 + n_2} = 5.94 \times 10^{-3}$$

Thus, the relative lowering of vapour pressure, $\left.p_1^0 - p\right/_{p_1^0} = 5.94 \times 10^{-3}$

And, lowering of vapour pressure, $\Delta p = p_1^0 - p = p_1^0 \chi_2$

$$= 17.537\ mm \times\ 5.94 \times 10^{-3}$$

$$= 0.104\ mm$$

Problem (4): The vapour pressure of water at 25℃ is 23.76 mm. Calculate — the vapour pressure of 20 % glucose in water. Repeat the same calculation when 38 g of sucrose is dissolved in 100 g of water. Is the results in this case is different? If not, why? Finally, calculate the vapour pressure of water at the same temperature when 20 g of glucose is dissolved in 100 g of water.

Solution: $1^{st}\ part = 23.19\ mm; 2^{nd}\ part = Same;\ 3^{rd}\ part = 23.29\ mm$

Problem (5): The vapour pressure of water at 20℃ is 17.54 mm and that for 10 % urea is 16.93 mm. Calculate its molecular weight.

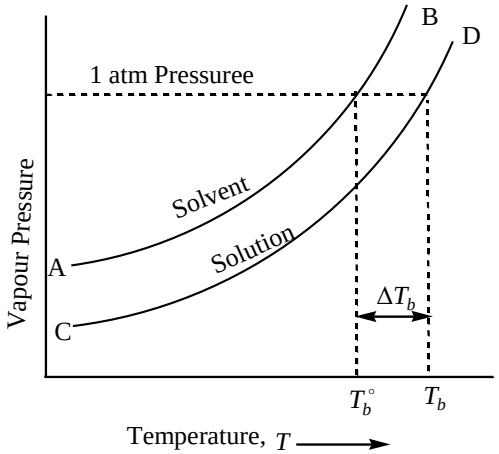
Solution: 33.56 $gmol^{-1}$

Problem (6): 126.28 g of compound 'A' was added in 1000 g of water. Calculate the relative lowering in vapour pressure of water at 20℃.

Solution: 17.38 mm

Elevation of Boiling Point by a Non-Volatile Solute:
[*Raoults law of Elevation of Boiling Point*]

The boiling point of a liquid is the temperature at which its vapour pressure becomes equal to the atmospheric pressure (760 $mm\ of\ Hg$). Since, the vapour pressure of a **solution** is always **lower** than that of the pure **solvent**; it follows that the boiling point of a solution will always be higher than that of the pure solvent. This fact can be readily understood from the vapour pressure curves against temperature as shown in the figure given below —



The upper curve (AB), represents the vapour pressure — temperature of the pure solvent and the lower curve (CD) represents the vapour pressure — temperature relationship of a dilute solution. It is evident that the vapour pressure of the solution (p) is lower than that of the pure solvent (p_1^0) at every temperature. The temperature T_1^0 gives the boiling point of the pure solvent and T that for solution, because at these temperatures the vapour pressure becomes equal to the external atmospheric pressure, as shown in the figure. From the **figure** it is clear that —

$$T > T_1^0$$

$$and, \qquad \Delta T_b = T - T_1^0$$

The term ΔT_b is known as the ***elevation of boiling point*** of a ***dilute solution*** of non-volatile solute in volatile solvent.

❖ Expression for Elevation of Boiling Point:

[From TD considerations *i.e.* Chemical Potential point of view]

Let us consider a dilute solution of non-volatile solute (2) is in equilibrium with the pure solvent (1). Hence, we have —

$$\mu_1^S = \mu_1^v \qquad \rightarrow (1)$$

Where, μ_1^S = Chemical potential of 1, the pure solvent in solution, and

μ_1^v = The chemical potential of 1, in the vapour state *i.e.* at its boiling point

If the solution behaves ideally, then —

$$\mu_1^S = \mu_1^0(S) + RT \ \ln \chi_1 \qquad \rightarrow (2)$$

Here, $\mu_1^0(S)$ is the chemical potential of the pure solvent in the liquid state and $\chi_1$is the mole fraction of 1 in the solution.

From equation (1) & (2), we have —

$$\mu_1^v = \mu_1^0(S) + RT \ \ln \chi_1$$

$$\Rightarrow \ln \chi_1 = \frac{\mu_1^v - \mu_1^0(S)}{RT}$$

$$or \quad \ln \chi_1 = \frac{\Delta G_{vap}}{RT} \qquad \rightarrow (3)$$

Where, $\Delta G_{vap} = \mu_1^v - \mu_1^0(S) =$ Change in free energy in the vapour state

Differentiating equation (3), with respect to χ_1 at constant pressure p , we have —

$$\frac{1}{\chi_1} = \frac{1}{R}\frac{d}{d\chi_1}\left[\frac{\Delta G_{vap}}{T}\right]_p$$

$$= \frac{1}{R}\left[\frac{\partial\left(\Delta G_{vap}/T\right)}{\partial T}\right]_p \times \left(\frac{\partial T}{\partial \chi_1}\right)_p \qquad \rightarrow (4)$$

Again, from ***Gibbs-Helmholtz*** equation —

$$\left[\frac{\partial\left(\Delta G_{vap}/T\right)}{\partial T}\right]_p = -\frac{\Delta H_{vap}}{T^2} \qquad \rightarrow (5)$$

Where, $\Delta H_{vap} =$ Enthalpy of vaporization per mole of the solvent

From equation (4) & (5), we have —

$$\frac{1}{\chi_1} = -\frac{1}{R}.\frac{\Delta H_{vap}}{T^2}.\left(\frac{\partial T}{\partial \chi_1}\right)_p \qquad \rightarrow (6)$$

Integrating equation (6), between the proper limits as shown, we have —

$$\int_1^{\chi_1} \frac{d\chi_1}{\chi_1} = -\frac{1}{R}\int_{T_0}^{T} \frac{\Delta H_{vap}}{T^2} dT \qquad \rightarrow (7)$$

Where the lower limit $\chi_1 = 1$, corresponds to the pure solvent having boiling point T_0; the upper limit χ_1 corresponds to a solution whose boiling point is T. Assuming that ΔH_{vap} is constant within the temperature range (***Kirchoff's equation***), we have from equation (7) —

$$\ln \chi_1 = -\frac{\Delta H_{vap}}{R}\left[-\frac{1}{T}\right]_{T_0}^{T}$$

$$= -\frac{\Delta H_{vap}}{R}\left[\frac{1}{T_0} - \frac{1}{T}\right]$$

$$= -\frac{\Delta H_{vap}}{R}\left[\frac{T - T_0}{TT_0}\right]$$

$$or \quad \ln \chi_1 = -\frac{\Delta H_{vap}}{R}\frac{\Delta T_b}{T_0^2} \qquad \rightarrow (8)$$

Where, $T - T_0 = \Delta T_b =$ elevation of boiling point and since for dilute solution T_0 & T are not much different, so $TT_0 = T_0^2$

Now, $\ln \chi_1 = \ln(1 - \chi_2) \qquad \because \chi_1 + \chi_2 = 1$

$$\Rightarrow \ln \chi_1 = -\chi_2 + \frac{\chi_2^2}{2} - \frac{\chi_2^3}{3} + \cdots$$

Since, χ_2 is the mole-fraction of the solute, which is very small in dilute solution (tends to zero). Therefore, —

$$\ln \chi_1 = -\chi_2 \quad (neglecting\ higher\ powers\ of\ \chi_2)$$

Hence, from equation (8), we have —

$$\ln \chi_1 = -\frac{\Delta H_{vap}}{R}\frac{\Delta T_b}{T_0^2} \qquad \rightarrow (8)$$

$$\Rightarrow -\chi_2 = -\frac{\Delta H_{vap}}{RT_0^2}\,\Delta T_b$$

$$\therefore \quad \boxed{\Delta T_b = \frac{RT_0^2}{\Delta H_{vap}}\chi_2} \qquad \rightarrow (9)$$

Therefore, we have —

$$\Delta T_b \;\propto\; \chi_2$$

Thus, the elevation of boiling point of a solution (ΔT_b) is directly proportional to the mole fraction of the solute (χ_2), hence, the ***elevation of boiling point is a colligative property***.

Generally in the study of colligative properties, ***molality*** (m) is used rather than mole – fraction of the solute. Molality of the solute is **defined** as the number of moles of the solute per kg (1000 g) of the solvent. If $n_1 \& n_2$ are the number of moles of 1 & 2 (*i.e.* solvent and solute) in the solution, then —

$$\chi_2 = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1} \qquad \because for\ dilute\ solution\ n_1 \gg n_2$$

Molality of the solute in the solution is given by —

$$m_2 = \frac{n_2}{n_1 M_1} [\Rightarrow n_2 = n_1 M_1 m_2]$$

Where, $M_1 =$ Molar mass of the solvent in $kg\ mol^{-1}$

$$\therefore\ \chi_2 = \frac{n_2}{n_1} = \frac{n_1 M_1 m_2}{n_1} = M_1 m_2$$

Therefore, from equation (9), we have —

$$\Delta T_b = \frac{RT_0^2}{\Delta H_{vap}} M_1 m_2$$

$$or \quad \boxed{\Delta T_b = \left(\frac{RT_0^2 M_1}{\Delta H_{vap}}\right) m_2} \qquad \rightarrow (10)$$

For a given solvent, the term within the bracket in equation (10) is a constant; known as the ***elevation of boiling point*** or ***ebullioscopic constant***, which is equal to the elevation of boiling point for $\mathbf{1}\ \boldsymbol{molal}$solution. It is represented by K_b and always expressed in the unit of $Kkgmol^{-1}$.

$$\therefore\ \boxed{\Delta T_b = K_b m_2}$$

$$\Rightarrow\ \Delta T_b \;\propto\; m_2$$

Thus, the elevation of boiling point is directly proportional to the molality of the solute. This is known as the Raoults law of elevation of boiling point.

To find the unit of K_b, the ebullioscopic constant:

Since, —

$$\Delta T_b = K_b m_2$$

$$\Rightarrow K_b = \frac{\Delta T_b}{m_2} = \frac{K}{mol\ kg^{-1}} = Kkgmol^{-1}$$

APPLICATION OF ELEVATION OF BOILING POINT:

Determination of Molecular Mass of the solute from Elevation of Boiling Point Measurement:

By measuring the elevation of boiling point of a solution of known concentration it is possible to calculate the molar mass of a non-volatile, non-electrolyte solute in the solution. Since, we have —

$$\Delta T_b = K_b m_2$$

Where, ΔT_b = Elevation of boiling point, and $\Delta T_b = T - T_0$
T_0 = The boiling point of the pure solvent, and
T = The boiling point of the solution
m_2 = The molality of the solute
K_b = Molal elevation of boiling point, and

$$K_b = \frac{RT_0^2 M_1}{\Delta H_{vap}}\ Kkgmol^{-1}$$

If $w_2\ kg$ of the solute of molar mass $M_2\ kg\ mol^{-1}$ is dissolved in $w_1\ kg$ of solvent, then —

$$m_2 = \frac{w_2}{M_2} \times \frac{1}{w_1}$$

$$\left\| m = \frac{a}{M} \times \frac{1000}{b\ (\text{in gram})} \right.$$

$$\left\| m = \frac{a}{M} \times \frac{1}{b\ (\text{in kg})} \right.$$

Therefore —

$$\Delta T_b = K_b \times \frac{w_2}{M_2} \times \frac{1}{w_1}$$

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

In the above expression all the quantities are known, hence the molar mass of the solute (M_2), can be easily calculated, and its unit will be $kg\ mol^{-1}$.

Problem (1): A sample of benzene that is contaminated with a non-volatile substance boils 3.1℃ higher than that of the pure benzene ($bp = 80.1$℃). What is the amount of impurity present in the sample? ($\Delta H_{vap} = 30.76\ kJmol^{-1}$)

Solution: We have —

$$\Delta T_b = K_b m_2, \quad and$$

$$K_b = \frac{RT_0^2 M_1}{\Delta H_{vap}}$$

Here, $\Delta T_b = T - T_0 = Elevation\ of\ bp = 3.1℃ = 3.1\ K$
$R = 8.314\ JK^{-1}mol^{-1}$

$T_0 = 80.1℃ = 80.1 + 273 = 353.1\ K$
$M_1 = molar\ mass\ of\ benzene = 78\ g\ mol^{-1} = 0.078\ kg\ mol^{-1}$
$\Delta H_{vap} = 30.76\ kJmol^{-1}$

On substituting the various values, we will have —

$$K_b = 2.63\ Kkg\ mol^{-1}$$

Now, from —

$$\Delta T_b = K_b m_2$$

$$\Rightarrow m_2 = \frac{\Delta T_b}{K_b} = \frac{3.1\ K}{2.63\ Kkg\ mol^{-1}} = 1.18\ mol\ kg^{-1}$$

Thus, the amount of impurity present $= 1.18\ mol\ kg^{-1}$ of benzene

Problem (2): A solution containing $2.44\ g$ of a solute dissolved in $75\ g$ of water boils at 100.413℃. Calculate the molar mass of the solute. ($K_b\ for\ water = 0.52$)

Solution: We have —

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

Here, $\Delta T_b = T - T_0 = 373.413 - 372 = 0.413\ K (= 0.413℃)$
$w_2 = 2.44\ g = 0.00244\ kg, \qquad w_1 = 75\ g = 0.075\ kg$
$K_b = 0.52\ Kkg\ mol^{-1}$

Hence, the molar mass of the solute, $M_2 = 0.04096\ kgmol^{-1}$

$$= 40.96\ gmol^{-1}$$

Problem (3): The molar hear of vaporization of water at 100℃ $is\ 40.585\ kJmol^{-1}$. At what temperature will a solution containing $5.60\ g\ glucose\ per\ 1000\ g$ of water boil?

Solution: We have —

$$\Delta T_b = T - T_0 = K_b m_2, \qquad and$$

$$K_b = \frac{RT_0^2 M_1}{\Delta H_{vap}}$$

$$= \frac{(8.314\ JK^{-1}mol^{-})(373\ K)^2(0.018\ kg\ mol^{-1})}{40585\ Jmol^{-1}}$$

$$\therefore K_b = 0.513\ Kkg\ mol^{-1}$$

Now, molality of solute (glucose, $M_2 = 180\ g$) is given by —

$$m_2 = \frac{w_2}{M_2} \times \frac{1}{w_1}$$

$$= \frac{5.60\ \times 10^{-3} kg}{180 \times 10^{-3} kg\ mol^{-1}} \times \frac{1}{1\ kg} = 0.0311\ mol\ kg^{-1}$$

$$\therefore \Delta T_b = K_b m_2 = 0.016\ K$$

$\therefore Boiling\ point\ of\ the\ solution, \qquad T = T_0 + \Delta T_b$

$$= 373\ K + 0.016\ K$$

$$= 373.016\ K = 100.016℃$$

Problem (4): A solution containing 2.5 g of a non-volatile solute in 100 g of benzene ($K_b = 2.67$) boiled at a temperature $0.42°$ higher than did the pure solvent. What is the molar mass of the solute?

Solution: 158.93 $g\ mol^{-1}$

Problem (5): $5g$ of a non-volatile solute compound is dissolved in $250g$ of water. If the molar mass of the compound is $140gmol^{-1}$, calculate the elevation of boiling point. ($\Delta H_{vap} = 40.66\ kJmol^{-1}$)

Solution: We have —

$$\Delta T_b = K_b m_2$$

$$where, \quad K_b = \frac{RT_0^2 M_1}{\Delta H_{vap}} = 0.5121\ Kkgmol^{-1}$$

And, molality of solute (m_2) is —

$$m_2 = \frac{w_2}{M_2} \times \frac{1}{w_1} = 0.1429\ mol\ kg^{-1}$$

$$\therefore \Delta T_b = K_b m_2 = 0.0732\ K = 0.0432℃$$

Problem (6): The boiling point of CCl_4 was raised by $0.325K$ when $5.141 \times 10^{-4} kg$ of anthracene ($C_{10}H_{10}$) was dissolved in $35 \times 10^{-3} kg\ CCl_4$. Calculate the molar mass of the solute (M_1). Given that for $CCl_4, K_b = 3.9\ Kkgmol^{-1}$

Solution: 176.3 $g\ mol^{-1}$

Problem (7): A solution containing $0.3g\ of\ camphor, C_{10}H_{16}O$ in $25.3g\ of\ chloroform$ boils at $334.3K$. Boiling point of chloroform is $334.0K$. Calculate the molar heat of vaporization and elevation of boiling point constant for chloroform.

Solution: Since —

$$\Delta T_b = K_b m_2$$

$$\Rightarrow K_b = \frac{\Delta T_b}{m_2} = \frac{\Delta T_b}{\frac{w_2}{M_2} \times \frac{1}{w_1}} = 3.8456\ Kkgmol^{-1}$$

Again —

$$K_b = \frac{RT_0^2 M_1}{\Delta H_{vap}}$$

$$\Rightarrow \Delta H_{vap} = \frac{RT_0^2 M_1}{K_b} = 28.82\ kJmol^{-1}$$

Problem (8): Show that the elevation of bp is a colligative property.

Solution: The elevation of boiling point, ΔT_b is given by —

$$\Delta T_b = K_b m_2 = \frac{RT_0^2 M_1}{\Delta H_{vap}} m_2$$

Again, the mole-fraction of the solute is given by —

$$\chi_2 = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1}, \qquad for\ dilute\ solution\ \ n_1 \gg n_2$$

$$\Rightarrow \Delta T_b = \frac{K_b}{n_1} \times n_2$$

$$= Constant \times n_2$$

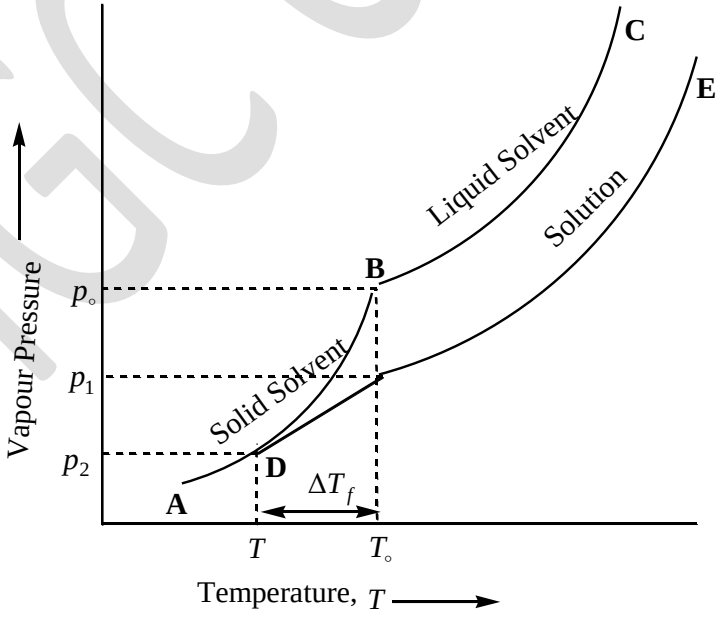
$$\Rightarrow \Delta T_b \ \propto \ n_2$$

Thus, for a given amount of a particular solvent (*i.e.* n_1 is known) ΔT_b, the elevation of boiling point is proportional to the number of moles of the solute present in the solution (n_2), and hence it is a colligative property. //

❖ Depression of Freezing Point (ΔT_f) of a Solution:

❖ [By a non-volatile solute/ substance]

Depression of Freezing Point: Freezing point is the temperature at which solid and liquid states of a substance have the same VP (vapour pressure). The VP curves of the pure solvent and that of a dilute solution in the freezing point range are shown in the figure. The VP curves of the solvent in the liquid and solid state are shown to meet at point B, corresponding to the temperature T_0, at which solid and liquid states have the same VP. Hence, T_0 corresponds to the **freezing point** of the pure solvent. As the VP of the solution is less than that of the pure solvent, the VP curves of the solution always lies between that of the pure solvent, as shown in the **figure** given below.



The VP curve of the solution is seen to intersect that of the solid at D, *i.e.* at a lower temperature T. Therefore, T gives the **freezing point** of the solution. Evidently, depression in freezing point ΔT_f is given by $T_0 - T$. Thus —

$$\Delta T_f = T_0 - T$$

Expression for Depression of Freezing Point from TD Considerations:

Let us consider a solution of a non-volatile solute (2) is in equilibrium with the vapour of the pure solvent (1). The equilibrium condition requires that —

$$(\mu_1)_{Solution} = (\mu_1)_{Solid}$$

Where, $(\mu_1)_{Solution}$ = Chemical potential of 1, the pure solvent in solution, and

$(\mu_1)_{Solid}$ = The chemical potential of the pure solvent in the solid state *i.e.* at its freezing point

If the solution behaves ideally, then —

$$(\mu_1)_{Solution} = \mu_1^0 + RT\ \ln \chi_1$$

Here, μ_1^0 is the chemical potential of the pure solvent in the liquid state and χ_1 is the mole fraction of the solvent in the solution. Therefore —

$$(\mu_1)_{Solid} = \mu_1^0 + RT\ \ln \chi_1$$

$$\Rightarrow \ln \chi_1 = -\frac{\mu_1^0 - (\mu_1)_{Solid}}{RT} = -\frac{(\Delta G)_{Fusion}}{RT} \qquad \rightarrow (1)$$

Where —

$(\Delta G)_{Fusion} = \mu_1^0 - (\mu_1)_{Solid}$

= Molar free energy of fusion of the solvent at equilibrium temperature T

Differentiating equation (1), with respect to χ_1 at constant pressure p, we have —

$$\frac{d}{d\chi_1}(\ln \chi_1) = -\frac{1}{R}\frac{d}{d\chi_1}\left[\frac{(\Delta G)_{Fus}}{T}\right]_p$$

$$\frac{1}{\chi_1} = -\frac{1}{R}\left[\frac{\partial\{(\Delta G)_{Fus}/T\}}{\partial T}\right]_p \times \left(\frac{\partial T}{\partial \chi_1}\right)_p \qquad \rightarrow (2)$$

Again, from ***Gibbs-Helmholtz*** equation —

$$\left[\frac{\partial(\Delta G_{Fus}/T)}{\partial T}\right]_p = -\frac{\Delta H_{Fus}}{T^2} \qquad \rightarrow (3)$$

Where: ΔH_{Fus} = The molar enthalpy of fusion of the solvent at temperature T

From equation (2) & (3), we have —

$$\frac{1}{\chi_1} = \frac{1}{R}\frac{\Delta H_{Fus}}{T^2}.\left(\frac{\partial T}{\partial \chi_1}\right)_p$$

$$or \quad \frac{d\chi_1}{\chi_1} = \frac{1}{R}\frac{\Delta H_{Fus}}{T^2}\ dT$$

Integrating the above equation between the proper limits as shown, we have —

$$\int_{1}^{\chi_1} \frac{d\chi_1}{\chi_1} = \int_{T_0}^{T} \frac{\Delta H_{Fus}}{R} \frac{dT}{T^2}$$

Where the lower limit $\chi_1 = 1$, implies a pure solvent having freezing point T_0 and the upper limit χ_1 corresponds to a solution whose freezing point T. Assuming that ΔH_{Fus} is a constant over the temperature range $T_0 \& T$, we have —

$$\ln \chi_1 = -\frac{\Delta H_{Fus}}{R}\left[\frac{1}{T}\right]_{T_0}^{T}$$

$$\Rightarrow \ln(1-\chi_2) = -\frac{\Delta H_{Fus}}{R}\left[\frac{1}{T} - \frac{1}{T_0}\right]$$

$$or \quad -\chi_2 = -\frac{\Delta H_{Fus}}{R}\left[\frac{T_0 - T}{TT_0}\right]$$

$$or \quad -\chi_2 = -\frac{\Delta H_{Fus}}{RT_0^2}\,\Delta T_f$$

Where, $T_0 - T = \Delta T_f =$ Depression of freezing point of the solution

Since for dilute solution $T_0 \& T$ are not much different, so $TT_0 = T_0^2$

Further, $\ln \chi_1 = \ln(1-\chi_2)$ $\quad \because \chi_1 + \chi_2 = 1$

$$\Rightarrow \ln \chi_1 = -\chi_2 + \frac{\chi_2^2}{2} - \frac{\chi_2^3}{3} + \cdots$$

Since, χ_2 is the mole-fraction of the solute, which is very small in dilute solution *i.e.* $\chi_2 \ll 1$. Therefore, we can neglect the higher powers of χ_2, and hence, $\ln \chi_1 = -\chi_2$. Thus —

$$\Delta T_f = \frac{RT_0^2}{\Delta H_{Fus}} \cdot \chi_2 \qquad \rightarrow (4)$$

Therefore, we have —

$$\Delta T_f \quad \propto \quad \chi_2$$

Thus, the depression of freezing point of a solution is directly proportional to the mole fraction of the solute (χ_2) in the solution *i.e.* it is a ***colligative property***.

Generally in the study of colligative properties, ***molality*** (m) is used rather than mole-fraction of the solute. ***Molality*** of the solute is ***defined*** as the number of moles of the solute ***per kg*** $(\mathbf{1000\ g})$ of the solvent. If $n_1 \& n_2$ are the number of moles of 1 & 2 (*i.e.* solvent & solute) in the solution, then —

$$\chi_2 = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1} [\because for\ dilute\ solution\ \ n_1 \gg n_2]$$

Molality of the solute in the solution is given by —

$$m_2 = \frac{n_2}{n_1 M_1}, \qquad \Rightarrow n_2 = n_1 M_1 m_2$$

Where, $M_1 =$ Molar mass of the solvent in $kg\ mol^{-1}$

$$\therefore\ \chi_2 = \frac{n_2}{n_1} = \frac{n_1 M_1 m_2}{n_1} = M_1 m_2$$

Therefore, from equation (4), we have —

$$\Delta T_f = \frac{RT_0^2}{\Delta H_{Fus}} . M_1 m_2$$

$$or \quad \Delta T_f = \left(\frac{RT_0^2 M_1}{\Delta H_{Fus}}\right) m_2 \qquad \rightarrow (5)$$

For a given solvent, the term within the bracket in equation (5) is a constant; known as the ***molal depression of freezing point*** or ***Cryoscopic*** constant represented by the symbol K_f. It is ***defined*** as the ***depression of freezing point*** of **1- *molal solution***. It is a constant for a given solvent and always expressed in the unit of $\boldsymbol{Kkgmol^{-1}}$. Thus —

$$K_f = \frac{RT_0^2 M_1}{\Delta H_{Fus}}$$

$$\therefore \quad \Delta T_f = K_f m_2 \qquad \rightarrow (6)$$

$$i.e. \quad \Delta T_f \ \propto \ m_2$$

Thus, the ***depression of freezing point is directly proportional to the molality of the solute***. This is known as the ***Raoults law*** of depression of freezing point.

APPLICATION OF ELEVATION OF BOILING POINT:

Determination of Molecular Mass of the solute from Freezing Point Measurement:

By measuring the freezing point depression of a solution of known concentration, it is possible to calculate the molar mass of a non-volatile, non-electrolyte solute in the solution. Since, we have —

$$\Delta T_f = K_f m_2$$

Where, ΔT_f = Depression of freezing point, and $\Delta T_f = T_0 - T$
T_0 = The freezing point of the pure solvent, and
T = The freezing point of the solution
m_2 = The molality of the solute
K_f = Molal depression of freezing point, and

$$K_f = \frac{RT_0^2 M_1}{\Delta H_{fus}}\ Kkgmol^{-1}$$

If $w_2\ kg$ of the solute of molar mass $M_2\ kg\ mol^{-1}$ is dissolved in $w_1\ kg$ of solvent, then —

$$m_2 = \frac{w_2}{M_2} \times \frac{1}{w_1}$$

$$\left\| m = \frac{a}{M} \times \frac{1000}{b\ (\text{in gram})} \right.$$

$$\left\| m = \frac{a}{M} \times \frac{1}{b\ (\text{in kg})} \right.$$

Therefore —

$$\Delta T_f = K_f \times \frac{w_2}{M_2} \times \frac{1}{w_1}$$

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

In the above expression all the quantities are known, hence the molar mass of the solute (M_2), can be easily calculated, and its unit will be $kg\ mol^{-1}$.

Problem (1): For benzene $T_0 = 278.6\ K$ & $\Delta H_{fus} = 9.83\ kJmol^{-1}$, calculate the value of K_f.

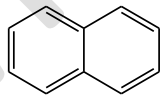
Solution: We have —

$$K_f = \frac{RT_0^2 M_1}{\Delta H_{fus}}$$

$$= \frac{(8.314\ JK^{-1}mol^{-1})(278.6\ K)^2(78 \times 10^{-3} kg\ mol^{-1})}{(9.83 \times 10^3\ Jmol^{-1})}$$

$$= 5.1205\ Kkgmol^{-1}$$

Problem (2): A solution containing 2.423 g of sulphur in 100 g of naphthalene ($fp = 80.1$°C) gave a freezing point depression of 0.64°C. The latent heat of fusion of naphthalene is 35.7 $cal\ g^{-1}$. What is the molecular formula of sulphur in solution?



Naphthalene,
$C_{10}H_8$ =128 g

Solution: Here —

$$w_1 = 100\ g = 0.1\ kg$$

$$w_2 = 2.423\ g = 2.423 \times 10^{-3}\ kg$$

$$M_1 = 128\ g\ mol^{-1} = 128 \times 10^{-3}\ kg\ mol^{-1}$$

$$\Delta T_f = 0.64°C = 0.64\ K$$

$$M_2 = ?$$

We have —

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

$$\Delta H_{\text{Fusion}} = 35.7\ \text{cal g}^{-1}$$
$$= 35.7 \times 128\ \text{cal mol}^{-1}$$
$$= 35.7 \times 128 \times 4.187\ \text{J mol}^{-1}$$

Here —

$$K_f = \frac{RT_0^2 M_1}{\Delta H_{fus}} = 6.9348\ Kkgmol^{-1}$$

$$\therefore\ M_2 = \frac{K_f}{\Delta T_f} \times \frac{w_2}{w_1} = 0.2626\ kg\ mol^{-1} = 262.6\ g\ mol^{-1}$$

Therefore, the atomicity of S- in solution will be —

$$= \frac{262.6\ g\ mol^{-1}}{= 32.0\ g\ mol^{-1}} = 8.2 \approx 8$$

$\therefore$ Molecular formula of S- in solution = S_8

Problem (3): Calculate the molal depression constant of water. The heat of fusion of ice is 334.7 Jg^{-1}.

Solution: Here —

$$\Delta H_{fus}(of\ ice) = 334.7J\ g^{-1}$$

$$= 334.7 \times 18\ Jmol^{-1} = 6024.6\ Jmol^{-1}$$

$$T_0 = 0℃$$

We have —

$$K_f = \frac{RT_0^2 M_1}{\Delta H_{fus}} = 1.85\ Kkgmol^{-1}$$

Problem (4): An aqueous solution containing 0.25 g of solute dissolved in 20 g of water froze at $-0.42℃$. Calculate the molar mass of the solute. The molar heat of fusion of ice at 0℃ is $334.7\ Jg^{-1}$ & $R = 8.314\ JK^{-1}mol^{-1}$.

Solution: Here —

$$w_1 = 20\ g = 0.020\ kg$$

$$w_2 = 0.25\ g = 0.025\ kg$$

$$M_1 = 18\ g\ mol^{-1} = 18 \times 10^{-3}\ kg\ mol^{-1}$$

$$\Delta T_f = 0.42℃ = 0.42\ K, \qquad T_0 = 0℃ = 273\ K$$

$$M_2 = ?, \qquad K_f = ?$$

Since —

$$K_f = \frac{RT_0^2 M_1}{\Delta H_{fus}}$$

$$\therefore K_f = 1.85\ Kkgmol^{-1}$$

Now —

$$\Delta T_f = K_f m_2 = K_f \frac{w_2}{M_2} \times \frac{1}{w_1}$$

$$\Rightarrow M_2 = \frac{K_f}{\Delta T_f} \times \frac{w_2}{w_1} = 0.055059\ kg\ mol^{-1} = 55.059\ g\ mol^{-1}$$

Problem (5): 4 g of a non-volatile solute is dissolved in 250 g of water. The depression in the freezing point of water observed is 0.087. Calculate the molecular weight of the solute. Given that K_f for water is $1.856\ Kkgmol^{-1}$.

Solution: We have —

$$\Delta T_f = K_f m_2 = K_f \frac{w_2}{M_2} \times \frac{1}{w_1}$$

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

$$= \frac{1.856\ Kkgmol^{-1}}{0.087\ K} \times \frac{4 \times 10^{-3} kg}{250 \times 10^{-3} kg}$$

$$= 0.3413\ kg\ mol^{-1} = 341.3\ g\ mol^{-1}$$

Problem (6): The lowering of freezing point of benzene was 2.33 when 4.12 g of a solute of unknown molar mass dissolved in $9.31 \times 10^{-3} kg$ of benzene. Calculate the molar mass of the solute. Molal depression constant for benzene is 5.1 $Kkgmol^{-1}$.

Solution: 96.864 $kg\ mol^{-1}$

Problem (7): A brass sample composed of 20 % Zn & 80 % $Cu\ by\ mass$ melts at 1268 K. Pure copper melts at $1357K$. What is the molal freezing constant for copper? ($Cu = 65\ gmol^{-1}$)

Solution: We have —

$$\Delta T_f = K_f m_2$$

$$\Rightarrow K_f = \frac{\Delta T_f}{m_2} = \frac{\Delta T_f}{\frac{w_2}{M_2} \times \frac{1}{w_1}}$$

$$i.e. \quad K_f = \Delta T_f \times \frac{w_1}{w_2} \times M_2$$

$$= (89K) \times \frac{80}{20} \times (65 \times 10^{-3} kgmol^{-1}) = 23.14\ Kkgmol^{-1}$$

Problem (8): $1g$ of urea when dissolved in $100g$ of a certain solvent decreases its freezing point by 0.2℃. But, if $1.6g$ of unknown compound when dissolved in $80g$ of the same solvent depresses its freezing point by 0.36℃. Calculate the molecular weight of the unknown compound.

Solution: 66.7 $gmol^{-1}$

Problem (9): $0.4g$ of glucose was dissolved in $100g$ of water and the depression in freezing point is -0.41℃ . Calculate the heat of fusion of water.

Solution: 6045.2 $Jmol^{-1}$