Solutions

Solution

It is a homogeneous mixture of two or more chemically non-reacting substances whose composition can be changed within certain limits.

A solution is regarded as a singular phase having more than one component.

A solution which contains two components is known as **binary solution**.

The component which is present in smaller quantities is called the solute and the other which present in larger amount is known as the **solvent**.

The below table shows the list of solutions and their examples.

Concept Ladder

A solution which contains as much solute as it can dissolve at a given temperature is called a saturated solution.

A solution which contains lesser solute than the amount of solute if can dissolve is called unsaturated solution.

Solute	Solvent	Examples
Solid	Solid	Alloys, stones
Solid	Liquid	Sugar, Salt in water
Solid	Gas	Iodine vapours in air
Liquid	Solid	Mercury in metal amalgams
Liquid	Liquid	Alcohol in water
Liquid	Gas	Moist air
Gas	Solid	Occluded Hydrogen on Pd, Pt, Ni, etc
Gas	Liquid	Aerated water
Gas	Gas	Air

Types of Solutions

Solutions of Solids in Liquids

- It is a solution which still in contact with excess of solute.
- The solubility of the solute is defined as the amount of solute dissolved per 100 g of solvent at a specific temperature for a saturated solution.
- For exothermic substances such as KOH, CaO, $Ca(OH)_2$, M_2CO_3, M_2SO_4 etc.,

Concept Ladder

A solution which contains more solute than the amount of solute it can dissolve at a particular temperature is called a super saturated solution.

solubility is inversely proportional to temperature. (M = Alkali metals)

- For endothermic substances such as NaCl, KNO_3, $NaNO_2$, glucose etc., solubility is directly proportional to temperature.

Solubility of Gases

- Solubility of gases is mostly described in terms of absorption coefficient, i.e., the volume of the gas (at normal temperature and pressure), dissolved by unit volume of solvent, at a specific temperature and 1 atm pressure.
- The solubility factor for a gas in a liquid depends upon:

1. **Temperature**
   Solubility have inverse relation with temperature as dissolution of a gas is exothermic in most cases.

$$\text{Gas} + \text{liquid} \Rightarrow \text{Dissolved gas}$$

$$\Delta H = -\text{ve}$$

2. **Nature of gas**
   The gas which can be easily liquified are more soluble as they contian higher value of van der Waal's force of attraction. For example, SO_2 and CO_2 are more soluble in water than O_2, N_2 and H_2.
3. **Nature of solvent**
   Gases which can be ionized in aq. solution are more soluble in H_2O as compared to the other solvents.
4. **Pressure of the gas (Henry's law)**
   This law states that the solubility of a gas in a given volume of liquid at constant temperature is directly proporitonal to the pressure of the gas.

$$m \propto P$$

$$m = KP$$

Rack your Brain

Why do aquatic species like fish feel more comfortable in the lakes in winter than in summer?

Previous Year's Questions

The beans are cooked earlier in pressure cooker because.

[NEET]

(1) Boiling point increases with increasing pressure
(2) Boiling point decreases with increassing pressure
(3) Extra pressure of pressure cooker softens the beans
(4) Internal energy is not lost while cooking in pressure cooker.

Concept Ladder

Solubility of gases in liquids decreases with rise in temperature. When dissolved, the gas molecules are present in liquid phase and the process of dissolution can be considered similar to condensation and heat is evolved in this process. As dissolution is an exothermic process. the solubility should decrease with increase of temperature.

or $\frac{m}{p} = K_H$ (At constant temperature)

P = Pressure of gas at equlilibrium with solution

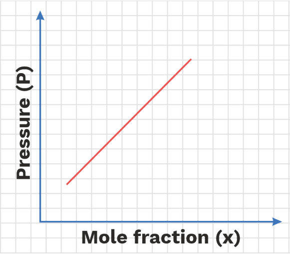
m = The mass of gas dissolved by unit volume of solvent.

Here K_H = Henry's constant (Function of nature gas)

When solubility is expressed as its mole fraction (X)

$$P \propto X \text{ or } P = K_H X$$

$$\text{Solubility} \propto \frac{1}{K_H}$$



- Henry's law is obeyed only when
  1. Gas does not dissociate.
  2. Pressure is not too high.
  3. In solvent, gas is not highly soluble.
  4. Temperature is not too low.
  5. Gas should be inert.

e.g. $NH_3 + H_2O \rightleftharpoons NH_4OH$

- The volume of the dissolved gas does not depend upon pressure at a particular Temperature.

Applications of Henry's Law:

(1) Soft drinks bottles are sealed at high pressures to increase solubility of CO_2 in water.

(2) Sea divers used a mixture of O_2 + He to minimize the painful effect by N_2 in decomposition.

Rack your Brain

Why does the solubility of exothermic substances decreases with increasing of temperatrue?

Concept Ladder

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

Concept Ladder

When air enters the lungs, partial pressure of oxygen is high. This oxygen combines with haemoglobin to form oxyhaemoglobin. Partial pressure of O_2 in tissues is low. Hence, O_2 is released from oxyhaemoglobin which is utilised for functions of the cells.

(3) At higher altitudes, breathing becomes tough as O_2 is less available in the air due to less pressure.

Expression of Concentration of Solution

Solubility

The amount of solute which is dissolved in a specific amount/volume of solution. It is denoted by C or S.

$$\text{C or S} = \frac{\text{Weight of solute in gram}}{\text{Volume in litre}} \text{ or } \frac{W}{V} \text{ g / L}$$

$$\boxed{C = N \times E}$$

N = Normality of solution,

E = Eqivalent weight of solute

Concentration in parts per million (ppm)

When any amount of solute is present in one million (10^6) parts of the solution, then it is known as ppm.

$$\text{ppm}_{(A)} = \frac{\text{Mass of A}}{\text{Total mass of the solution}} \times 10^6$$

Concentration in parts per billion (ppb)

When any amount of solute is present in one billion (10^9) parts of the solution, then it is known as ppb.

$$\text{ppb}_{(A)} = \frac{\text{Mass of A}}{\text{Total mass of the solution}} \times 10^9$$

Molarity (M)

It is the no. of moles of solute present in one litre of the solution, and it is denoted by M.

- When molarity of a solution is one, it is called one molar solution.

$$M = \frac{\text{Weight of solute in gram}}{\text{Molar mass} \times \text{Volume in litre}}$$

In case of dilution or mixing,

$$\boxed{M_1V_1 = M_2V_2 = M_3V_3}$$

$$M_R = \frac{M_1V_1 + M_2V_2}{V_1 + V_2} \text{ or } \frac{M_AV_A - M_BV_B}{V_A + V_B}$$

A → Acid; 1 → Solute (1)

B → Base; 2 → Solute (2)

(Both don't react with each other)

Concept Ladder

Air quality measurement are commonly reported in terms of: micrograms per cubic meter (μg/m^3) part per meilion (ppm) or parts per billion (ppb)

Previous Year's Questions

How many grams of concentrated nitric acid solution should be used to prepare 250 mL of 2.0 M HNO_3? The concentrated acid is 70% HNO_3. **[NEET]**

(1) 70.0 g conc. HNO_3

(2) 54.0 g conc. HNO_3

(3) 45.0 g conc. HNO_3

(4) 90.0 g conc. HNO_3

Concentration Of Solution

(1) % by weight

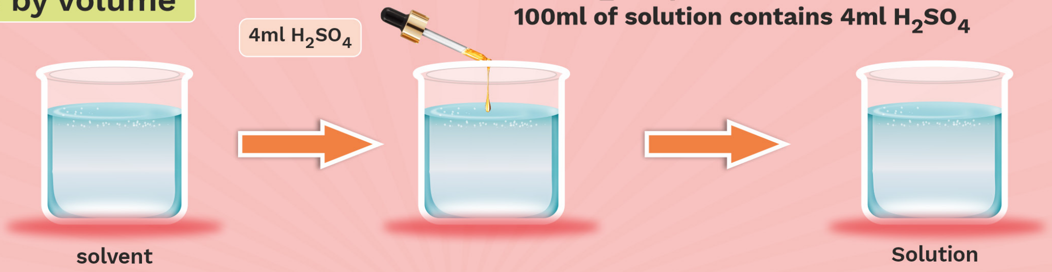
4.9% H_2SO_4 by weight means

100gm of solution contains 4.9gm H_2SO_4

(2) % by volume

4% H_2SO_4 by Volume means

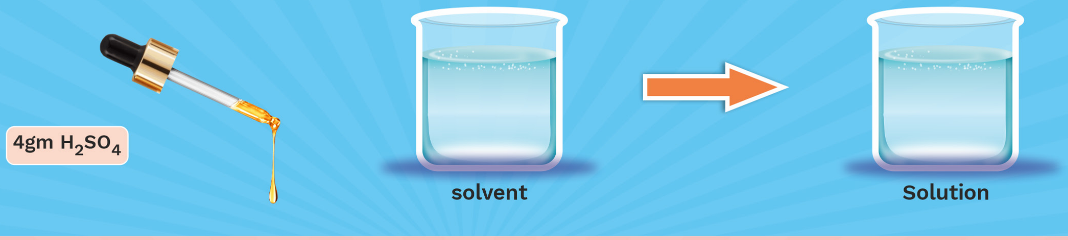
100ml of solution contains 4ml H_2SO_4



(3) % weight by volume

4% H_2SO_4 w/v means

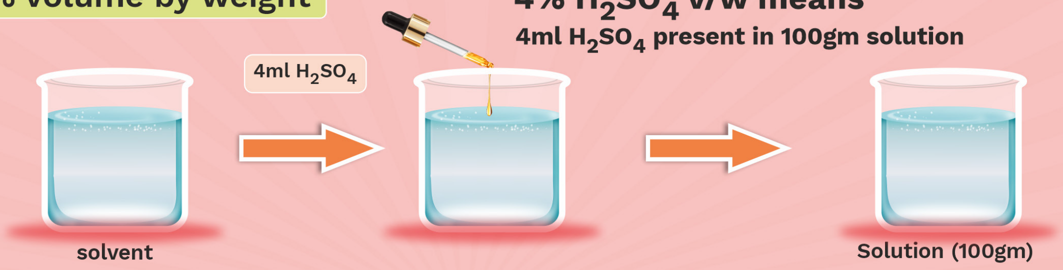
4gm H_2SO_4 present in 100ml solution



(4) % volume by weight

4% H_2SO_4 v/w means

4ml H_2SO_4 present in 100gm solution



Molality (m)

No. of moles of solute dissolved in 1 kg of solvent. It is denoted by m.

$$m = \frac{\text{Weight of solute in gram}}{\text{Molar mass} \times \text{wt. of solvent in kg}}$$

- If molality of a solution is one, it is called molal solution.
- Concentration of one molal solution is less than that of one molar solution.
- Molality is used preferably over molarity in experimental calculations as molality is temperature independent while molarity is affected by temperature.

Normality (N)

It is the no. of gram equivalents of a solute present in a litre of solution, and is denoted by N.

$$N = \frac{\text{Weight of solute in gram}}{\text{Equivalent mass} \times \text{Volume in litre}}$$

- Relation between normality and molarity.

$$\text{N} \times \text{Eq. wt.} = \text{Molarity} \times \text{Molar mass}$$

$$\text{N} = \text{Molarity} \times \text{Valency}$$

$$\text{N} = \text{Molarity} \times \text{Number of H+ or OH ion.}$$

Formality (F)

It is the no. of gram formula present in a litre of solution for an ionic solute. It is denoted by F.

$$F = \frac{\text{Weight of solute in gram}}{\text{Formula wt.} \times \text{Volume in litre}}$$

- It is applicable for ionic solids like NaCl.

Previous Year's Questions

If molality of the dilute solution is doubled, the value of molal depression constant (K_f) will be **[NEET]**

(1) halved
(2) tripled
(3) unchanged
(4) doubled

Concept Ladder

Normality is gram equilvalents/L or number of miliequivalents (meq) per cc of the solution and molarity is mol/L or number of milimoles (mmol) per cc of the solution.

No. of equivalent of solute in solution (V) = N × V

No. of Moles of solute in solution (V) = M × V [V = Volume of Solution]

Concentration Terms

1 Molarity (M)

Molarity is no. of moles of a solute per litre of the solution

$$M = \frac{\text{Mole of solute}}{\text{Volume of solution (in litre)}}$$

2 Molality (m)

Molality is the no. of moles of solute per kilogram of the solvent.

$$m = \frac{\text{Mole of solute}}{\text{weight of solvent (in kg.)}}$$

3 Normality(N)

Normality is the gram equivalent weight per litre of solution.

$$N = \frac{\text{gram equivalents of solute}}{\text{volume of solution (in litre)}}$$

4 Formality (F)

Formality is the no. of gram formula masses of the ionic solute dissolved per litre of solution.

$$F = \frac{\text{weight in gram}}{\text{formula weight x volume of solution (litre)}}$$

5 Mole fraction (χ)

Mole fraction is the number of moles of one component divided by total no. of moles of whole components of solution XA = The Mole fraction of A in binary solution(A+B).

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

6 Parts per million (ppm)

It is the solute present in one million (10^6) parts by mass of the solution.

$$\text{ppm} = \frac{\text{mass of solute}}{\text{mass of solvent}} \times 10^6$$

Mole fraction

Mole fraction of a component is given by the moles of one component divided by the total no. of moles present in that solution. It is expressed by X, for example, for a binary solution two component A and B,

$$\text{Mole Fraction of A}\,(X_A) = \frac{n_A}{n_A + n_B}$$

$$\text{Mole Fraction of B}\,(X_B) = \frac{n_B}{n_A + n_B}$$

n_A = no. of moles of A. (Solute)
n_B = no. of moles of B. (Solvant)

Weight per cent $= \left(\frac{w}{W} \times 100\right)$ It is weight of solute present in 100 g of solution.

Volume per cent $= \left(\frac{v}{V} \times 100\right)$ It is volume of solute present in 100 mL of solution.

$$\text{Mole per cent} = \frac{\text{Moles of solute}}{\text{Total moles present in solution}} \times 100$$

Previous Year's Questions

What is the mole fraction of the solute in a 1.00m aqueous solution?

[NEET]

(1) 1.770
(2) 0.0354
(3) 0.0177
(4) 0.177

Mass fraction

The ratio of the mass of the component to the total mass of the solution is known as Mass Fraction. It is given for a solution which contains w_A g of A and w_B g of B,

$$\text{Mass fraction of A}\ (X_A) = \frac{W_A}{W_A + W_B}$$

$$\text{Mass fraction of B}\ (X_B) = \frac{W_B}{W_A + W_B}$$

So, $x_A + x_B = 1$

Concept Ladder

Sum of mole fraction of solute and solvent will be always equal to 1.

- When one mole of a solute is present in one litre of solution at 0°C it is called one demal solution.
  1 Molar > 1 molal.

Relation Between Molarity (M) and Molality (m)

⇒ Let Molarity = M
Molality = m

= Mass of solute = w (in gram)
Mass of solvant (in gram) = W
M_2 = Molar mass of solute
d = density of solution
So mass of solvent = 1000d − MM_2 g

$$\text{As } m = \frac{w}{M_2} \times \frac{1000}{W}$$

$$\text{So } m = \frac{M}{1000d - MM_2} \times 1000$$

$$m = \frac{M}{d - \frac{MM_2}{1000}}$$

Vapour Pressure

Vapour Pressure of a Liquid

- When the vapour phase is in equilibrium with the liquid is for a given temperature then the pressure forced by the vapours is known as vapour pressure of a liquid. Nature of the liquid and temperature are the two dependent properties for it.
- Vapour pressure of a solution is always lesser than the vapour pressure form of its pure liquid state.
- For having an idea of attractive force between the molecles of a liquid, vapour of a liquid is used. Force of attraction has inverse relation with vapour pressure.

  e.g., → $P^{\circ}_{C_2H_5OC_2H_5} > P^{\circ}_{C_2H_5OH} > P^{\circ}_{H_2O} > P^{\circ}_{Glycol}$

- With increase in temperature, vapour pressure of liquid increases as kinetic energy of molecules increases.
- The variation of vapour pressure with temperature can be given by Clausius-Clapeyron equation as follows:

$$\log_{10}\frac{P_2}{P_1} = \frac{\Delta H_{vap}}{2.303\ R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

Definitions

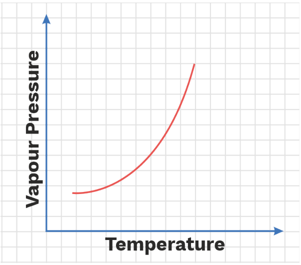
Vapour pressure of a liquid/ solution is the pressure exerted by the vapour in equilibrium with the liquid/solution at a particular temperature.

Rack your Brain

Which unit is useful in relating concentration of solution with its vapour pressure?

Concept Ladder

A substance with a high vapour pressure at normal temperature is often referred to as volatile. So, alcohol is more volatile than water because of presence of hydrogen bonding between molecules of water.



Vapour Pressure of a Solution

- When the pure solvent is added to a miscible solute then they form a solution. There is decrease in escaping tendency of solvent molecules as some molecules of solute replace the molecules of the solvent from the surface. This causes decrease in the vapour pressure.
- The vapour pressure of a pure solvent is more than that of its solution.
- If the vapour pressure of a solvent is p^o and that of solution is p_s then, lowering of vapour pressure = $p^o - p_s$
- When there is decrease in surface area occupied by the solvant molecules and increase in density, the vapour pressure of a solution decreases.

Raoult's Law

Raoult's Law for Volatile Solutes

It states that for a given solution, the vapour pressure of a component for a given temperature is equal to the multiplication of mole fraction of the component in the solution and V.P. of that component in its pure state for the same temperature. For a solution containing two components A and B the total vapour pressure P is :

$$p_A = p^0_A \times x_A$$

$$p_b = p^0_b \times x_B$$

$$P = p_A + p_B = p^0_A\, x_A + p^0_B\, x_B$$

Rack your Brain

Why vapour pressure of aqueous solution of glucose lower than that of water?.

Concept Ladder

In a solution, the vapour prssure of a componenet at a given temperature is equal to the mole fraction of that component in the solution multiplied by the vapour pressure of that component in the pure state.

Previous Year's Questions

In which case Raoult's Law is not applicable?

[AIIMS]

(1) 1M NaCl
(2) 1M Urea
(3) 1M glucose
(4) 1M sucrose

As we know that:

$$x_A + x_B = 1$$

$$x_A = (1 - x_B)$$

$$P = (1 - x_B)\, p^0_A + p^0_B\, x_B$$

$$P = (p^0_B - p^0_A)\, x_B + p^0_A$$

As P^0_A, P^0_B are constant at a particular temperature hence P_T is a linear function of the mole fraction (x_B).

Raoult's Law for Non-volatile Solutes

Raoult's law states that the relative lowering of vapour pressure of a solution containing a non-volatile solute is equal to the mole fraction of the solute in the solution.

$$\frac{P^{0} - P_s}{P^0} = \frac{n_2}{n_1 + n_2} = x_2$$

Here,

x_2 = Mole fraction of solute
n_1 = Moles of solvent
n_2 = Moles of solute
p_s = Vapour pressure of the solution
p^0 = Vapour pressure of pure solvent

Ideal Solutions

Ideal solutions are the solutions in which solute-solute and solvent-solvent interactions are almost similar to solute-solvent interactions (A—B = A—A or B—B interactions) and such solutions satisfy the following requirements:

1. They obey Raoult's law for all ranges of concentrations and temperature.
2. ΔH (mix) = 0
3. ΔV(mix) = 0
4. $(V{\cdot}P)_{obs} = (V{\cdot}P)_{exp.}$
   $(B{\cdot}P)_{obs} = (V{\cdot}P)_{exp.}$
5. No dissociation or association takes place here.

Concept Ladder

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

Previous Year's Questions

Which of them is not equal to zero for an ideal solution?

[NEET]

(1) ΔV_{mix}
(2) $\Delta P = P_{observed} — P_{Roult}$
(3) ΔH_{mix}
(4) ΔS_{mix}

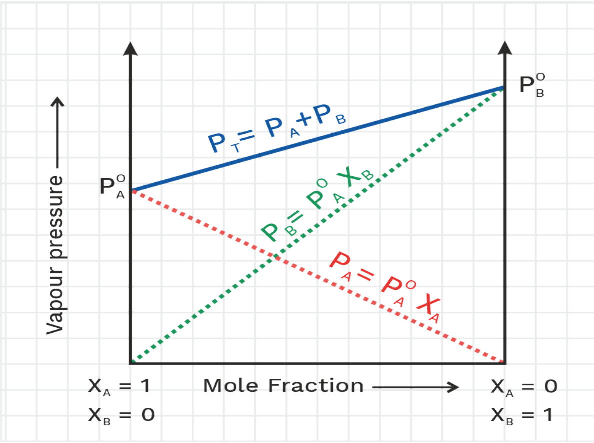
Definitions

An ideal solution is that solution in which each component obeys Raoult's law under all conditions of temperature and concentrations.

6. No chemical reaction between solute and solvent.
7. It does not form azeotrope mixture.

Examples:

1. Benzene + toluene
2. Hexane + heptane
3. Ethyl bromide + ethyl iodide
4. Chlorobenzene + bromobenzene
5. CCl_4 + $SiCl_4$
6. All dilute solutions



Non-ideal Solutions

Non-ideal solutions are the solutions in which solutesolvent interactions are different from solute-solute and solvent-solvent interactions. These solutions do not obey Raoult's law for all concentrations and:

1. ΔH (mix) ≠ 0
2. ΔV (mix) ≠ 0

Types of Non-ideal Solutions

(a) Non-ideal solutions showing positive deviations: Positive deviation occurs when total vapour pressure for any mole fraction is more than what is expected according to Raoult's law. This happens when the new interactions are weaker than the interaction in the pure component (A—B < A—A or B—B interactions).

Previous Year's Questions

A solution containing components A and B follows Raoult's law

[AIPMT]

(1) A—B attraction force is greater than A—A and B—B.
(2) A—B attraction force is less than A—A and B—B.
(3) A—B attraction force is remains same as A—A and B—B.
(4) Volume of solution is different from sum of volume of solute and solvent.

Definitions

A non-ideal solution is that solution in which solute and solvent molecules interact with one another with a different force than the forces of interaction between the molecules of the pure components.

- $\Delta H = +ve, \Delta V = +ve, \Delta S = +ve, (V.P)_{obs} > (V.P)exp.$

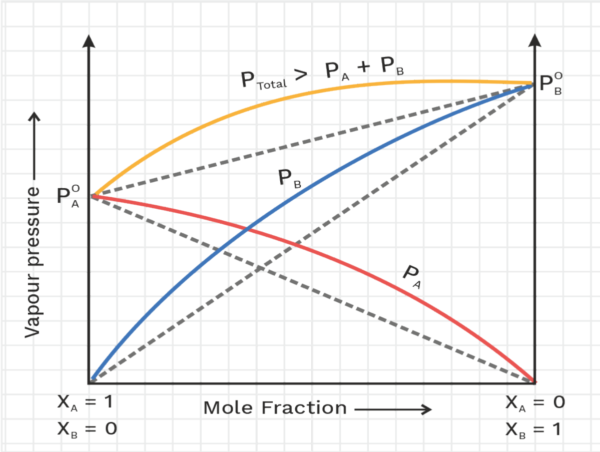
$$P_A > P_A^0 \cdot X_A,\ P_B > P_B^0 \cdot X_B$$

$$P_T > P_A^0\ X_A + P_B^0 \cdot X_B$$

- It forms minimum boiling azeotrops, for example, C_2H_5OH + cyclohexane. The H-bonding present in pure C_2H_5OH are cut off on adding cyclohexane. For such solution, ΔV and ΔH are positive.

Examples:

1. Acetone + carbon disulphide,
2. Acetone + benzene
3. Carbon tetrachloride + chloroform or Toluene
4. Methylalcohol + water
5. Acetone + C_2H_5OH



(b) Non-ideal solutions showing negative deviations: Negative deviation is seen when total vapour pressure for any mole fraction is less than that expected from Raoult's law. This happens when the new interactions are stronger than the interactions in the pure components
(A—B > A—A or B—B interactions).

- $\Delta H = -ve, \Delta V = -ve, \Delta S = +ve$
$(V \cdot P)_{obs.} < V \cdot P_{exp.}$

$$P_A < P_A^0 . x_A,\ P_B < P_B^0 \cdot x_B\ ;\ P_T < P_A^o.x_A + P_B^o.x_B$$

Previous Year's Questions

A solution of acetone in ethanol **[AIPMT]**

(1) obeys Raoult's Law
(2) shows a negative deviation from Raoult's Law
(3) shows a positive deviation from Raoult's Law
(4) behaves like a near ideal solution.

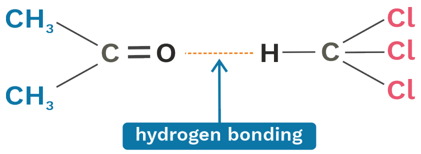
Rack your Brain

Why does a solution of ethanol and cyclohexane show positive deviation from Raoult's Law?

Rack your Brain

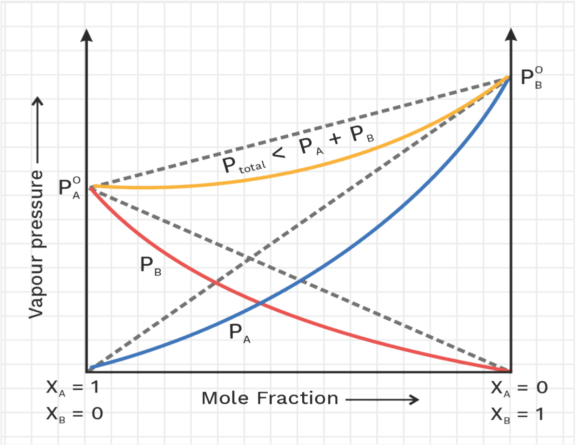
Two liquids A and B on mixing produce a warm solution. Which type of deviation from Raoult's law does it show?

- It forms maximum boiling azeotrope, for example, $CHCl_3 + CH_3COCH_3$. For such solutions, ΔV and ΔH are negative.



Examples:

1. Chloroform + benzene ordiethyl ether
2. Acetone + aniline
3. Nitric acid (HNO_3) + water
4. Acetic acid + pyridine



Azeotropic Mixture

It is a mixture of two liquids having the same boiling point. Because of same boiling point the two liquids cannot be separated by simple distilation. These mixtures are therefore called constant boiling mixtures. These are formed by non-ideal solutions.

Azeotropic mixture and composition curves

- These are the mixture of two liquids which boils at one particular temperature like a pure liquid and distils over in the same composition i.e., these are constant boiling mixtures. These are formed by non-ideal solutions.

Rack your Brain

Cutting onions taken from the fridge is more comfortable than cutting those lying at room temperature. Why?

Concept Ladder

Azeotropic mixtures cannot be separated into their constituents by fractional distillation. For example, if we try to concentrate a dilute solution of alcohol, we can do so only till it becomes 95.4% because after that it becomes a constant boiling mixture (azeotrope). The mixture containing 95.4% alcohol and 4.6% water is called rectified spirit.

RAOULT'S LAW

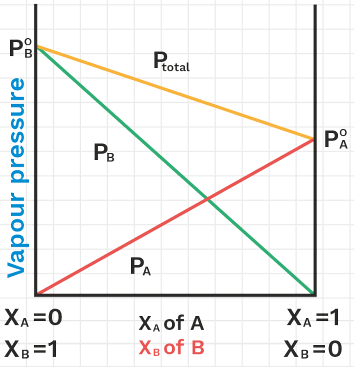
The vapour pressure of a solution of a non-volatile solute is equal to the vapour pressure of the pure solvent at that temperature multiplied by its mole fraction.

$$P_{Solution} = \chi_{solvent} \; P^o_{solvent}$$

Vapour pressure of the solution

Mole Fraction of the solvent

Vapour pressure of the pure solvent

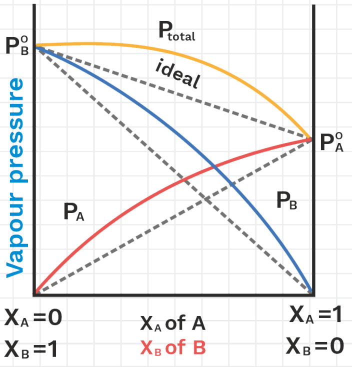


$P_A = X_A P^o_A$

$P_A = X_B P^o_B$

$P_{total} = P_A + P_B$

Raoult's Law

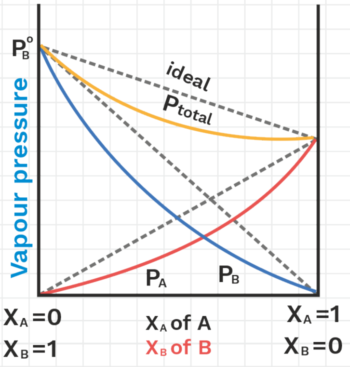


$P_A > X_A P^o_A$

$P_B > X_B P^o_B$

$P_{total} > P_{ideal}$

Positive deviation from Raoult's Low



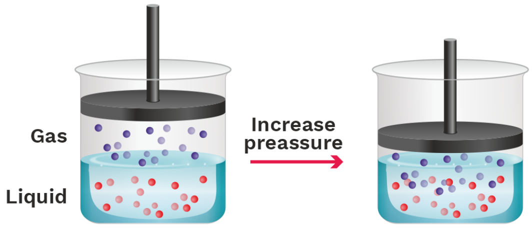
$P_A < X_A, P^o_A$

$P_B < X_B, P^o_B$

$P_{total} < P_{ideal}$

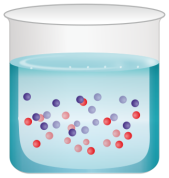
Negative deviation from Raoult's Low

Henry's law



At constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid.

Vapour pressure



$P_{total} = P_A + P_B$

$P_A = X_A, P^o_A$

$P_B = X_B, P^o_B$

Each substance has a lower vapour pressure from that of a pure substance !

Even though it looks like the mix may be "50/50", "A" particles have a higher vapour pressure (evaporate more easily) than the "B"

- For the separation of constituent particles of the liquid mixtures by distilation, the study of vapour pressure curves of the mixtures will make it easy.
- By fractional distilation method the separation will be possible only when the composition of vapour phase is different from that of the boiling liquid phase.

Concept Ladder

To obtain pure alcohol (100% alcohol) called absolute alcohol from rectified spirit, the method used to called azeotropic distillation. For this purpose, rectified spirit is mixed with a suitable amount of benzene. The mixture is then subjected to fractional distillation.

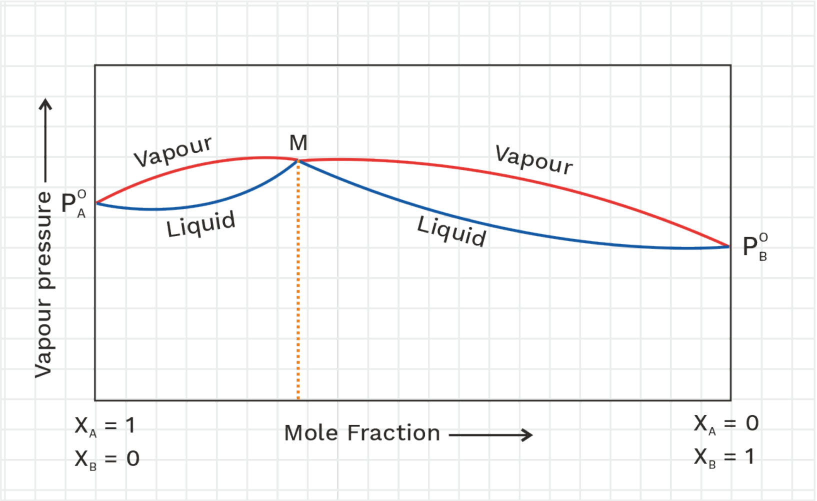
Types of azeotropic mixtures

These are of the following two types:

1. **Azeotropic mixtures with minimum boiling point:** Azeotropic mixture is the mixture of two liquids in which the boiling point of the mixture is lesser than either of the two pure components.

- It is formed by the composition of a non-ideal solution which shows positive deviation to the solution having maximum vapour pressure.
- This mixture consists non-ideal solutions showing positive deviation Raoult's law and for which, the vapour pressure is maximum.

For example, C_2H_5OH (95.5%) + H_2O (4.5%) mixture boils at 351.5 K.
(B.P. of C_2H_5OH = 78.1° C, B.P. of H_2O = 100° C)



- Such mixtures on distillation will give first fraction upto point M in pure state. After this the temperature will rise and the second component will pass over. Hence in such solutions also complete separation is not possible.
- The figure shows maximum vapour pressure at point M and therefore solution has lowest boiling point.

2. Azeotropic mixtures with maximum boiling point: Azeotropic mixture is the mixture of two liquids in which the boiling point of the mixture is larger than either of the two pure components.

- It is formed by the composition of a non-ideal solution which shows negative deviation to the solution having minimum vapour pressure.

  E.g., Nitric acid (68%) + water (32%) mixture boils at 393.5 K.

  An aqueous solution of HCl initally gives pure water when subjected to distillation and later forms a constant boiling mixture at a temperature of 100°C containing 20.24% acid.
- During distillation when two volatile liquids A and B are mixed, for condition having A is more volatile and present in excess, the vaopur part will be richer in component A and liquid part will be for component B. Lastly, A point is reached 'N' where the boiling point is maximum and the vapour pressure is minimum as shown in the figure.
- For this stage from this type of solution, complete separation of components into its pure state is impossible.

Rack your Brain

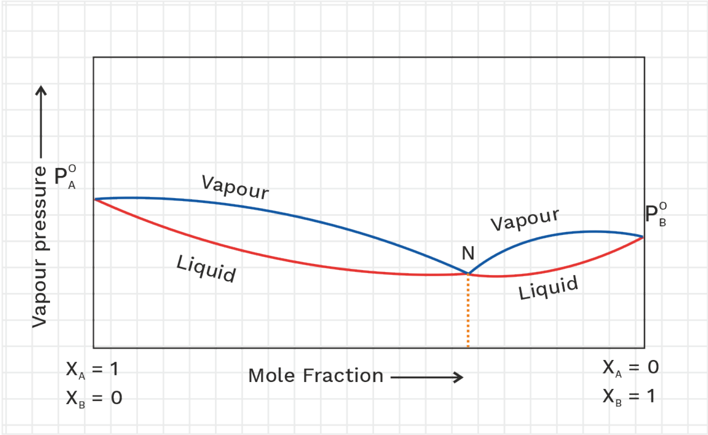
The dissolution of ammonium chloride in waster is an endothermic process but still it dissolves in water readily. Why?

Concept Ladder

Tertiary azeotrope is a mixture of water (7.4%), Benzene (74.1%) and Alcohol (18.5%). Whereas binary azeotrope is a mixture of Benzene (67.7%) and Alcohol (32.2%).

Rack your Brain

Can we separate the componenets of azeotropic mixture by distillation?

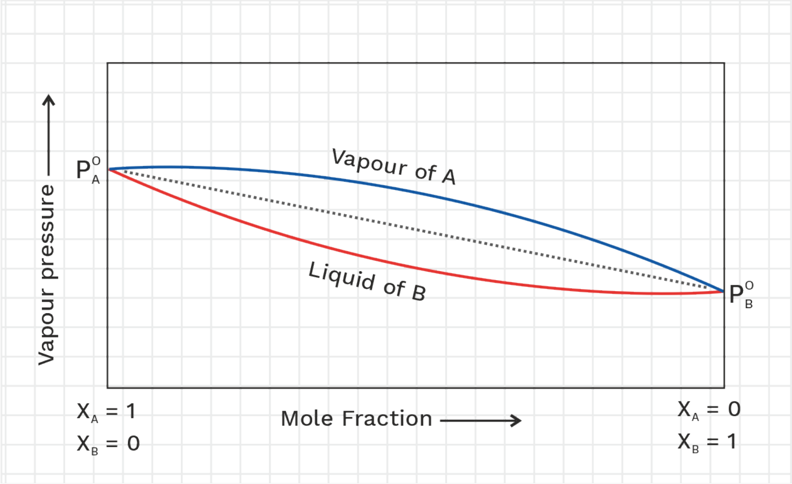


3. **Mixture Showing ideal behaviour or zeotropic mixture:** Zeotropic mixture is defined as the liquid mixture which get distilled whenever there is change in its concentration.

- For zeotropic mixture, the vapour pressure composition curve for liquids A and B is a straight line. A will be collected distillate as it become more volatile on distillation.
- The remaining fraction will be richer in B and poorer in A. We can get A and B in their pure state, on repeating the process of distillation again and again, e.g., methanol-water mixture.

Concept Ladder

Absolute alcohol is prepared by azeotropic distillation method. Rectified spirit is mixed with a suitable amount of benzene and subjected to fractional distillaton.



Solubility of Partially Miscible Liquids

Conjugate solutions

Many liquids are partially miscible and form two liquid layers at a particular temperature. Such liquid solutions in which different compositions of components coexist are called conjugate solutions, for example, phenol and water.

Critical temperature

With change in temperature the miscibility of liquids changes. For a certain temperature the two layers become completely miscible. This certain temperature is termed as critical temperature or consolute temperature.

Colligative Properties

The properties of a solution which depend only on the number of particles like molecules or ions of the solute in a definite amount of the solvent but not on the nature of the solute, are termed as Colligative Properties. These are as follows:

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

- VP, BP, FP, MP and Osmosis are not colligative properties.
- These are properties of dilute solution non-volatile solute without any dissociation or association.

Relative Lowering of Vapour Pressure

When a non-volatile solute is mixed with a volatile solvent, the vapour pressure of solution becomes less than the vapour pressure of pure solvent. It is due to increase in density which decreases rate of evaporation.

Mathematically, $\pi \propto \frac{1}{\sqrt{d}}$

If p^0 = vapour pressure of pure solvent

p = vapour pressure of solvent in solution

Definitions

Those properties of ideal solutions which depend only on the number of particles of the solute (molecules or ions) dissolved in a definite amount of the solvent and do not depend on the nature of solute are called colligative properties.

Previous Year's Questions

Pure water can be obtained from sea water by

[AIPMT]

(1) centrifugation
(2) plasmolysis
(3) reverse osmosis
(4) sedimentation

- The lowering of vapour pressure

$$\Delta p = (p^0 - p)$$

- The ratio in the lowering of vapour pressure and the vapour pressure of pure solvent is define as the relative lowering of vapour pressure.

$$\frac{\Delta p}{p^0} = \frac{p^0 - p}{p^0} = \text{Relative lowering of vapour pressure}$$

- When a solution is prepared by mixing the non-volatile solute B and solvent A

$$x_A + x_B = 1$$

$$x_B = 1 - x_A$$

Here, x_B is the mole fraction of solute.

$$\text{As } \frac{p_A}{p_A^0} = x_A$$

$$1 - \frac{p_A}{p_A^0} = 1 - x_A = x_B; \quad (\because 1 - x_A = x_B)$$

$$\frac{p_A^0 - p_A}{p_A^0} = x_B = \frac{\Delta p}{p_A^0} = \frac{n}{n + N}$$

Here, n = Number of moles of the solute
N = Number of moles of the solvent

- In a dilute solution, N is far greater than n, and hence,

$$x_B = \frac{n}{N} = \frac{w / m}{W / M} = \frac{wM}{Wm}$$

Here,
W = Weight of solvent
w = Weight of solute
M = Molecular weight of solvent
m = Molecular weight of solut

$$\text{So, } \frac{p_A^0 - p_A}{p_A^0} = \frac{\Delta p}{p^0} = \frac{wM}{Wm}$$

Previous Year's Questions

A solution has a 1 : 4 mole ratio of pentane to hexane. The vapour pressures of the pure hydrocarbons at 20°C are 440 mm Hg for pentane and 120 mm Hg for hexane. The mole fraction of pentane in the vapour phase would be

[AIPMT]

(1) 0.200
(2) 0.549
(3) 0.786
(4) 0.478

- The molecular weight of a solute can be determined with the help of the relative lowering of vapour pressure method

- R.L.V.P is measured by ostwald walker method.

$$\frac{P^0 - P_S}{p^0} = \frac{\text{Loss in Mass of Solvent bulbs}}{\text{Gain in } CaCl_2 \text{ tube}}$$

Osmosis

In osmosis, there is a net flow of solvent molecules from a less concentrated solution to a more concentrated solution or from the solvent to the solution or across a semi-permeable membrane (membranes of animal origin, membranes made from

$Cu_2[Fe(CN)_6]$, $Ca_3(PO_4)_2$ etc.)

Osmosis was first observed by Abbe Nollet in 1748. e.g.

(1) Absorption of water from soil by cell walls of roots.

(2) Water movement from root to upper parts of plants.

Osmotic Pressure

- When the column is formed as a result of osmosis, then the equilibrium hydrostatic pressure is known as Osmotic Pressure.
- To restrict the entry of the solvent into the solution through the semi-permeable membrane, the min. pressure that is to be applied on the solution is osmotic pressure.
- It is the min. pressure needed to apply on a solution for making its vapour pressure equal to vapour pressure of the solvent.
- It is denoted by P or π.
- It is measured by Pfeffer's method, Berkely-Hartley's method, Townsend's method.

Previous Year's Questions

During osmosis, flow of water through a semipermeable membrane is

[AIPMT]

(1) from solution having lower concentration only

(2) from solution having higher concentration only

(3) from both sides of semipermeable membrane with equal flow rates

(4) from both sides of semipermeable membrane with unequal flow rates.

Rack your Brain

What will happen if pressure greater than the osmotic pressure is applied on the solution separated by a semi-permeable membrane from the solvent?

Van't Hoff equation of osmotic pressure

$$\pi = CST$$

Here,

π = Osmotic pressure

S or R = Solution constant

($\approx$ 0.0821 Latm/K. mol)

C = Concentration of solution in mol/L

T = Absolute temperature in K

So, $\pi \propto C$ (At constant temperature)

$$\pi = \frac{n}{V} ST \ (C = n/V)$$

$$\pi V = nST$$

Here,

n = Numbers of moles the solute,

V = Volume of solution

$$\pi V = \frac{w}{M} RT$$

As n = w/M

M = Molar mass of solute

w = Gram weight of solute

Determination of molecular weight from osmotic pressure

π = CST

C = n/V

C = Concentration of solution.

n = No. of moles of solute in solution.

- When solute is dissolved in V litre then

$$\pi V = nST \qquad (n = W/M)$$

$$\pi V = \frac{W}{M} ST$$

$$M = \frac{W \times ST}{\pi \times V}$$

- Accurate molecular weight is obtained under the following conditions:

Concept Ladder

When the membrane permits the solvent molecules to come out through the membrane, it is called exomosis (exo-osmosis). When the membrane permits the solvent molecules to enter inside, it is called endosmosis (endo-osmosis).

Previous Year's Questions

From the colligative properties of solution, which one is the best method for the determination of molecular weight of proteins and polymers?

[AIPMT]

(1) Osmotic pressure

(2) Lowering in vapour pressure

(3) Lowering in freezing point

(4) Elevation in boiling point

1. Solution must be very dilute.
2. Solute must be non-volatile.
3. Solute should not undergo dissociation or association in the solution.

- When height is involved then, $\pi = hdg$
- d = density of solution.
- h = hight difference in both vessel (due to osmosis)

Isotonic solution

Solutions having equal molar concentrations or equal osmotic pressures are called isotonic solutions. For example, 0.91% solution of pure aqueous NaCl is isotonic with human RBC.

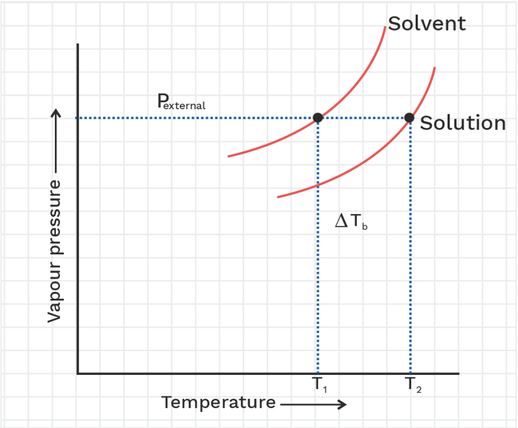
$$P_1 = P_2 \text{ or } \pi_1 = \pi_2$$

$$\frac{w_1}{M_1V_1} = \frac{w_2}{M_2V_2}$$

- In an isotonic solution net osmosis is zero. When RBCs are placed in distilled water (Hypotonic medium) they swell as water flows into them, but when they are taken in 5% NaCl solution (Hypertonic) they shrink as water comes out from the cells.

Elevation in Boiling Point

Boiling point is the temperature of a liquid at which its vapour pressure becomes equal to the atmospheric pressure.



T_1 = Boiling point of solvent
T_2 = Boiling point of solution

Concept Ladder

If two solutions have same osmotic pressure and hence same molar concentration, they are called isotomic. If of lower osmotic pressure, it is called hypotonic with respect to the more concentrated solution. The more concentrated solution is said to be hypertonic with respect to the dilute solution.

Concept Ladder

$$K_b = \frac{RT_0^2}{1000\, l_v} = \frac{M_1RT_0^2}{1000\, \Delta_{vap}H}$$

$$\text{where, } l_v = \frac{\Delta_{vap}H}{M_1}$$

T_0 = Boiling point of the liquid (pure solvent)
l_v = latent heat of vaporisation (per gm)
$\Delta_{vap}H$ = latent heat of vaporisation (per mole)
M_1 = M.M of solvent
R = Gas constant

- Elevation in the boiling point is also termed as ebullioscopy.
- It is the increase in boiling point of a solvent due to the addition of non-volatile solute in it. It is denoted by ΔT_b.
- It is measured by Lands Berger's method and Koltrell's method.
- The elevation in B.P. is given as

  m = molality of solution

  $$\Delta T_b \ \alpha \ m \text{ or } \Delta T_b = K_b.m$$

  $$\text{So, } \Delta T_b = K_b \times \frac{w}{M} \times \frac{1000}{W}$$

  $$\text{Molecular weight of solute, } M_W \ \frac{M_w = k_b \times w \times 1000}{\Delta T_b \times W}$$

  Here,
  W = Weight of solvent
  w = Weight of solute
  K_b = Molal elevation constant or ebullioscopic constant.
  If molality of the solution is one, then

  $$\Delta T_b = K_b$$

  $$K_b = \frac{RT^2}{1000 \ L_v}$$

  $$L_v = \frac{\Delta H_v}{M}$$

  Here, L_v = Latent heat of vaporization.
- If molar elevation in boiling point constant (K) is to be calculated, then replace 1000 with 100 in the above mentioned formula, that is, $K = 10 \ K_b$.

Depression in Freezing Point

Freezing point is a measure of temperature for the substance having the same solid and liquid forms in equilibrium, also having same vapour pressure. Solid form of a solution separates out at a lower temperature because of lower vapour pressure of the solution.

Definitions

Molal elevation constant may be defined as the elevation of boiling point when the molality of the solution is unity, i.e., 1 mole of the solute is dissolved in 1 kg (1000 g) of the solvent. The units of K_b are, therefore, degree/molality, i.e. K/m or °C/m or K kg mol^{-1}.

Rack your Brain

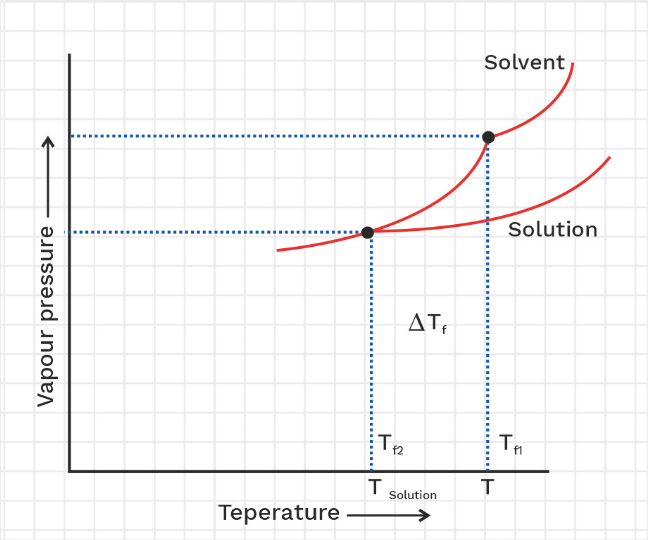
Why elevation of boiling point is a colligative properte?

Previous Year's Questions

The freezing point depression constant for water is -1.86°C m^{-1}. If 5.00g Na_2SO_4 is dissolved in 45.0g H_2O, the freezing point is changed by -3.82°C. Calculate the van't Hoff factor for Na_2SO_4.

[AIPMT]

(1) 2.05 (2) 2.63
(3) 3.11 (4) 0.381



- It is the decrease in freezing point of a solvent due to the addition of a non-volatile solute.
- This is also termed as **cryoscopy**.
- Depression in freezing point (ΔT_f) = Freezing point of pure solvent – Freezing point of solution
- It is measured by Beckmann's thermometer method and Rast's method.

$$\Delta T_f = K_f.m.$$

- $$\Delta T_f = K_f \frac{w}{m_w} \times \frac{1000}{W}$$
- $$M \text{ or } m_w = \frac{K_f \times w \times 1000}{\Delta T_f \times W}$$

Here,
W = Weight of solvent
w = Weight of solute
K_f = Molal depression constant or cryoscopic constant

- If molality of the solution is one, then

$$\Delta T_f = K_f$$

- $$K_f = \frac{RT^2}{1000\ L_f}$$

Rack your Brain

Sodium chloride solution freezes at lower temperature than water but boils at higher temperature than water. Explain.

Concept Ladder

$$K_f = \frac{RT_0^2}{1000\, l_f} = \frac{M_1RT_0^2}{1000\ \Delta_{fus}H}$$

$$\text{where, } l_f = \frac{\Delta_f H}{M_1}$$

T_0 = freezing point of the liquid (pure solvent)
l_f = latent heat (per gram)
$\Delta_{fus}H$ = latent heat of fusion
M_1 = M.M of solvent
R = Gas constant

COLLIGATIVE PROPERTY

A property that depends on the concentration of solute particles but not on the identity of the solute

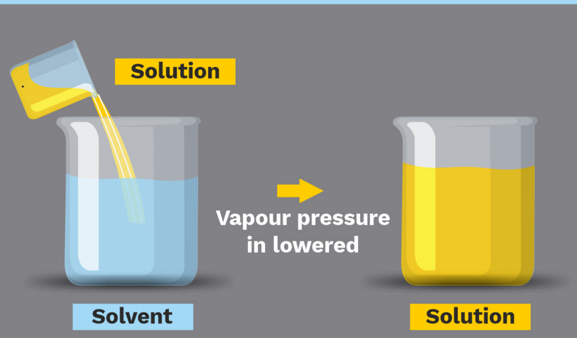
Colligative properties include :

- Vapour pressure lowering
- Boiling point elevation
- Freezing point depression

VAPOUR PRESSURE

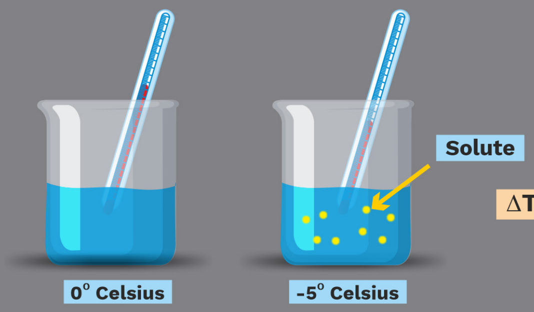
vapour pressure is the pressure of the vapour over a liquid at equilibrium.

A non-volatile solute will lower the vapour pressure of a solvent

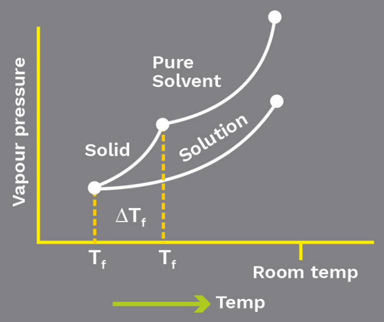


Freezing Point Depression

Freezing Point Depression is the decrease in the freezing point of a solvent due to the presence of solute particles.

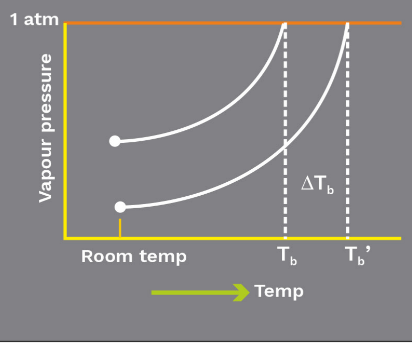


$\Delta T_f = K_f.m$

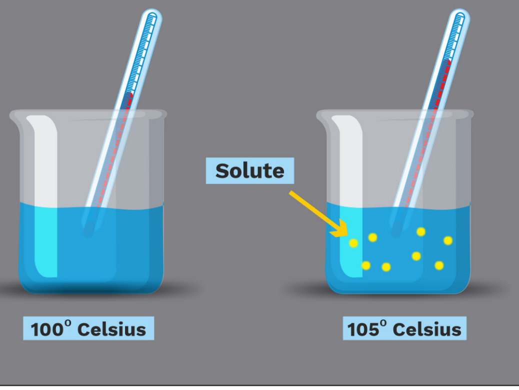


Boiling Point Elevation

Boiling Point elevation is the increase in the boiling point of a solvent due to the presence of solute particles



$\Delta T_b = K_b.m$



$$K_f = \frac{RT_f^2}{l_f \times 1000}$$

Here, l_f = Latent heat of fusion

- If molar depression in freezing point constant (K) is to be calculated, then replace 1000 with 100 in the above-mentioned formula, that is, $K = 10\ K_f$

Van’t Hoff Factor

- Certain solutes which undergo dissociation or association in solution, are found to show abnormal molecular mass. Due to this, the colligative property becomes abnormal which can be explained by Van’t Hoff factor.

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

$$i = \frac{\text{Observed colligative property}}{\text{Normal colligative property}}$$

$$i = \frac{\text{Actual number of particles or species}}{\text{Expected number of particles or species}}$$

- For solutes showing dissociation, the van’t Hoff factor i > l.

For example, $Fe^{3+} + 3Cl^- \longrightarrow Fe^{3+} + 3Cl^-$ Here $i = 4$

$$\left.\begin{array}{l} i = 2 \text{ for } MX,\ MNO_3,\ MSO_4 \\ i = 3 \text{ for } MX_2,\ M_2O,\ M(NO_3)_2 \\ i = 4 \text{ for } MX_3,\ K_3[Fe(CN)_6] \\ i = 5 \text{ for } M_2X_3,\ M_2(SO_4)_3, \\ \qquad M_3(PO_4)_2, K_4[Fe(CN)_6] \end{array}\right] \text{When } \alpha = 1$$

- For solutes showing association, the van’t Hoff factor i < 1. For example, dimerization of acids like benzoic acid in benzene.
- For solutes showing neither dissociation nor association, the van’t Hoff factor i is 1, for example, urea, glucose, sucrose.

Definitions

Molal depression constant may be defined as the depression of freezing point when the molality of the solution is unit i.e., one mole of the solute is dissolved in 1000 g (1 kg) of the solvent. The units of K_f are, therefore, degrees/molality i.e., K/m or [K] [kg] $[mol]^{-1}$

Rack your Brain

Value of i (Van’t Hoff Factor) for aqueous KCl solution is close to 2, while the value of ethanoic acid in benzene is nearly 0.5 why?

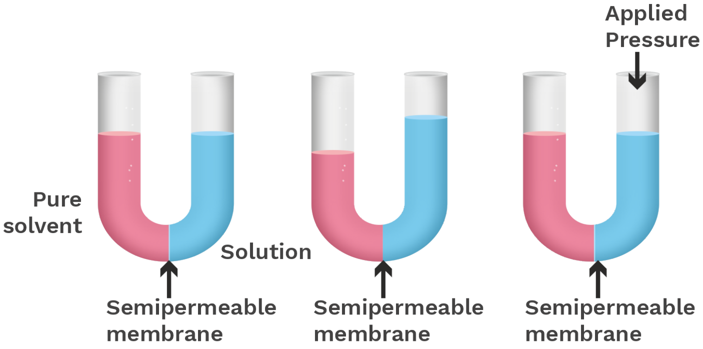
Concept Ladder

Van’t Hoff factor, (i)
- i > 1 (in case of dissociation)
- i < 1 (in case of association)

WHAT IS OSMOTIC PRESSURE ? & WHAT IS HOFF FACTOR ?

WHAT IS OSMOTIC PRESSURE ?

The minimum pressure that stops the osmosis is equal to the osmotic pressure of the solution



$$\pi = i\,\mathrm{MRT}$$

π = Osmotic Pressure

i = Osmotic Pressure

M = Molar concentration of solution (mol/L)

R = Ideal gas constant (0.08206 L atm Mol^{-4} K^{1})

R =Temperature in Kelvin (K)

WHAT IS HOFF FACTOR ?

Colligative properties are directly proportional to the number of mole of solute, dissociation or association may cause some abnormal increase or decrease in the measured values of colligative properties. Van't Hoff factor is a factor that takes into account this abnormal behaviour

$$i = \frac{\text{Observed magnitude of any colligative properties}}{\text{Normal magnitude of the same colligative properties}}$$

Since, colligative properties are inversely related to molar mass of the solute hence one can write

$$i = \frac{\text{Normal molar mass}}{\text{Observed molar mass (obtained froma colligative property)}}$$

Thus the value of depends upon the state of solute in the solution. Following cases are possible :

when $i = 1$ then the solute remains unaffected (i.d., normal) in solution

when $i > 1$ then the solute undergo dissociation in solution

when $i < 1$ then the solute undergo association in solution

- Degree of dissociation, $\alpha = \frac{i-1}{n-1}$

  Here n = Number of species formed after dissociation

  Degree of association, $\alpha = \frac{n(1-i)}{n-1}$

  Here n = Number of species formed after association.

Measuring Molecular Mass of Polymers

Molecular mass of polymers is best determined by osmotic pressure method; firstly, because the values given by other colligative properties are so low that they cannot be measured accurately, and secondly, osmotic pressure measurements can be made at room temperature and do not require heating which may change the nature of the polymer.

Q.1 Distinguish between the boiling point of a liquid and the normal boiling point of a liquid.

A.1 B.P. is the temperature at which the vapour pressure of the liquid becomes equal to the surrounding pressure. The normal B.P. is the temperature at which the vapour pressure is 1 atm.

Q.2 Briefly explain the underlying principle of the purification of water by reverse osmosis.

A.2 When pressure greater than osmotic pressure is applied on the salt water side of a semi-permeable membrane, water molecules flow through the membrane towards pure water side.

Q.3 Components of a binary mixture of two liquids A and B were being separated by distillation. After some time separation of components stopped and the composition of the vapour phase became the same as that of a liquid phase. Both the components started coming in the distillate. Explain why this happened.

A.3 Both the components started coming for distillation, the liquid and vapour phase will have the same composition. This shows an azeotropic mixture. Therefore it can’t be separated by distillation.

Q.4 Explain why on the addition of 1 mol of NaCl to 1 litre of water, the boiling point of water increases, while the addition of 1 mol of methyl alcohol to one litre of water decreases its boiling point.

A.4 NaCl is a non-volatile solute. On adding NaCl to water, vapour pressure is lowered and hence boiling point of water increases. Methyl alcohol is more volatile than water. On adding methyl alcohol into water, vapour pressure of solution is greater than that of water. hence, boiling point of water decreases.

Q.5 Explain the solubility rule “like dissolves like” in terms of intermolecular forces that exist in solutions.

A.5 For one substance to dissolve into another substance, the two substances should have similar intermolecular interactions. This is so only when either both the substances (solute and solvent) are polar or both are non-polar. This rule is called “like dissolves like”.

Q.6 Concentration terms such as mass percentage, parts per million, mole fraction and molality are independent of temp., however, molarity is a function of temperature. Explain.

A.6 Change in molarity of a solution is due to the change in volume which is cause due to change in temperature. Hence, terms such as ppm, mole fraction, mass percentage and molality are independent of temp., as their calculations are based on mass and do not involve volume.

Q.7 What is the significance of Henry's Law constant K_H?

A.7 Higher the value of Henry'ss law constant, K_H, lower is the solubility of gas in the liquid

Q.8 Why are aquatic species more comfortable in cold water in comparison to warm water?

A.8 Due to the increase in solubility and availability of O_2, aquatic species are more comfortable in cold water

Q.9 Why soda water bottle kept at room temperature fizzes on opening?

A.9 Both pressure inside the bottle and solubility of carbon dioxide reduces, when a soda water bottle is opened at room temp. and normal pressure conditions, therefore causing the gas bubbles to escape and soda water fizzing.

Q.10 Why is the vapour pressure of an aqueous solution of glucose lower than that of water?

A.10 In pure water, the entire surface is occupied by water molecules which are volatile. On adding glucose, some water molecules on the surface are replaced by glucose molecules which are non-volatile. Hence, vapour pressure is lowered.

Q.11 Mixing of acetone with chloroform takes place with reduction in volume ? What type of deviation from Raoult's law is shown in this case ?

A.11 The solution has negative deviation from Raoult's law because decrease in volume indicates strong forces of interaction between the molecules in solution.

Q.12 How does sprinkling of salt help in clearing the snow-covered roads in hilly areas? Explain the phenomenon involved in the process.

A.12 When salt is spread over snow covered roads, depression in freezing point of water takes place. At the ambient temperature, snow starts melting and it helps in clearing the roads.

Q.13 What is a "semi-permeable membrane"?

A.13 A semi-permeable membrane is a continuous sheet or film of suitable material (natural or synthetic) which has pores such that solvent molecules can pass through but big molecules of the solute cannot.

Q.14 Write an example of a material used for making semi-permeable membrane for carrying out reverse osmosis.

A.14 Cellulose acetate and polyamides are the examples of materials used for the semi-permeable membrane include.

Q.15 Molarity of H_2SO_4 is 0.8 and its density is 1.06 g/cm^3. What will be its concentration in terms of molality and mole fraction?

A.15 Molarity of H_2SO_4 = 0.8, it means 0.8 mole H_2SO_4 are present in 1 L of the solution 0.8 mole H_2SO_4 = 0.8 × 98g = 78.4 g;

1L H_2SO_4 solution = 1000 × 1.06g = 1060g

$$\therefore \text{Mass of solvent (water)} = 1060 - 78.4\text{g} = 981.6\text{ g} = \frac{981.6}{18}\text{moles} = 54.53\text{moles}$$

Thus, 981.6g of water contain 0.8 mole of H_2SO_4.

$$\therefore \text{ Molality } = \frac{0.8\,\text{mol}}{981.6\,\text{g}} \times 1000 \text{ mol kg}^{-1} = 0.815\,\text{mol kg}^{-1}$$

Further, the solution contains 0.8 mole of solute in 54.53 moles of solvent.

$$\therefore \text{ Mole fraction of solute } = \frac{0.8}{0.8 + 54.53} = 0.014$$

Q.16 At a given temperature, the vapour pressure in mm of Hg of a solution of two volatile liquids A and B is given by the equation p = 120 - 80 X_B (X_B = mole fraction of B)

Calculate the vapour pressures of a pure A and B at the same temperature.

A.16 When $X_B = 0$, we have pure A $\therefore p_A^0 = 120 - 80 \times 0 = 120$ mm

The given expression can be written as $p = 120 - 80\,(1 - X_A)$

When $X_A = 0$, we have pure B $\therefore p_B^\circ = 120 - 80\,(1 - 0) = 40$ mm

Alternatively, for pure B, $x_B = 1$. Hence, $p_B^0 = 120 - 80 \times 1 = 40$ mm

Q.17 CCl_4 and water are immiscible whereas ethanol and water are miscible in all proportions. Correlate this behavior with molecular structure of these compounds.

A.17 CCl_4 is a non-polar covalent compound hence it can neither form H-bonds with water molecules nor it can break H-bonds in water molecules whereas water is a polar compound. Therefore, CCl_4 is insoluble in water.

Ethanol is a polar compound hence it can form H-bonds with water. Therefore, it is miscible with H_2O in all proportions.

Chapter Summary

- Alloys are solutions of solids in solid
- Henry's Law determines solubility of gas in a liquid.
- When two non-reacting solutions of different normalities are mixed, the normality of final solution can be calculated by using following equation.

$$N_1V_1 + N_2V_2 = N_3(V_1 + V_2)$$

- Human RBC is isotonic with 0.91% NaCl
- Osmotic pressure is best colligative property to determine molecular mass of a non volatile solute and polymers.
- Plasmolysis is shrinking of living (plant or animal) call when placed in hypertonic solution.
- Reverse osmosis takes place when pressure applied on solution is more than osmotic pressure. The solvent starts flowing from solution to pure solvent e.g., desalination of sea water to obtain pure water.
- Substance having high vapour pressure evaporate easily.
- Clausius Clapeyron equation is used to calculate boiling point of solution at given temperature when boiling point at some other pressure is given.

$$\log \frac{P_2}{P_1} = \frac{\Delta H}{2.303\ R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

- (i) Aerosol - solid in gas or liquid in gas
  (ii) Gel - liquid in solid
  (iii) Emulsion - liquid in liquid
- Bredig's arc method and petisation are method of preparation of colloids and dialysis is method of purification of colloid.
- Negatively charged colloids are metals and coagulated by +vely charged ions.
- Colloidal gold is called purple of cassius.
- Colloidal antimony is used in treatment of kalazar.
- Proteins are coagulated by Ag^+.
- CMC is critical micellisation concentration, the surfactants at this concentration associate to form micells. For soaps, the CMC value to 10^{-3} mole/litre.
- Surface tenstion of lyophilic colloids is lower than water.