

Solutions and Colligative Properties





Homogeneous mixture i.e., a single phase containing more than one component dispersed on a molecular scale.



Homogeneous Mixture

When salt is dissolved in water it forms a homogeneous mixture. Composition is same throughout the salt solution.

Solutions around us

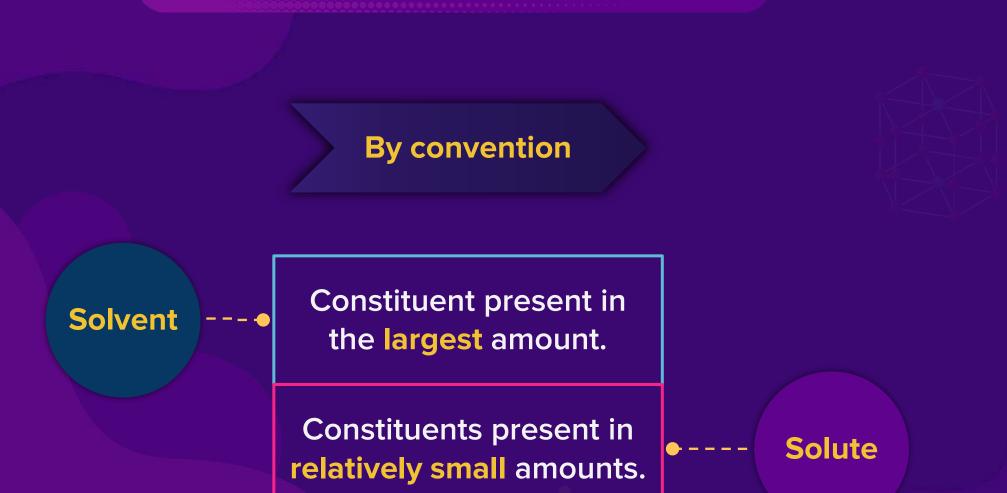
Soda can

Saline solution

Components of a Solution



Components of a Solution

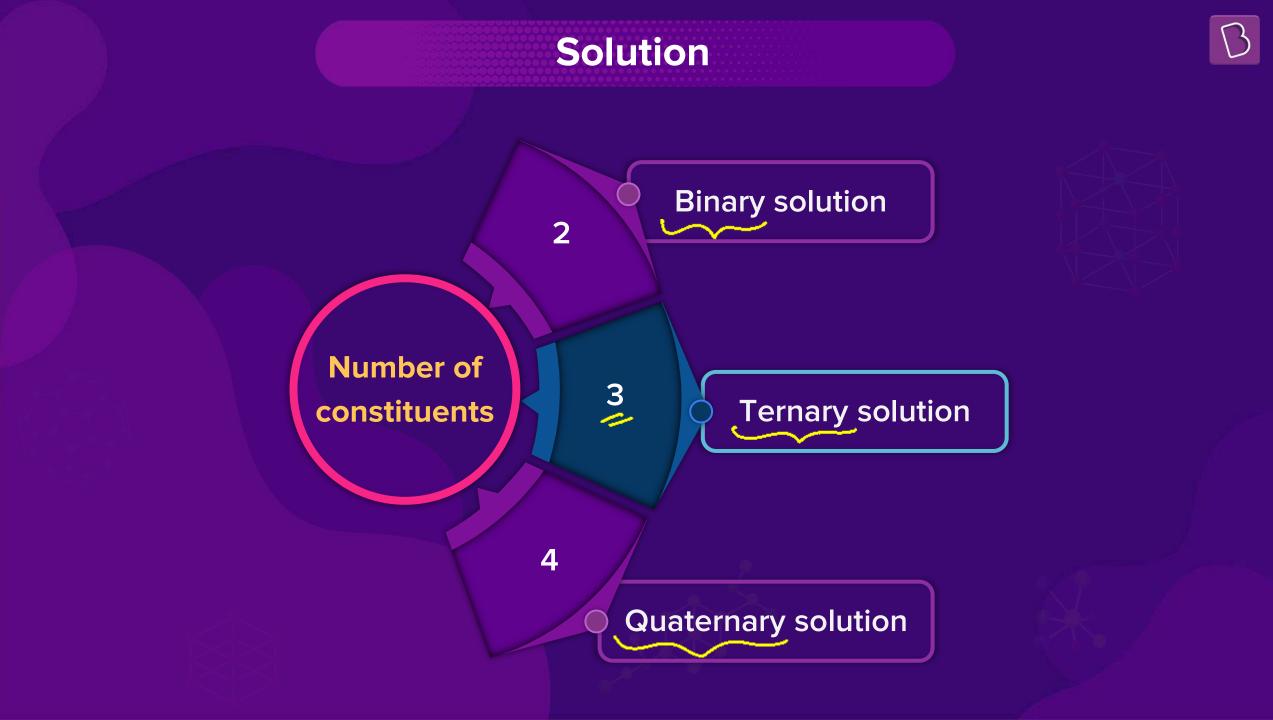




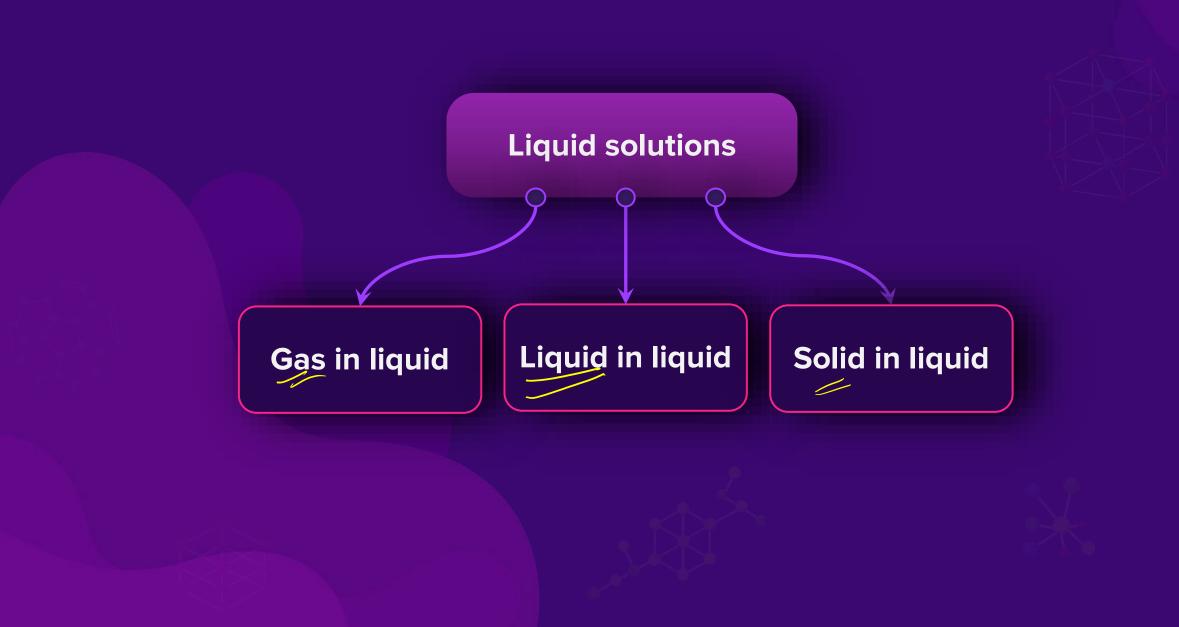


Solvent determines the physical state in which the solution exists.

If one of the components of a solution is water, it will always be considered as a solvent even when it is present in a very less amount.



Types of Liquid Solutions



Types of Liquid Solutions

1) Gas in liquid :

Solvent - Liquid & Solute - Gas Example: CO_2 dissolved in water.

2) Liquid in liquid :

Solvent - Liquid & Solute - liquid Example: Methanol dissolved in water .

3) Solid in liquid :

Solvent - Liquid & Solute - solid Example: Sugar in water, common salt dissolved in water.



Concentration Term

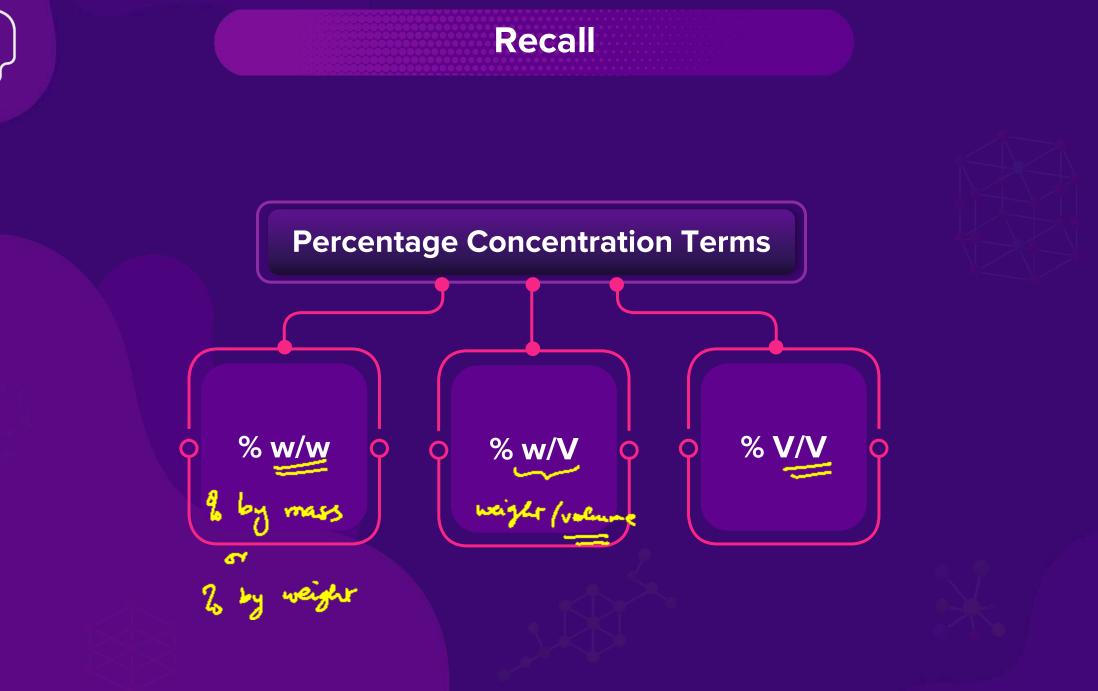
Composition of a solution can be described by expressing its concentration.

Concentration can be expressed either qualitatively or quantitatively.

Concentrated and dilute

Concentration terms









Amount of solute in grams dissolved per 100 g of solution.

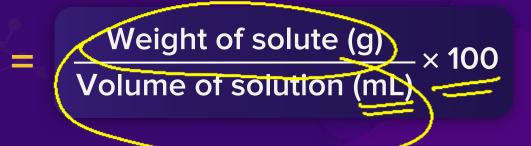
% w/w

Weight of solute (g) Weight of solution (g) × 100 B



Amount of solute in grams dissolved per 100 mL of solution.

% w/V





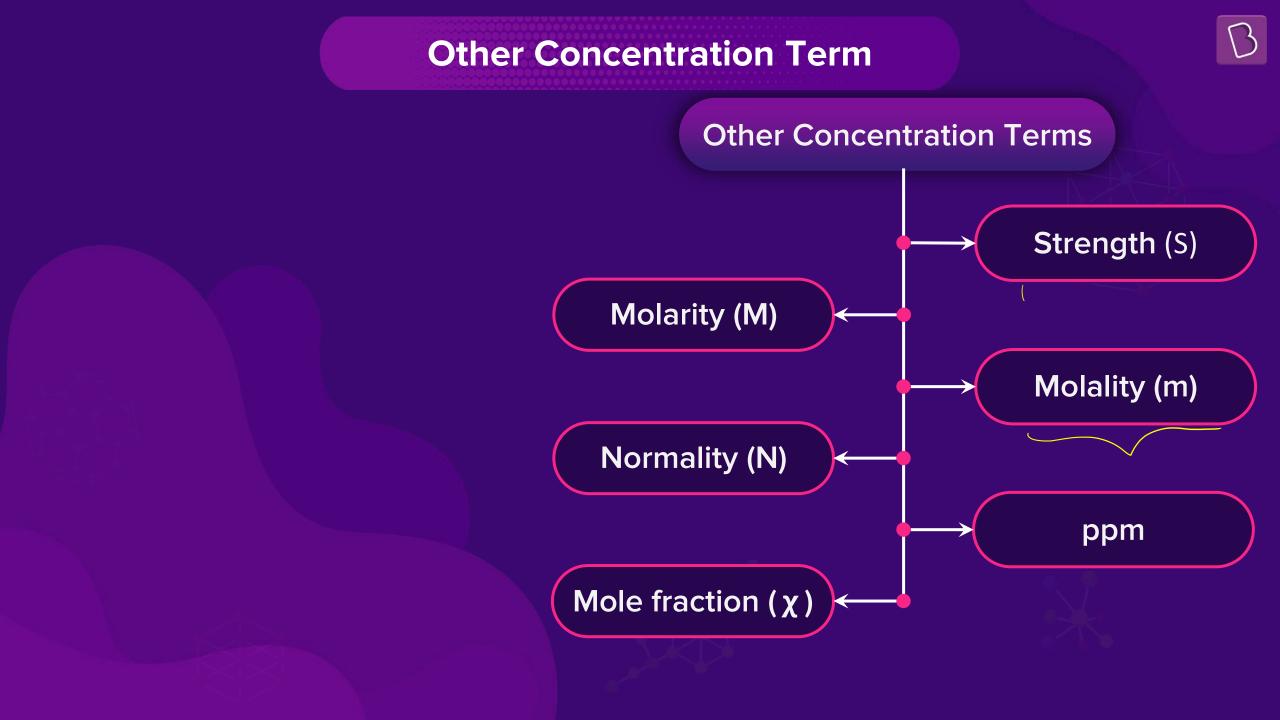
Volume of a solute (in mL) dissolved per 100 mL of solution.

% V/V

% V/V

_

Volume of solute (mL) Volume of solution (mL)





Strength of Solution = 10x (7, w/v)

Weight of solute (in gram) per litre (1000 mL) of solution.



If we have 6% w/w urea solution with density 1.060 g/mL, then its strength in g/L is:

Solution

Given: % w/w = 6% Density of solution = 1.060 g mL⁻¹ Strength of solution = ?

6% w/w urea solution means 6 g urea present in 100 g solution Therefore, mass of the solution= 100 g

Density is defined as the ratio of mass and volume. Thus,

Density of solution = Mass of solution Volume of solution Volume of = solution

100 g 1.060 g mL⁻¹ Volume of solution = 94.34 mL or volume of solution = 0.09434 L

Strength of the solution is given as follow:

Strength of solution =

Mass of the solute (g) Volume of solution (L)

6 g

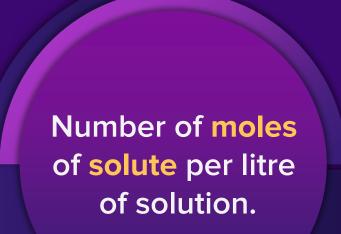
0.09434 L

Strength of solution

Hence, strength of solution = 63.6 %







Μ

No. of moles of solute (n) Volume of solution (L)





 6.02×10^{20} molecules of urea are present in 100 mL of its solution. The concentration of urea solution is:

Solution

Number of molecules of urea = 6.02×10^{20} molecules

Number of moles of urea
$$= \frac{N}{N_A} = \frac{6.02 \times 10^{20}}{6.02 \times 10^{23}}$$

Number of moles of urea = 0.001 mol

Volume solution = 100 mL = 0.1 L





Therefore, molarity of urea solution = 0.01 M



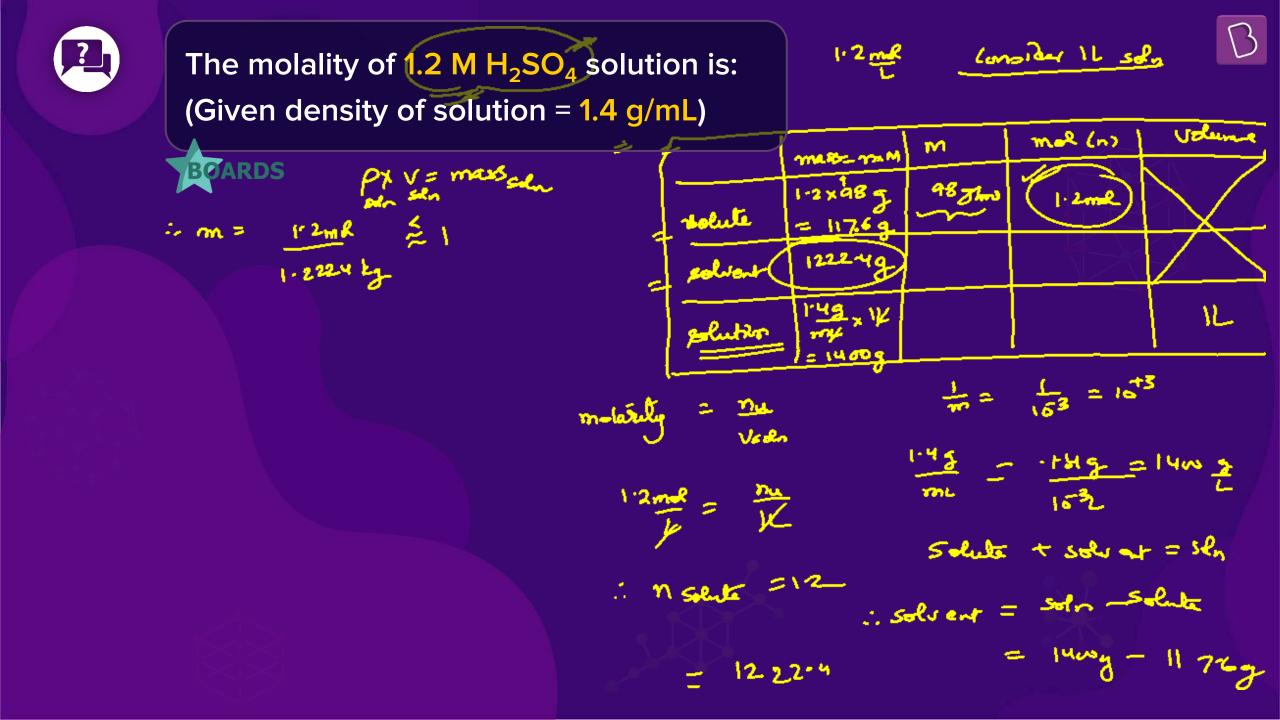
Number of moles of the solute per 1000 g or 1 kg of solvent.

m

No. of moles of solute (n)

Mass of solvent (kg)





Number of gram equivalents of solute dissolved per litre of solution.

Normality (N)





Normality (N)

-

B

Normality

Number of equivalents of solute

Volume of solution (L)

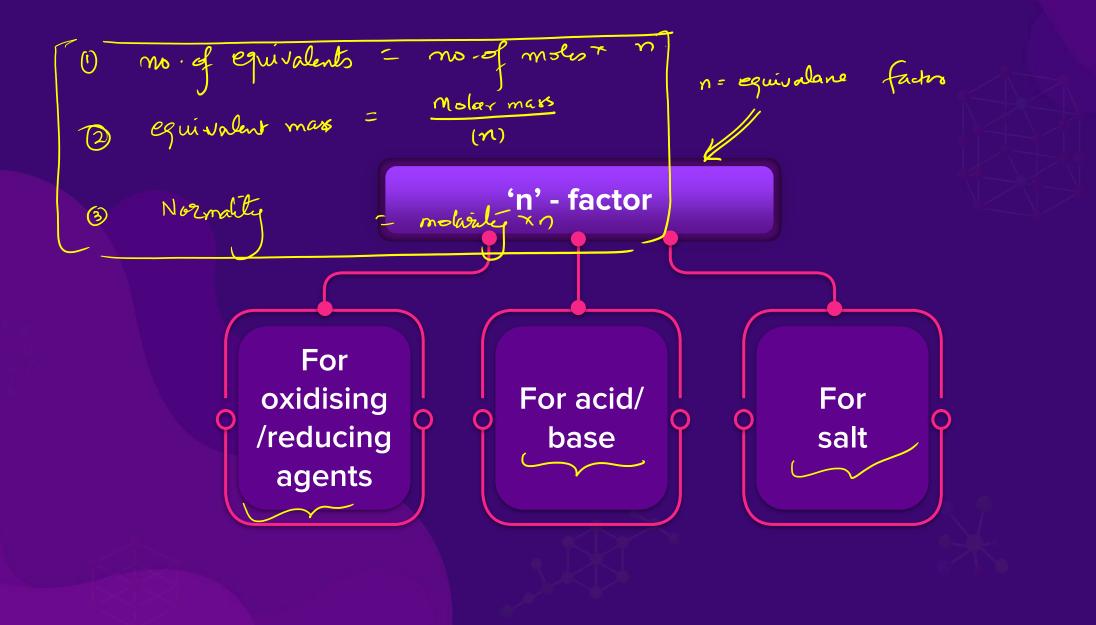
Number of equivalents

Mass of the species Equivalent mass

Mass of the species

Molar mass

n - factor



B

For Oxidising/Reducing Agents

Number of electrons involved in oxidation/ reduction half reaction per mole of oxidising/ reducing agent.

$$5e^{-} + 8H^{+} + MnO_{4}^{-} \longrightarrow Mn^{2+} + H_{2}O$$

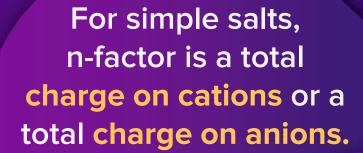
n-factor = 5

For Acid/Base

Number of H⁺ ions displaced/OH⁻ ions displaced per mole of acid/base.

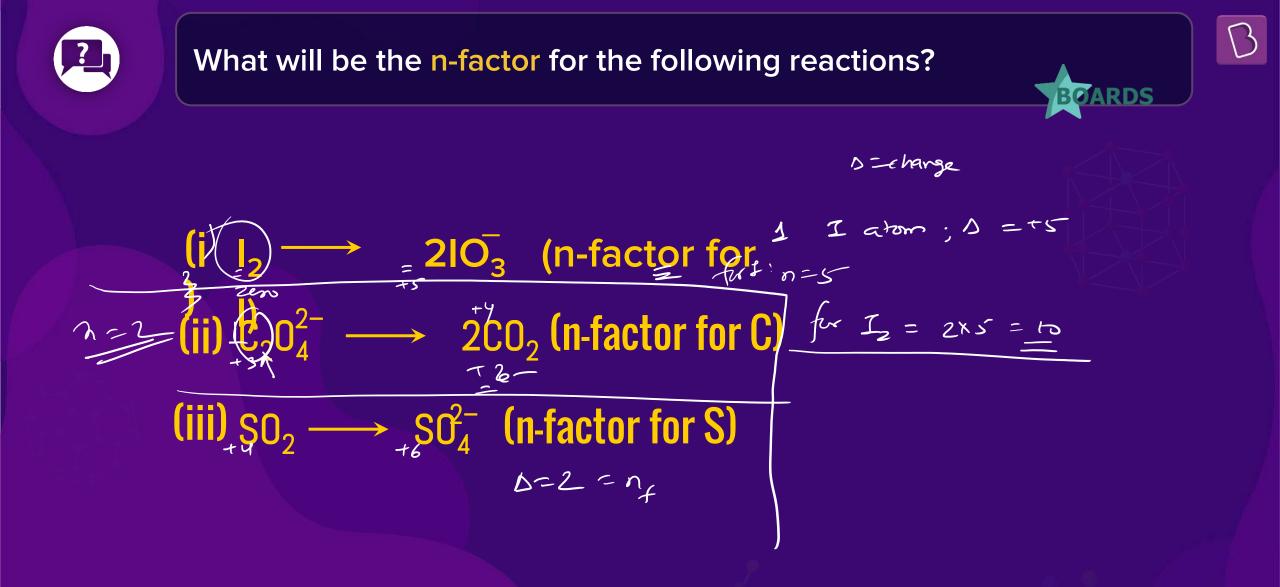
Example: H_2SO_4 n-factor = 2





Example: $Al_2(SO_4)_3$

n-factor = charge on the cation = $2 \times 3 = 6$



Hence, n-factor is 10, 2 and 2 respectively for the given reactions.

Parts per Million (ppm)

The number of parts of solute present in 1 million parts of solution.



Parts per Million (ppm)





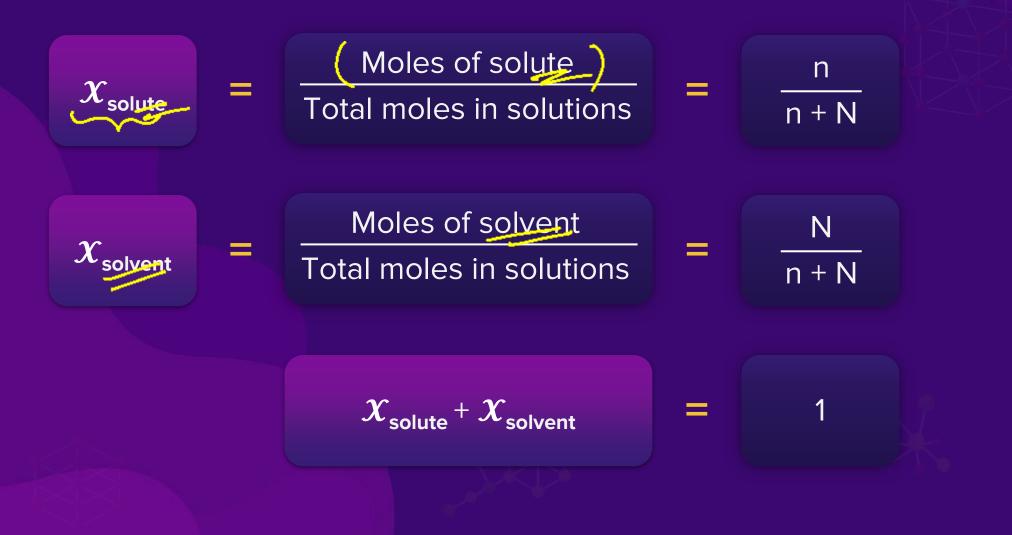
ppm (moles/moles)

 $\frac{\text{Moles of solute}}{\text{Moles of solution}} \times 10^{6}$

Mole Fraction (X)

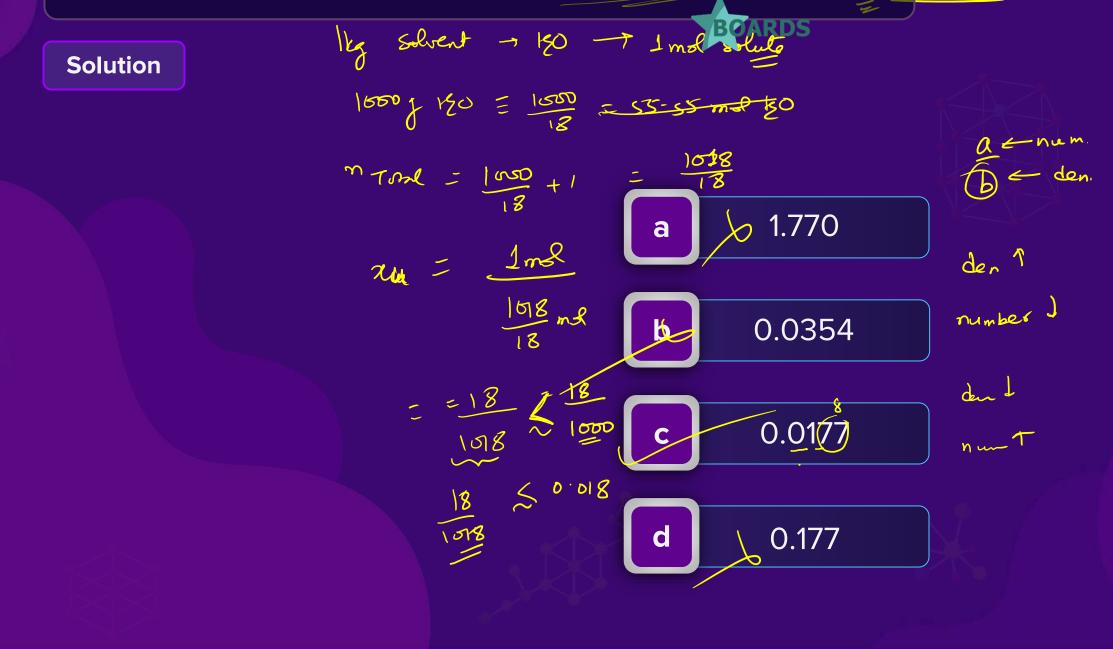
Ratio of the number of moles of a particular component to the total number of moles of all the components. Mole Fraction (X)

For a binary solution,

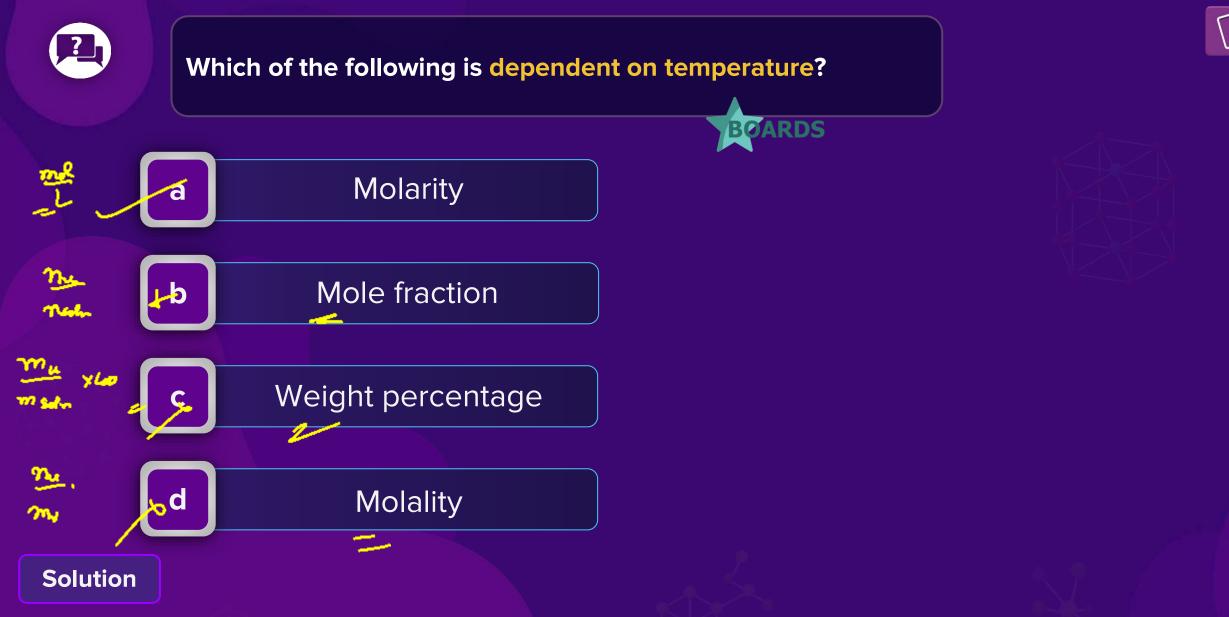




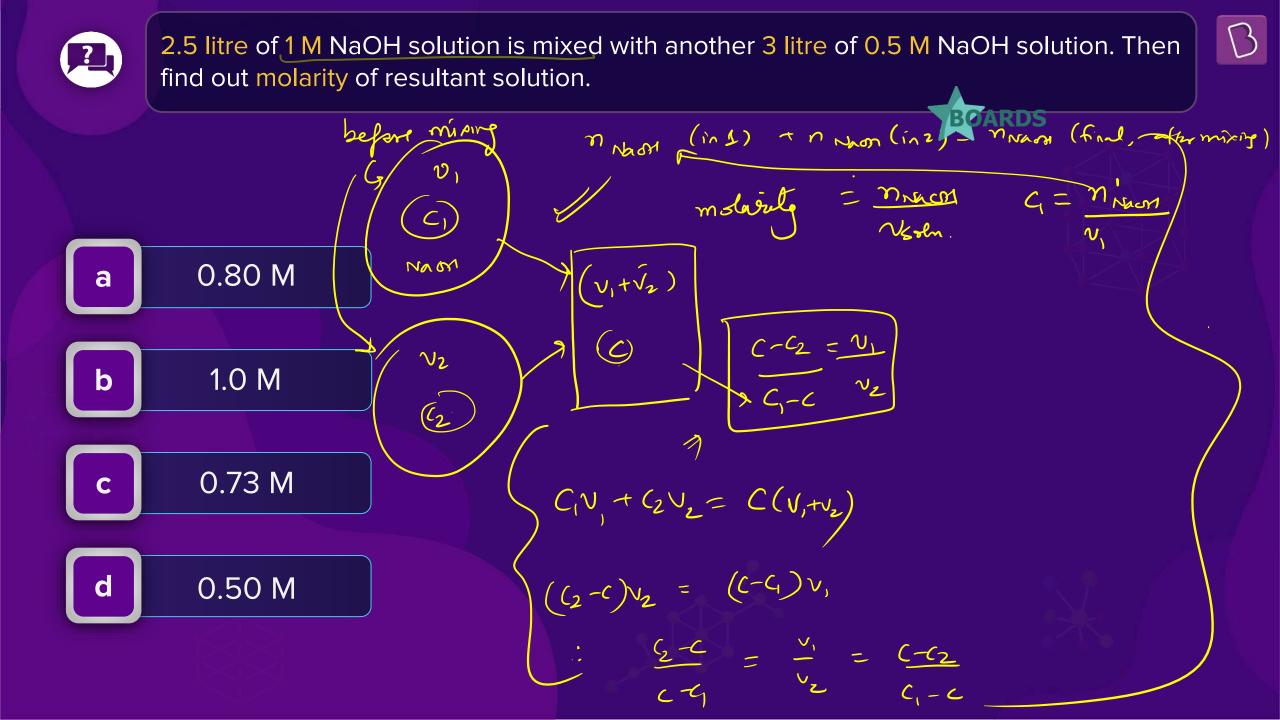
What is the mole fraction of the solute in a 1.00 m aqueous solution?



All volume dependent concentration terms are dependent on **temperature**.



Volume dependent concentration terms are temperature dependent, here, molarity is volume dependent and it also dependent on temperature. <u>Hence, option (a) is the correct answer.</u>





Solution

2.5 litre of 1 M NaOH + 3 litre of 0.5 M NaOH = 5.5 litre of 'x' M NaOH

 $\frac{x - 0.5}{1 - x} = \frac{v_1}{v_2} = \frac{2.5}{3}$

On solving we will get, 3x - 1.5 = 2.5 - 2.5x $x = \frac{4}{5.5} = 0.73 \text{ M}$

Hence, option (c) is the correct answer.

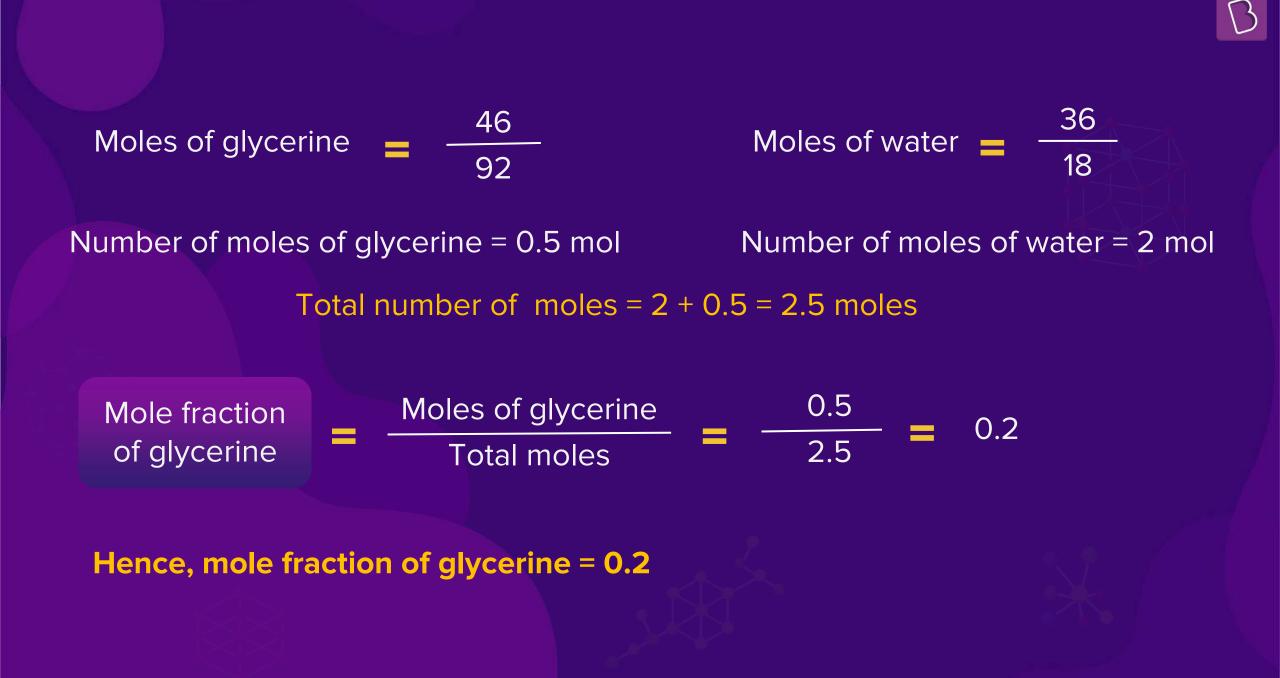




Mole fraction of glycerine ($C_3H_8O_3$) in a solution of 36 g of water and 46 g of glycerine is:

Solution

Given: Mass of glycerine = 46 g Molar mass of glycerine = 92 g mol⁻¹ Mass of water = 36 g Molar mass of water = 18 g mol⁻¹





Density of a 2.05 M solution of acetic acid in water is 1.02 g/mL. The molality of the solution is:

(a) 3.28 mol kg⁻¹

(c) 0.44 mol kg⁻¹

(b) 2.28 mol kg⁻¹

(d) 1.14 mol kg⁻¹

BOARDS

Solution

Given: Density of the solution $= 1.02 \text{ g mL}^{-1}$ Let the volume of the solution = 1 L = 1000 mL

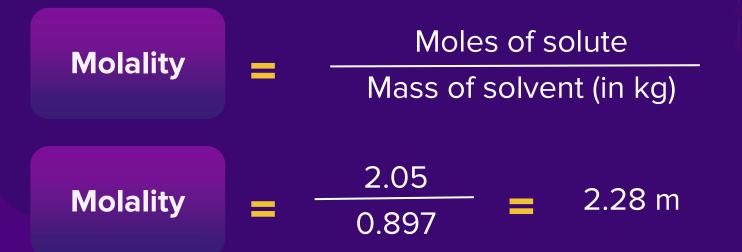
Density
$$=$$
 $\frac{Mass (g)}{Volume (mL)}$
1.02 g mL⁻¹ $=$ $\frac{Mass (g)}{1000 mL}$

Thus, mass of solution = 1020 g



Given: Molarity of acetic acid = 2.05 Mass of acetic acid n **Molarity** Volume (L) Molar mass of acetic acid x V Mass of acetic acid 2.05 60 x 1 Thus, mass of acetic acid = 123 g

Mass of solvent = Mass of solution – Mass of solute = 1020 - 123 = 897 g Mass of solvent = 897 g = 0.897 kg



Therefore, molality of acetic acid solution = 2.28 molal

Hence, option (b) is the correct answer.



The mole fraction of benzene in solution containing 30% by mass in carbon tetrachloride is:

Solution

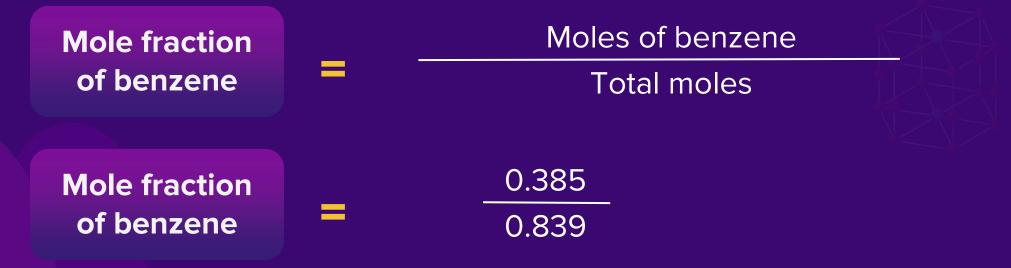
Let the mass of solution = 100 g Molar mass of benzene = 78 g mol⁻¹ Molar mass of $CCl_4 = 154$ g mol⁻¹

30% by mass means that 30 g of solute is present in 100 g of solution. Therefore, mass of benzene = 30 g Mass of $CCl_4 = 100 - 30 = 70$ g Moles of
benzene $\frac{30}{78}$ 0.385Moles of
 CCl_4 $\frac{70}{154}$ 0.454

Total moles = 0.385 + 0.454 = 0.8395

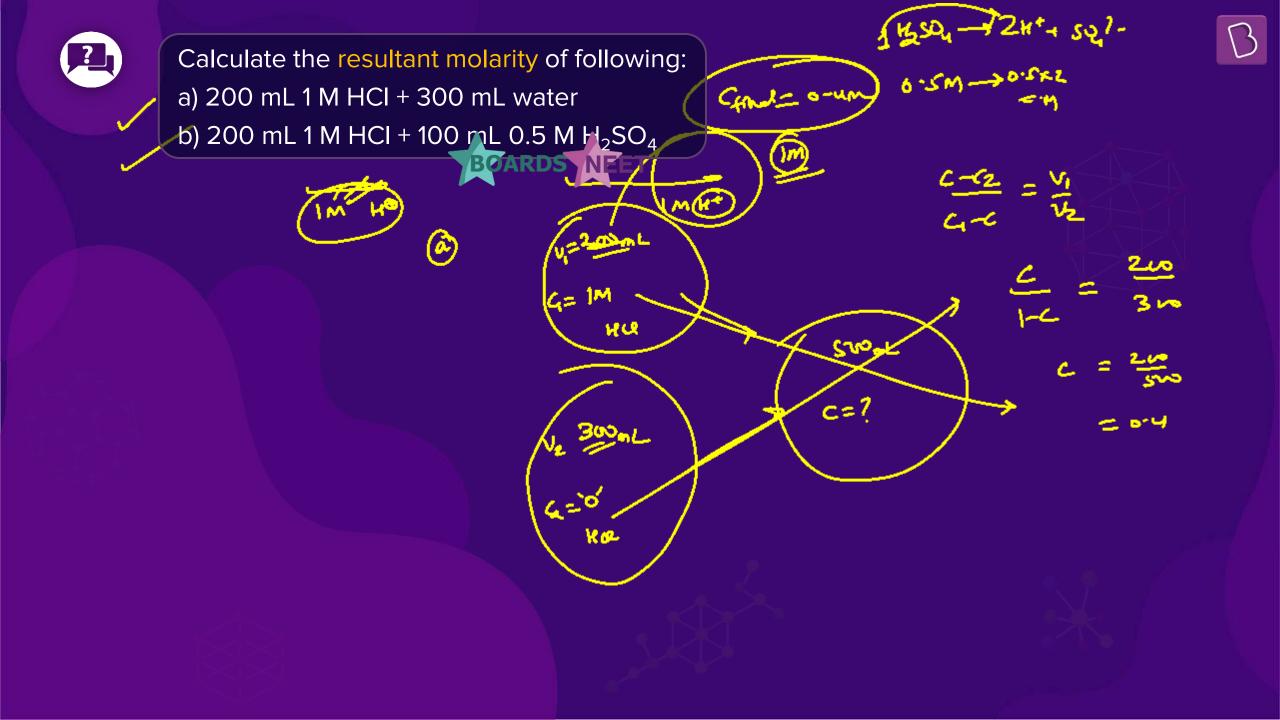






Mole fraction of benzene = 0.459

Hence, mole fraction of benzene is 0.459.



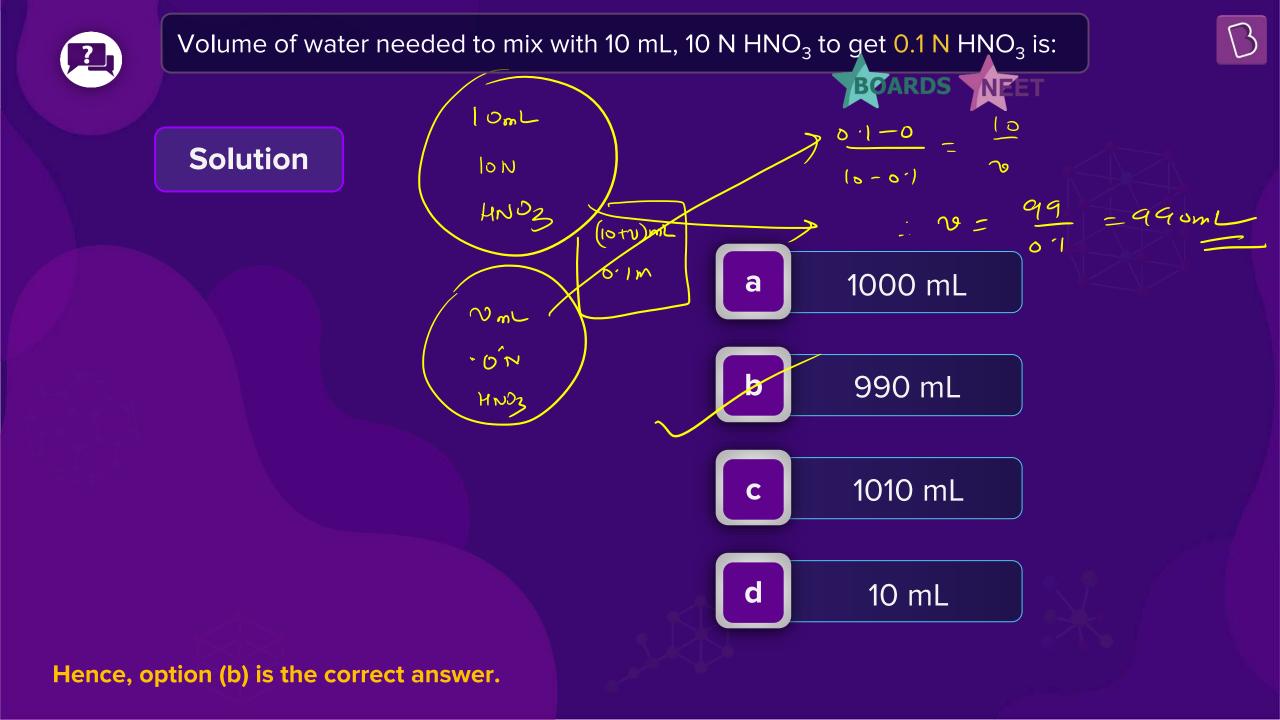


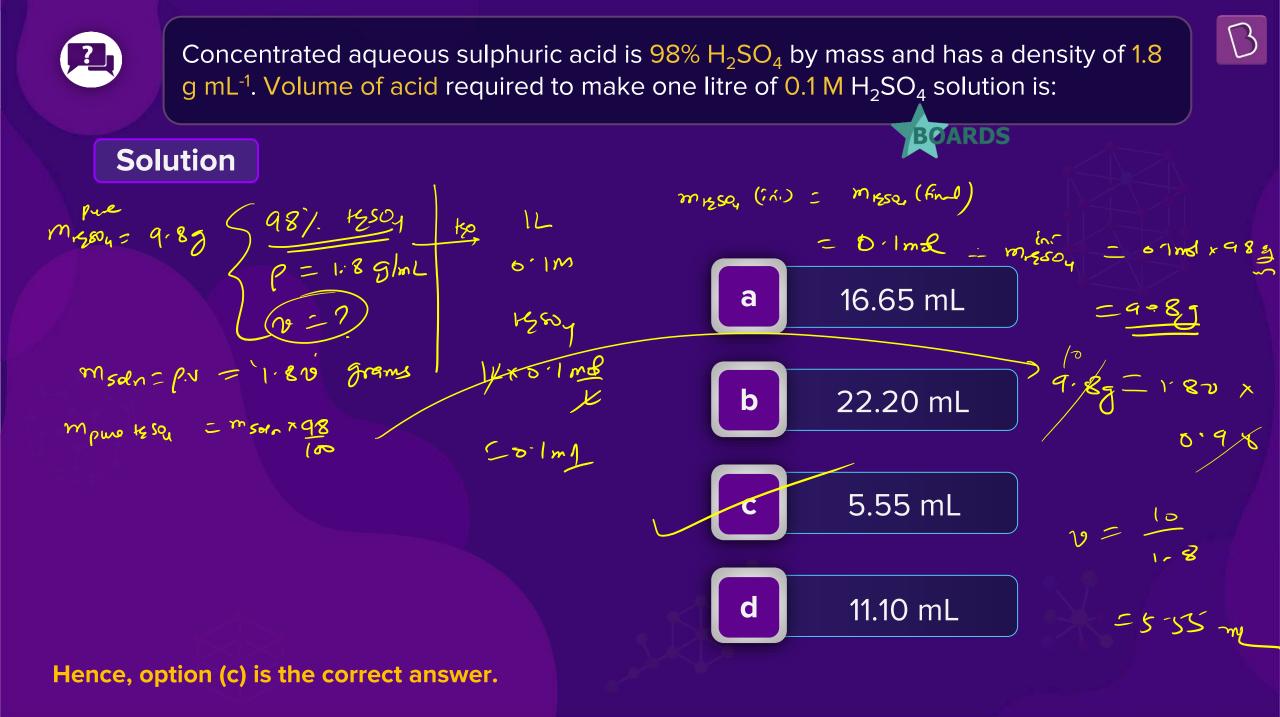
(b) $M_1 = 1 M$ $V_1 = 200 ml$ $M_2 = 0.5$ $V_2 = 100 ml$ n = 2 **Using the formula** $M_1 V_1 + nM_2 V_2 = MV$

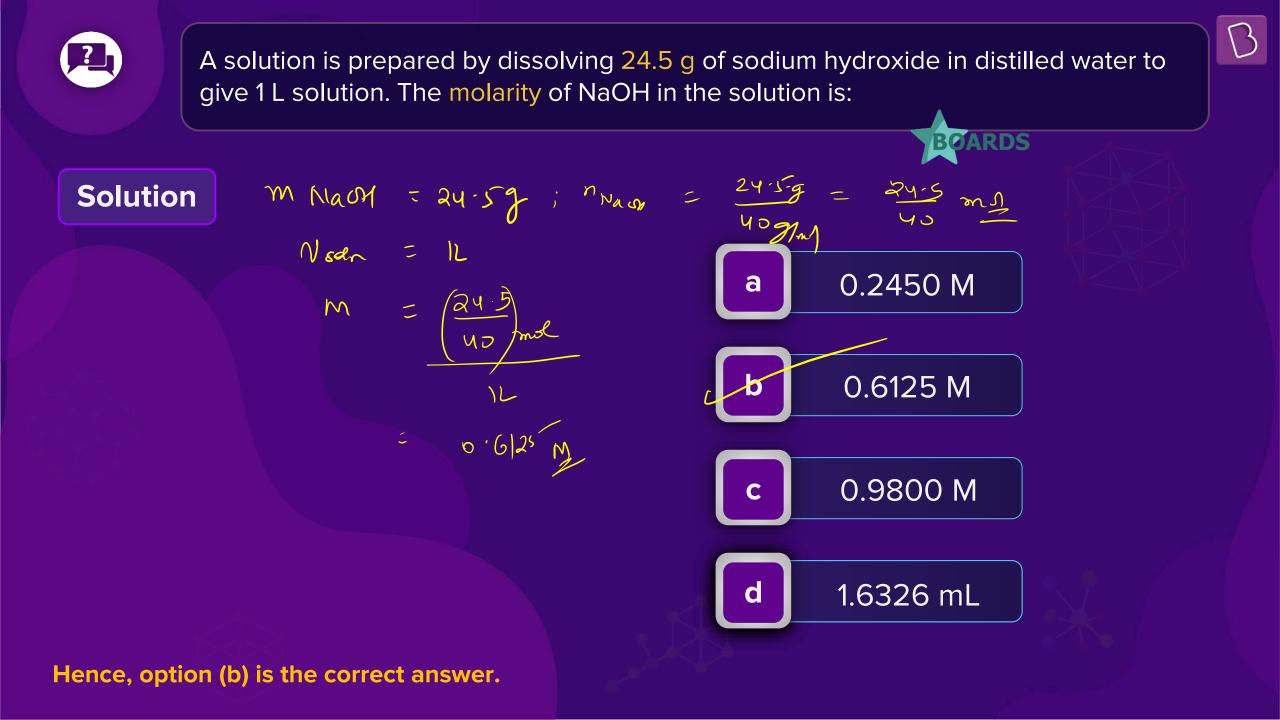
Where M is the resultant molarity and V is the total volume

 $(1 \times 200) + (2 \times 0.5 \times 300) = M \times 500$ M= 1 M Resultant molarity is 1 M.



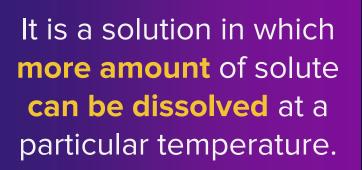








Unsaturated Solution







Saturated Solution







Supersaturated Solution

A solution which contains more amount of the solute than in the saturated solution at a particular temperature and pressure.



Solubility of a substance is its maximum amount that can be dissolved in a specified amount of solvent (generally 100 g of solvent) at a specified temperature to form a saturated solution.







Solubility of one substance into another depends on

Nature of the solute and solvent

Temperature

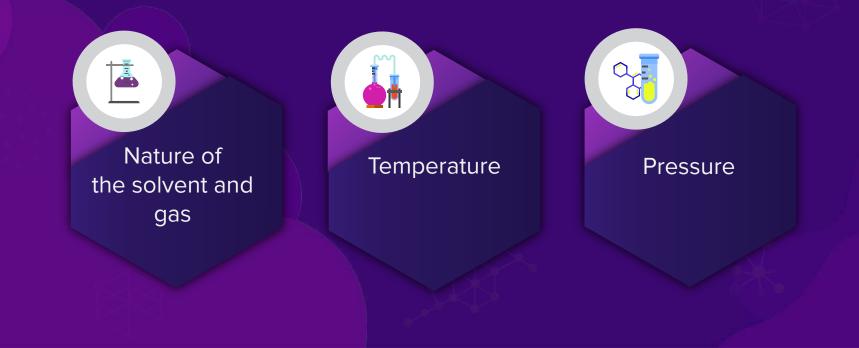
Pressure

2

3



There are three major factors that affect the solubility of a gas in a liquid:



Nature of the solvent and gas

Like dissolves like

Polar gases dissolve in polar solvents and non-polar gases dissolve in non-polar solvents.

- Polar gases : SO₂, NH₃ etc.
- Polar solvents : H_2O and alcohol etc.
- NH₃ is highly soluble in water, because both are polar and due to H-bonding.





(Water) Polar

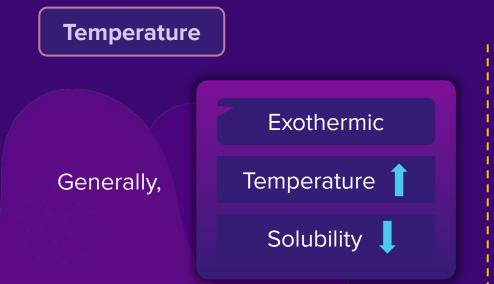
- Non polar gases : $O_2^{}$, $N_2^{}$ and $CO_2^{}$ etc.
- Non polar solvents : CCl₄, benzene etc.

Question : O_2 in water is : (a) Highly soluble (b) Moderately soluble (c) Poorly soluble **Answer :** O_2 in water is poorly soluble. Because O_2 is non-polar in nature whereas water is a polar solvent.

When a gas undergoes ionisation in a solvent, then it is highly soluble in that solvent.

E.g. **HCI** is highly soluble in **water.**

- When HCl (g) reacts completely with H₂O and gives H₃O⁺ and Cl⁻ and it becomes highly soluble because equilibrium shifts forward, increasing the solubility of HCl.
- If the solvent reacts with the gas. It can dissolve greater amounts of that gas.



For exothermic reaction as temperature increases solubility of gases in liquid decreases according to Le chatelier's principle. Consider any gas is dissolved in water.

Gas + aq ⇐ Gas (aq) + Heat

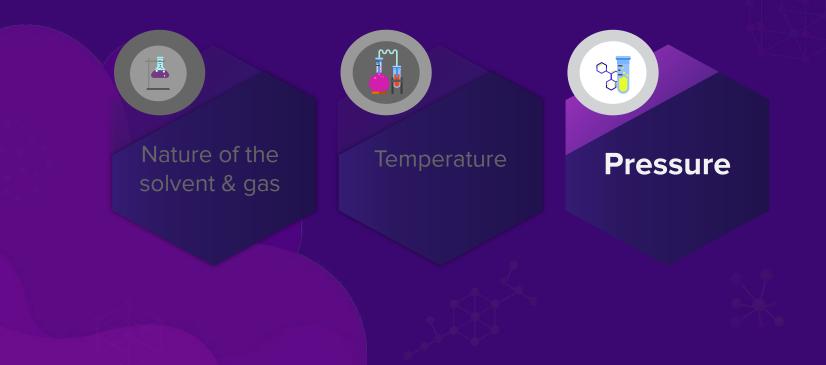
Solubility of gas increases in the forward direction if the temperature is lowered. According to Le chatelier's principle, if the reaction is exothermic in forward direction and temperature of reaction is increased, the reaction shifts to the backward direction.

Application:

Oxygen dissolves only to a **small extent** in water. It is this dissolved oxygen which sustains all **aquatic life.**

Solubility of gases **increases** with **decrease of temperature**. It is due to this reason that aquatic species are more comfortable in cold water rather than in warm water.

X

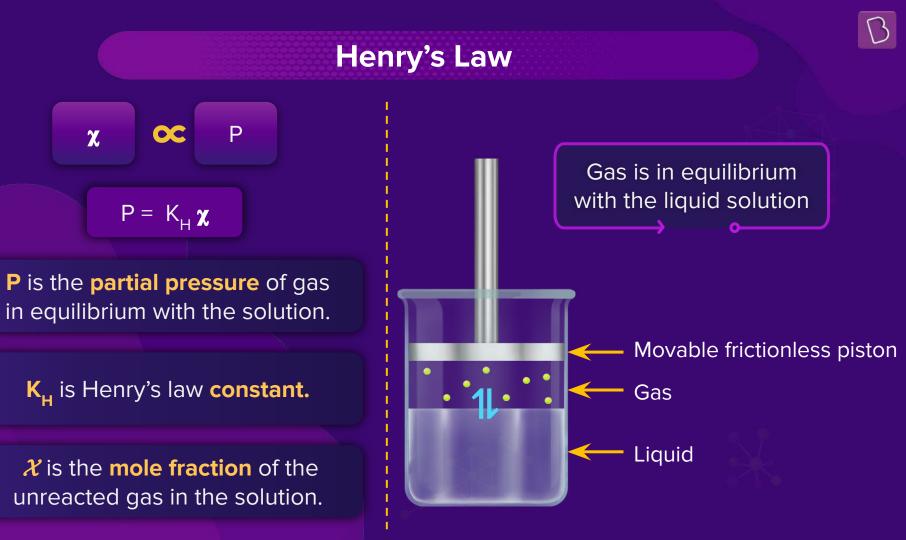




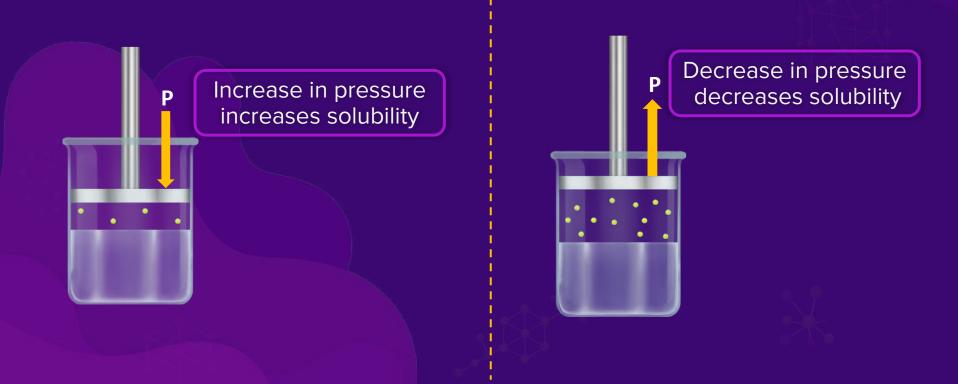
Henry gave a **quantitative relation** between pressure and solubility of a gas in a solvent which is known as **Henry's law**.

Henry's Law

The solubility of a gas in a liquid at a given temperature is directly proportional to its partial pressure, at which, it is dissolved.



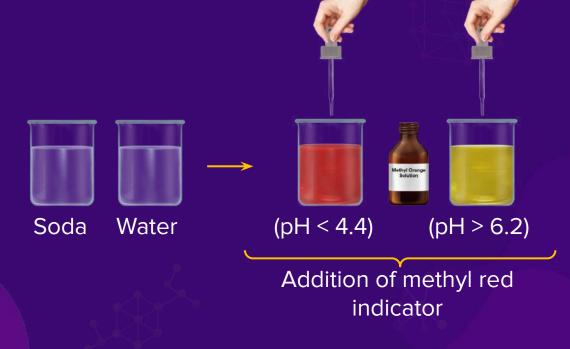




Henry's Law

Example:

Let us take two beakers. The first beaker has soda and the second has water. As we add some drops of methyl red indicator in both the beakers, the first beaker (that has soda) has a red colour (pH < 4.4) and the second beaker has a yellow colour (pH > 6.2).



Henry's Law

Henry's Law

Now, some coloured soda solution is taken in a syringe and its nozzle is closed. If we pull the syringe up, then the colour of the solution changes from red to yellow. This means that the amount of CO_2 dissolved in the soda water decreases. However, when we press the syringe again, the colour of the solution changes back to red. This means that the amount of CO_2 dissolved in the solution changes back to red. This means that the amount of CO_2 dissolved in the solution changes back to red. This means that the amount of CO_2 dissolved in the solution changes back to red. This means that the amount of CO_2 dissolved in the solution changes back to red. This means that the amount of CO_2 dissolved in the solution changes back to red.



Characteristics of Henry's Law Constant

d

е

K_H has same unit as that of **pressure: torr or bar**

а

h

Different gases have **different K**_H for the **same solvent**.

> K_H value of gas is **different** in **different solvents.**

K_H value **increases** with increase in **temperature**.

Higher the value of K_H of a gas, **lower** will be its **solubility**.

Since,

=



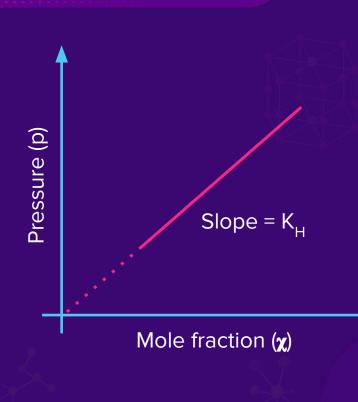
Graphical Analysis (Henry's Isotherm)

The Henry's law expression is given as follows:

 $\mathbf{p} = \mathbf{K}_{\mathbf{H}} \times \boldsymbol{\chi}$

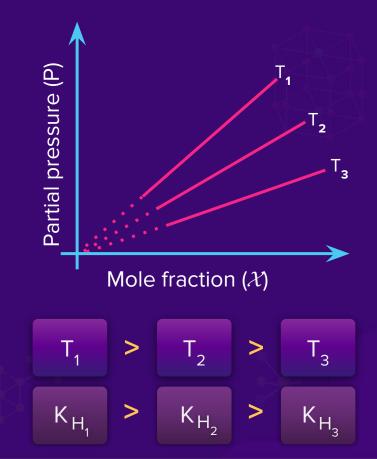
By comparing it with the straight line equation; (y = mx + c), we get, Intercept (c) = 0 Slope (m) = K_H

Plot of P vs χ is a straight line passing through the origin with **slope equal to K_H**.



Graphical Analysis (Henry's Isotherm)

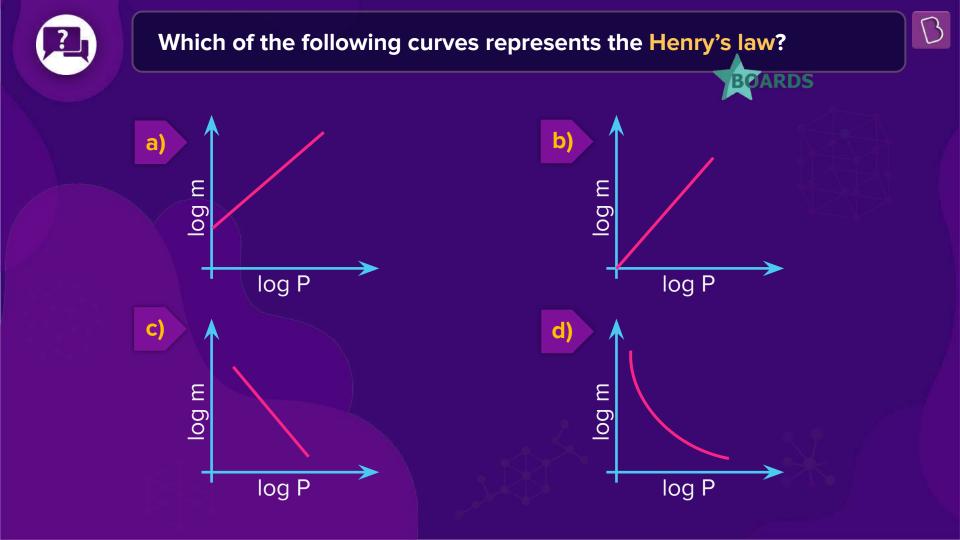
- Let us assume that $T_1 > T_2 > T_3$, temperature T_1 has the highest slope, and T_3 has the lowest. Thus, for the fixed value of the partial pressure, as the temperature increases, the slope of the graph also increases.
- However, to maintain the fixed value of the partial pressure of any gas, the mole fraction of the gas in the solution decreases. This indicates that the solubility of the gas also decreases as the temperature increases. This occurs only in case of exothermic reactions.



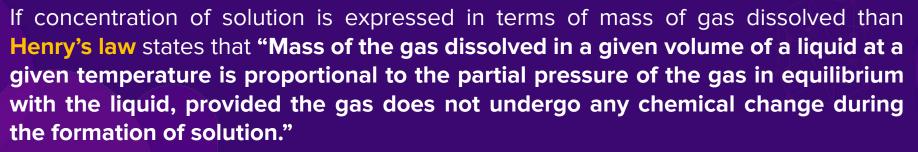
Graphical Analysis (Henry's Isotherm)

If a mixture of gases is brought in contact with a solvent, each constituent gas dissolves in **proportion to its partial pressure**.

Henry's law applies to each gas **independent** of the pressure of other gas.



Solution



 $m = K_{H} P$ Taking log on both sides; log m = log (K_{H} P) log m = log K_{H} + log P
By comparing it with the straight line equation; (y = mx + c), we get, Intercept (c) = log K_{H}

Hence, option (a) is the correct answer.

Applications of Henry's Law

To increase the solubility of CO₂ in soft drinks and soda water, the bottle is sealed under high pressure. Therefore, when the bottle is opened, the pressure decreases, so the solubility of CO₂ also decreases. As a result, the CO₂ escapes from the bottle.



Bottle is sealed under high pressure

Fizzes as CO₂ comes out

Variation of solubility of gas with the pressure

Application of Henry's Law

- recourse of everyone is loss there that at the everyond
- At high altitudes, the partial pressure of oxygen is less than that at the ground level because the population density of the oxygen particles is less at the higher altitudes as compared to that of on the ground level. At heights low blood oxygen level causes anoxia.

Applications of Henry's Law

• Scuba diving tanks are diluted with helium.

Scuba divers must cope with **high concentration** of dissolved gases while, breathing air at high pressure under water.

Increased pressure, increases solubility of atmosphere gases in the blood which are released when the diver comes towards the surface; as the pressure decreases and results in **formation of nitrogen bubbles** in blood. The bubble blocks the capillaries and creates a medical condition known as bends that are painful and dangerous to life.

To avoid bends as well as toxic effects of high concentration of nitrogen in blood, tanks used by scuba divers are filled with air diluted with helium.

Limitations of Henry's Law

Henry's law is valid only under the following conditions:

4

Pressure of the gas is not too high.

2 Temperature is not too low.

The gas should **not undergo** any **chemical reaction** with the solvent.

The gas should **not undergo dissociation** in solution. 8×10^{-x} moles of gas A is dissolved in 36 *mL* of water when pressure of gaseous mixture above water is 4 *atm*. Mole percentage of gas A in mixture is 25. Henry's constant for gas A in water is 2.5×10^3 *atm*. Find x.

ARDS

Solution

$$n_A = 8 \times 10^{-X}$$
, $V_w = 36 mL$, $P = 4 atm$, $\chi(A) = 0.25$
 $p(A) = \chi(A) \times P = 0.25 \times 4 = 1 atm$

According to Henry's Law:

 $p(A) = K_{H} \times \chi(A)$ $K_{H} = 2.5 \times 10^{3} atm$ $p(A) = K_{H} \times \chi(A)$ $1 = 2.5 \times 10^{3} \times \frac{n_{A}}{n_{A} + n_{H_{2}}0}$



Mass of water = V_{w} × density of water $= 36 \ mL \times 1 \ g \ mL^{-1} = 36 \ g$ $n_{H_2O} = \frac{36}{18} = 2 \text{ moles}$ $1 = 2.5 \times 10^3 \times \frac{n_A}{n_A + n_{H_2}O_1}$ $1 = 2.5 \times 10^3 \times \frac{n_A}{n_A + 2} \Rightarrow \frac{n_A}{n_A + 2} = 4 \times 10^{-4}$ $\frac{n_A}{2} = 4 \times 10^{-4}, n_A = 8 \times 10^{-4} = 10^{-4}$





Evaporation and Condensation

- Some of the more **energetic particles** on the **surface** of the liquid move fast enough to **escape** from the attractive forces holding the liquid together.
- As the gaseous particles bounce around, some of them will hit the surface of the liquid again, and be trapped there.
- At this stage, partial pressure of vapours is called vapour pressure of the liquid.

There will rapidly be an **equilibrium set up** in which, the number of particles leaving the surface is **exactly balanced** by the number rejoining it.

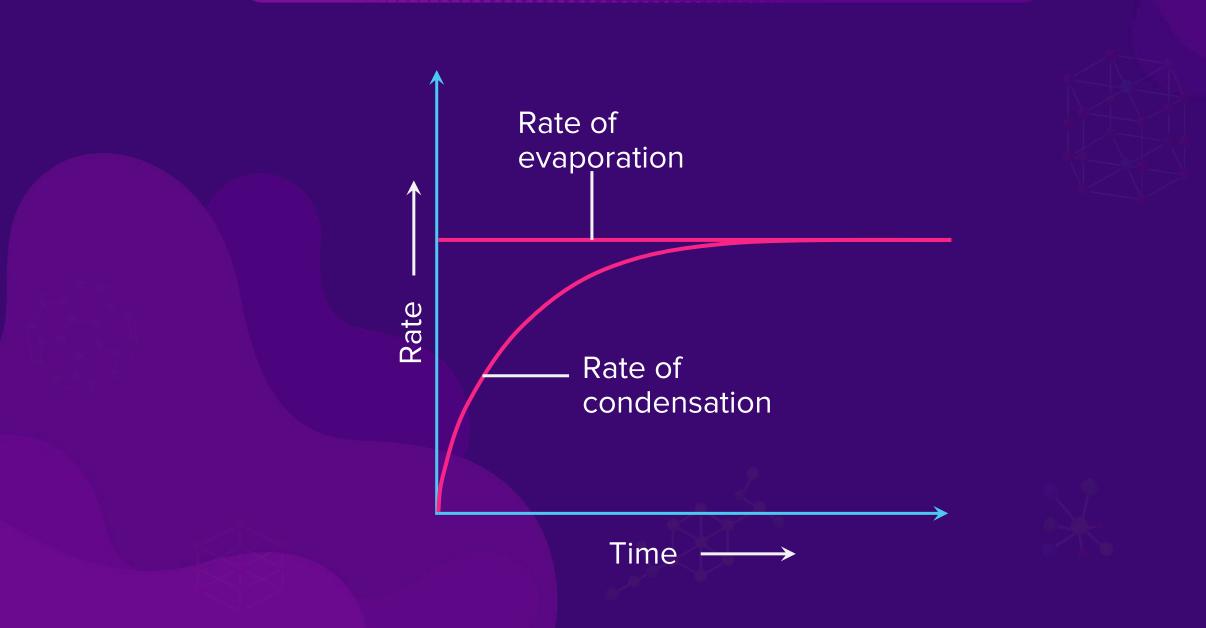
At equilibrium

=

Rate of evaporation

Rate of condensation

Evaporation and Condensation



Vapour Pressure (V.P.)

Pressure exerted by the vapours over the liquid surface **at equilibrium**.

Partial pressure of vapours which are in equilibrium with their pure solid or liquid is called vapour pressure of that substance.

$H_2O(I) \rightleftharpoons H_2O(g)$



V.P.

К_Р =



The solubility of N₂(g) in water exposed to the atmosphere, when its partial pressure is 593 *mm Hg* is 5.3×10^{-4} *M*. Its solubility at 760 *mm Hg* and at the same temperature is:

(c) 1500 M

(b) 6.8 × 10⁻⁴ M

(d) 2400 M

(a) 4.1 × 10⁻⁴ M

Solution

 $p_1 = 593 \text{ mm of Hg}$, $s_1 = 5.3 \times 10^{-4} \text{ M}$, $p_2 = 760 \text{ mm of Hg}$, $s_2 = ?$

 $p = K_H \times \chi$, for dilute solutions p is directly proportional to $K_H \times M$

$$\frac{p_1}{p_2} = \frac{s_1}{s_2}$$

$$s_2 = \frac{p_2}{p_1} \times s_1 \implies \frac{760}{593} \times 5.3 \times 10^{-4} = 6.79 \times 10^{-4}$$

Hence, option (b) is the correct answer.

Henry's law constant for O₂ dissolved in water is 4.34×10^4 atm at 25 °C. If the partial pressure of oxygen in air is 0.4 atm. The concentration (M) of dissolved oxygen in water in equilibrium with air at 25 °C is 5 × 10^{-P}. What is the value of P?

(c) 4

(b) 6

Solution

(a) 5

 $K_{H_{(O_2)}} = 4.34 \times 10^4 atm$ $p_{(O_2)} = 0.4 atm$

According to Henry's law:

$$p_{(O_2)} = K_{H_{(O_2)}} \times \chi_{(O_2)}$$

0.4 $atm = 4.34 \times 10^4 atm \times \chi_{(O_2)}$ $\Rightarrow \chi_{(O_2)} = 0.092 \times 10^{-4}$ Consider total one moles of solution,

(d) 8



ARDS



$$n_{O_2^+} n_{H_2O}^- = 1$$

 $n_{H_2O}^- = 1 - 0.092 \times 10^{-4} \approx 1 \text{ mol}$

Volume of solution will be almost equal to volume of 1 mole of water i.e., 18 *mL*.

Molarity of $O_2 =$ Moles of O_2 Moles of solution in L Molarity of $O_2 =$ Molarity of $O_2 =$ Molarity of $O_2 =$ Moles of O_2 $\frac{0.092 \times 10^{-4}}{18 \times 10^{-3}}$ Molarity of $O_2 =$ 5.11×10^{-4}

Hence, value of P = 4.

Hence, options (c) is the correct answer.



According to Henry's law, the solubility of a gas in a given volume of liquid increases with increase in:

- (a) Temperature
- (b) Pressure
- (c) Both (a) and (b)
- (d) None of the above

Solution

Henry's law states that, "The solubility of a gas in a liquid at a given temperature is directly proportional to its partial pressure, at which, it is dissolved."

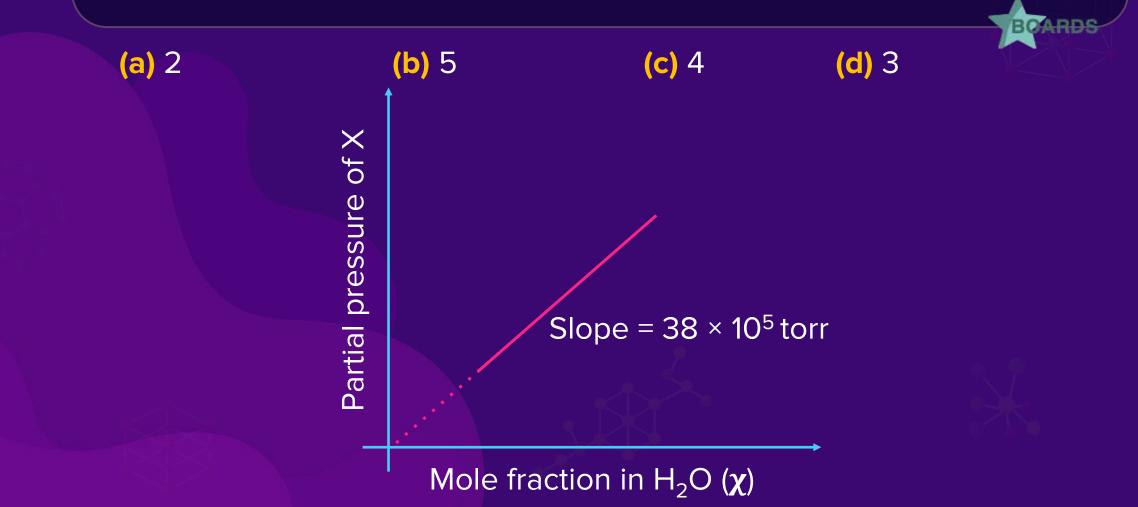
Hence, option (b) is the correct answer.





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A gas 'X' is present with saturated water vapour over water liquid at a total pressure of 1.5 *atm*. Vapour pressure of H_2O at the same temperature is 0.5 *atm*. The solubility of gas 'X' in terms of moles in 10 moles $H_2O(I)$ is given by P × 10⁻³. What is the value of P?





Solution

 $p^{o}_{(X)} + p^{o}_{H_2O} = 1.5 atm$ $p^{o}_{(X)} + 0.5 atm = 1.5 atm$ $p^{o}_{(X)} = 1.5 - 0.5 = 1 atm = 760 torr$

According to Henry's Law:

 $p^{o}_{(X)} = K_{H} \times \chi_{(X)}$ $K_{H} = 38 \times 10^{5}$ torr (from graph)

$$\mathbf{\chi}_{(X)} = \frac{760}{38 \times 10^5} = 2 \times 10^{-4}$$

Hence, option (a) is the correct answer.

1 *mol* of solution has 2×10^{-4} *mol* of X X is almost negligible hence 1 *mol* of water is only present. That means 1 *mol* of water has 2×10^{-4} *mol* of X 10 moles of water will have 2×10^{-3} *mol* of X

Hence, the value of P is 2.





The solubility of gases in liquids:



- (b) Decreases with increase in pressure and temperature
- (c) Increases with increase in pressure and decrease in increase in temperature
- (d) Decreases with increase in pressure and increase in temperature

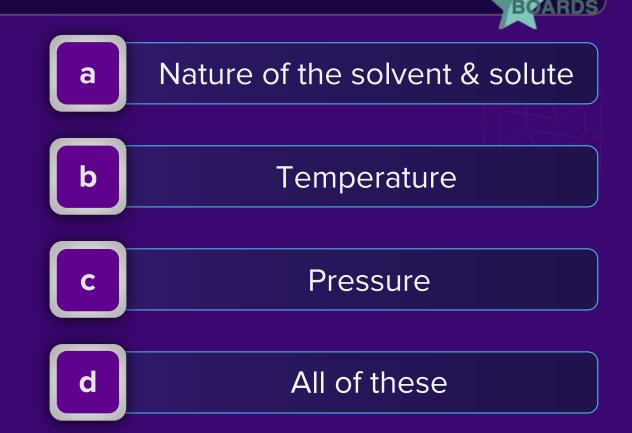
Solution

According to Henry's law, the solubility of gases in liquids increases with increase in pressure while solubility decreases with increase in temperature.

Hence, option (c) is the correct answer.



Solubility of one substance into another depends on:



Solution

Solubility of one substance into another depends on the nature of the solvent and solute, temperature and pressure.

Hence, option (d) is the correct answer.



Which one of the following statements regarding Henry's law is not correct?



(a) Different gases have different K_H (Henry's law constant) values at the same temperature.

(b) The value of K_{H} increases with increase of temperature and K_{H} is function of the nature of the gas.

(c) The partial pressure of the gas in vapour phase is proportional to the mole fraction of the gas in the solution.

(d) Higher the value of K_{H} at a given pressure, higher is the solubility of the gas in the liquids.

Solution

(a) Different gases have different K_{H} (Henry's law constant) values at the same temperature. This is true statement.

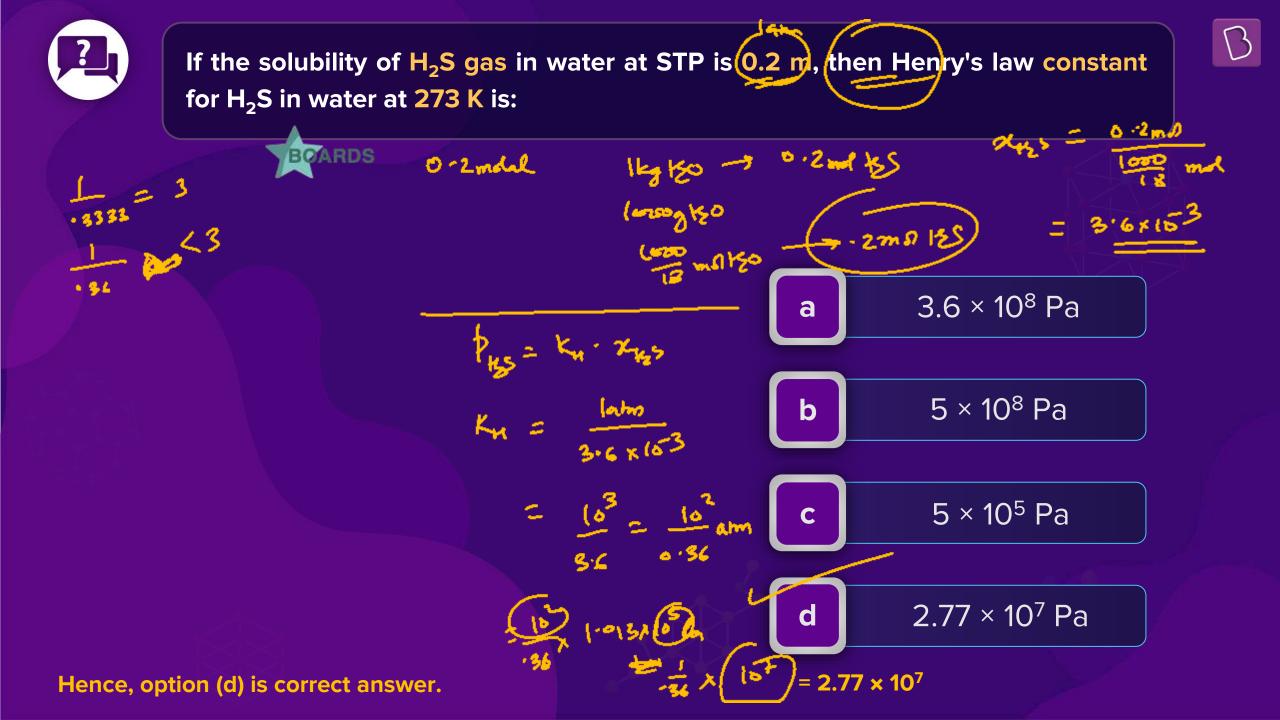


(b) The value of K_{H} increases with increase of temperature and K_{H} is a function of the nature of the gas. This is also a true statement as temperature increases, solubility decreases so, K_{H} increases.

(c) The partial pressure of the gas in the vapour phase is proportional to the mole fraction of the gas in the solution. This is also true as this is Henry's law.

(d) Higher the value of K_{H} at a given pressure, higher is the solubility of the gas in the liquids. This statement is not true as at higher values of K_{H} the solubility will be less.

Hence, option (d) is correct answer.



Features of Vapour Pressure (V.P.)



Amount of liquid taken

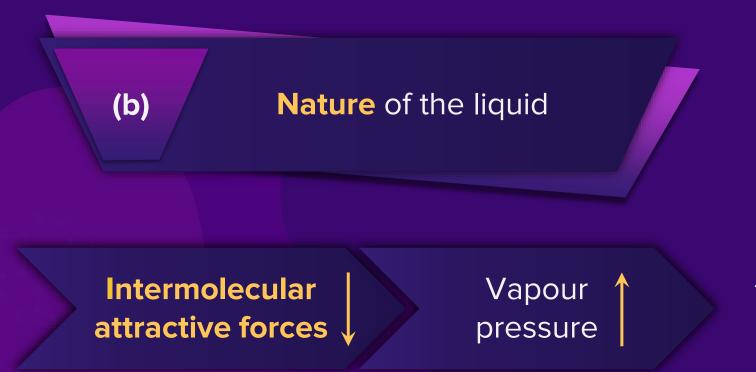
Surface area of the liquid

2

3

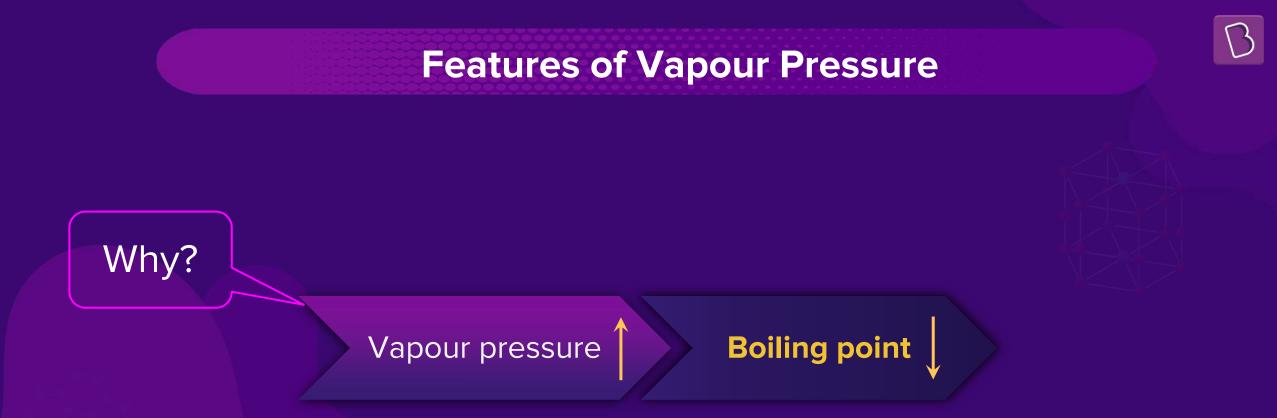
Volume or shape of the container

Features of Vapour Pressure (V.P.)



Loosely held molecules escape more easily into the vapour phase.

Example : In O_2 gas, the bond is nonpolar which means the attraction is very low and in H_2O , the bond is polar and there will be more attraction between H and O in H_2O . So at same temperature the vapour pressure of O_2 is high because of less attractive force.

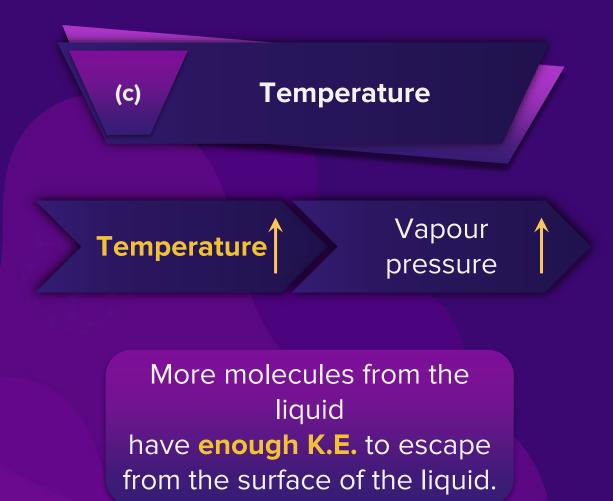


As vapour pressure increases, the tendency to go in vapour state increases and hence boiling point decreases.

Boiling point

- Temperature at which the vapour pressure of a liquid is equal to the external pressure.
- On increasing the temperature, liquid starts boiling and there comes a point where on heating, temperature remains constant and heat absorbed, which is called latent heat of vapourisation. After crossing that point liquid converts into vapour. The maximum temperature of liquid is boiling point.
- Boiling point is dependent on pressure.
- On increasing the external pressure, boiling point increases.
- In a pressure cooker the pressure increases and hence boiling point of water increases. For instance, now the boiling point of water is around 110 °C. Now rice has the opportunity to stay at that high temperature and hence they will cook faster as compared to the open container.
- Temperature at which the vapour pressure of a liquid is equal to the external pressure; P_(liq) = P_{ext}, T = Boiling point
- At normal boiling point, the vapour pressure of the pure liquid = 1 atm

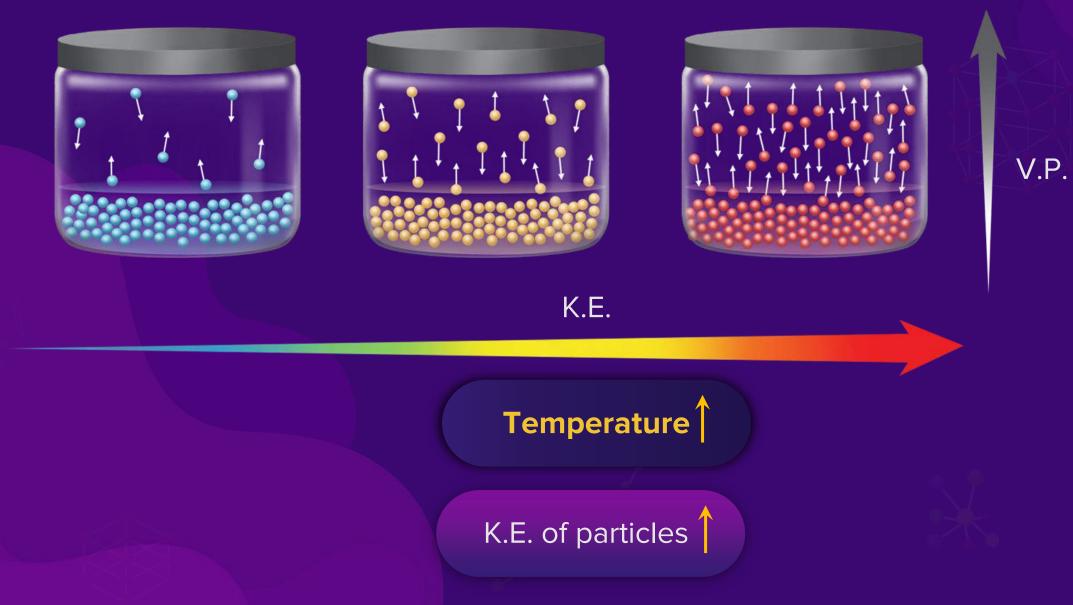
Features of Vapour Pressure

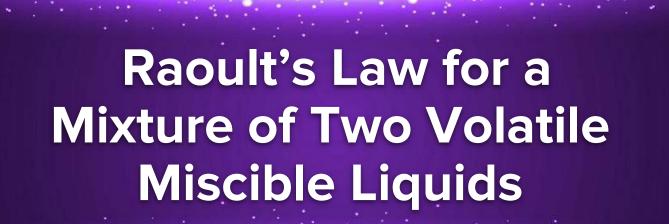


 $H_2O(I) \Rightarrow H_2O(g)$ $\Delta H > 0$

According to Le Chatelier's principle, increasing the temperature of a system in a dynamic equilibrium, favours the endothermic change.

Features of Vapour Pressure





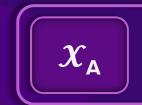


In the solution of volatile liquids, the partial vapour pressure of each component is directly proportional to its **mole fraction**.





Partial vapour pressure of component 'A'



Mole fraction of component 'A' in solution



Vapour pressure of pure component 'A' at a given temperature





In the solution of volatile liquids, the partial vapour pressure of each component is directly proportional to its **mole fraction**.



Partial vapour pressure of component 'A'



Mole fraction of component 'A' in solution



Vapour pressure of pure component 'A' at a given temperature

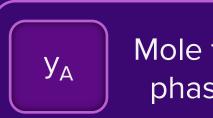
Raoult's Law For Binary Solutions of A & B



$$P_T = P_A + P_B$$

$$\mathsf{P}_{\mathsf{T}} = \boldsymbol{x}_{\mathsf{A}}\mathsf{P}_{\mathsf{A}}^{\mathsf{O}} + \boldsymbol{x}_{\mathsf{B}}\mathsf{P}_{\mathsf{B}}^{\mathsf{O}}$$

P_T in Terms of Composition of Vapour Phase

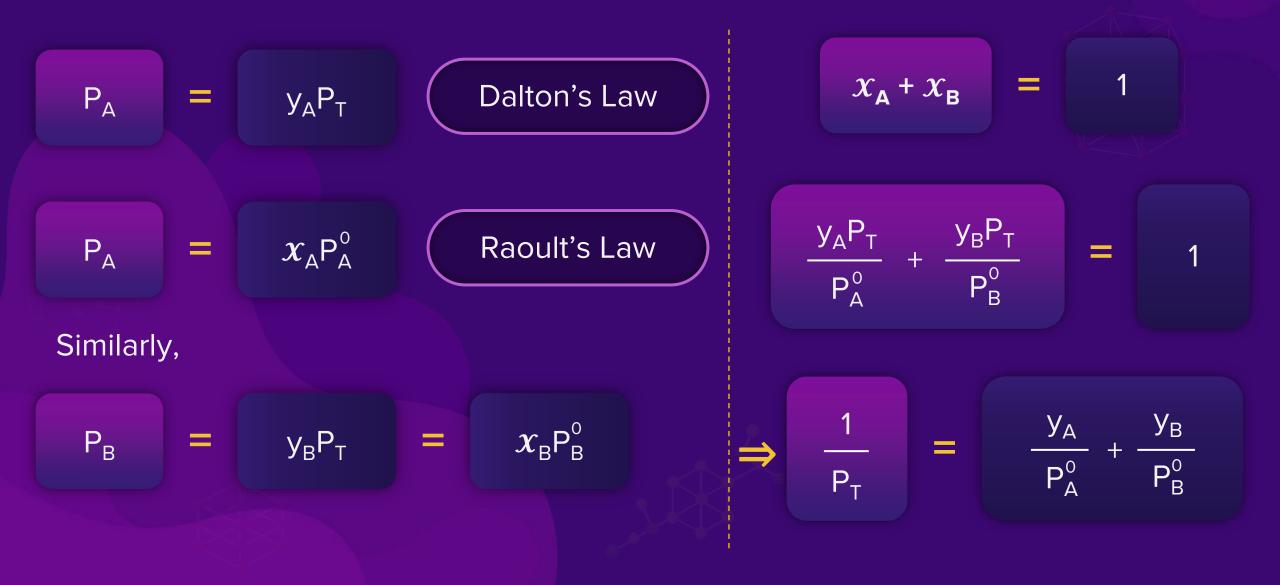


Mole fraction of A in vapour phase above the solution



Mole fraction of B in vapour phase above the solution

P_T in Terms of Composition of Vapour Phase





P_T in Terms of Composition of Vapour Phase

Solutions which obey **Raoult's law** over the entire range of concentration are known as **ideal solutions.**

$$x_{A} + x_{B} = 1$$

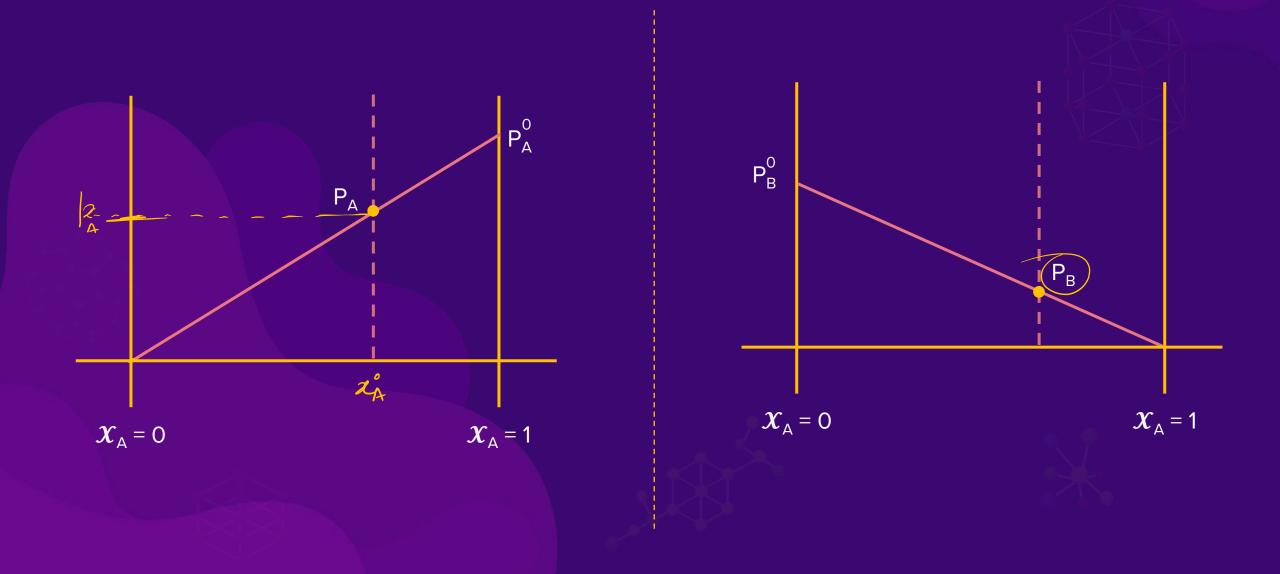
Relation between **total pressure vs mole fraction** in liquid phase.

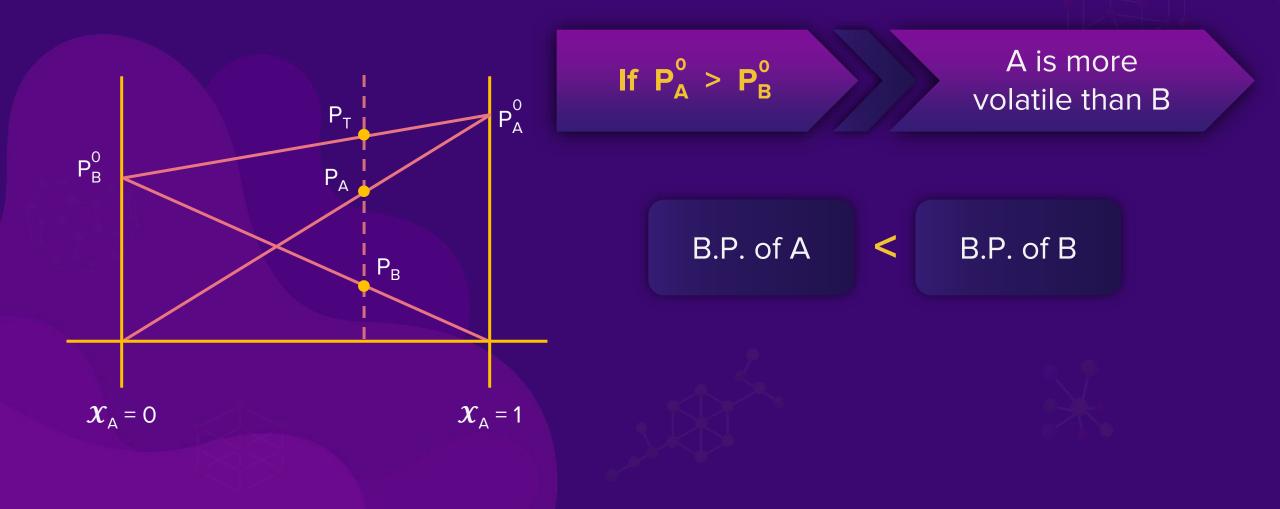
P₁

 $x_{A}P_{A}^{0} + x_{B}P_{B}^{0}$

(
$$\mathsf{P}_\mathsf{A}^\mathsf{O}$$
 - $\mathsf{P}_\mathsf{B}^\mathsf{O}$) $\boldsymbol{\mathcal{X}}_\mathsf{A}$ + $\mathsf{P}_\mathsf{B}^\mathsf{O}$

This represents equation of a straight line of P_T vs X_A





Did You Know?

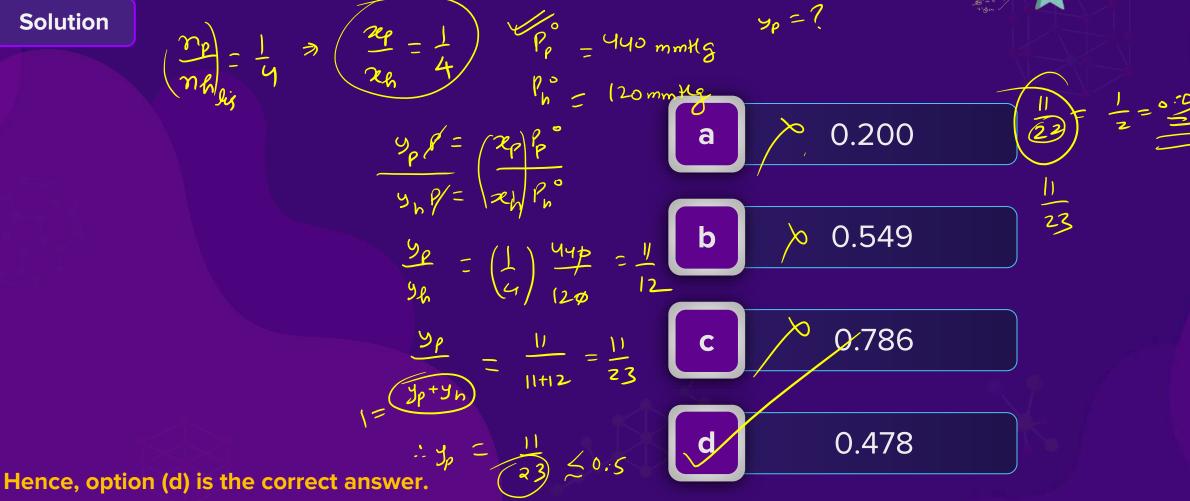
Compositions of the liquid and vapour that are in **mutual equilibrium** are **the same**.

The vapour will be **richer** in the **more volatile** component, if the mole fraction of components in liquid phase is comparable.



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

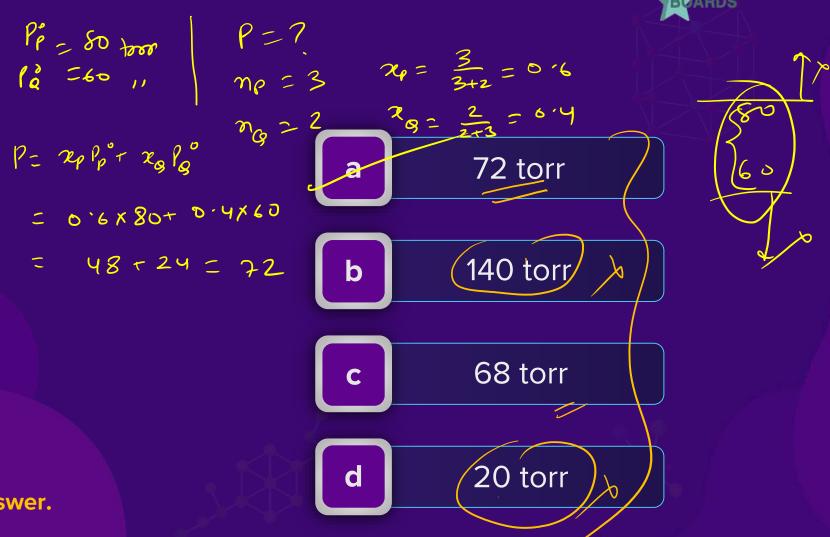
Solution





The vapour pressure of two liquids P and Q are 80 and 60 *torr*, respectively. The total vapour pressure of solution obtained by mixing 3 moles of P and 2 moles of Q would be :





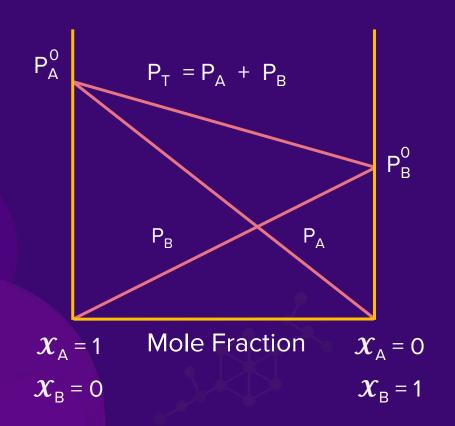
Hence, option (a) is the correct answer.



Solutions that obey Raoult's law over the entire range of concentration If the forces of attraction between A—A, B—B is similar to A—B, then A and B will form ideal solution.

(i)

Raoult's law is **obeyed**.





(ii) $\Delta_{mix}H = 0$, i.e., there should not be an enthalpy change when components of ideal solutions are mixed.

> Δ_{mix}V = 0, (1L + 1L = 2L) i.e., there should not be a change in volume on mixing.

(iii)

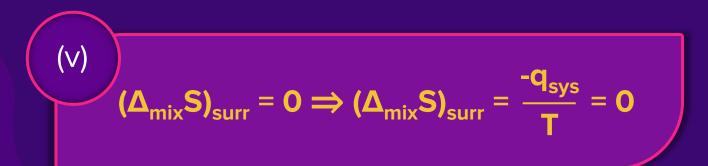


(iv)
$$\Delta T_{mix} = 0$$

 $\Delta V_{mix} = 0$
 $(\Delta_{mix}S)_{sys} > 0 \Rightarrow$ randomness
increases on mixing.



Probability of picking red ball is less as it has more randomness



(Δ_{mix}S)_{univ} > 0 ⇒ Mixing is a spontaneous process

(vi)





n-Hexane and n-Heptane

Ethyl bromide and Ethyl iodide

Benzene and Toluene

Chlorobenzene and Bromobenzene



Non-Ideal Solution



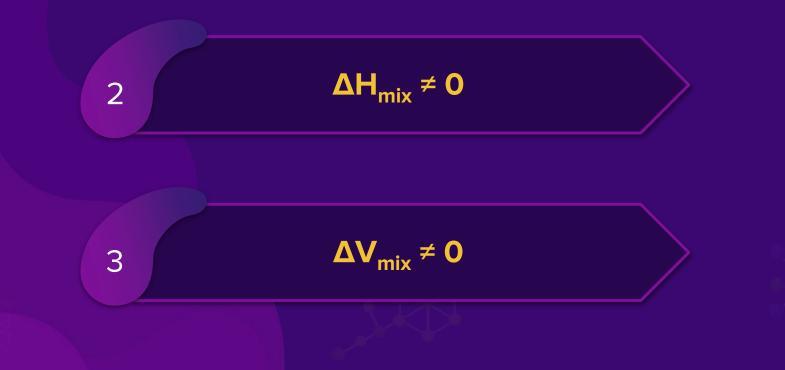


Non-Ideal Solution

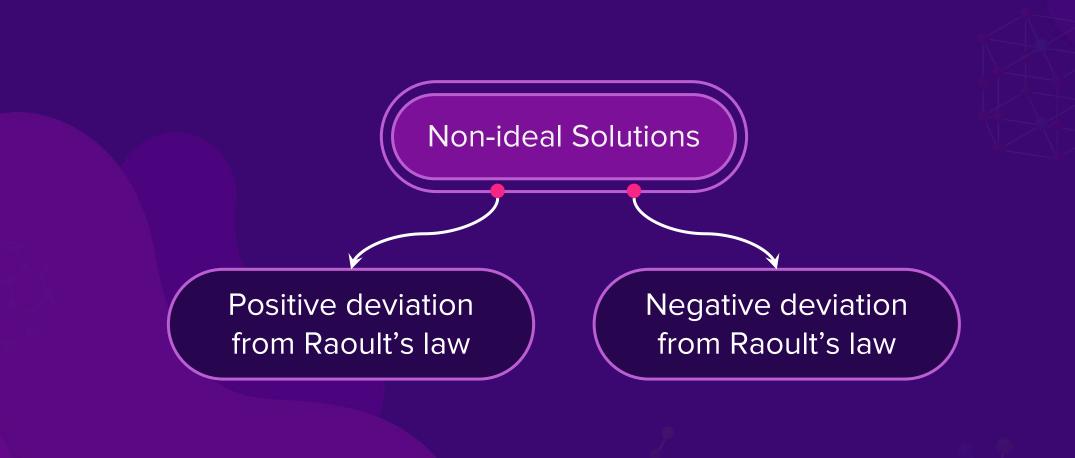
If the forces of attraction between A—A, B—B is different from A—B, then A and B will form non-ideal solution.



1



Non-Ideal Solution

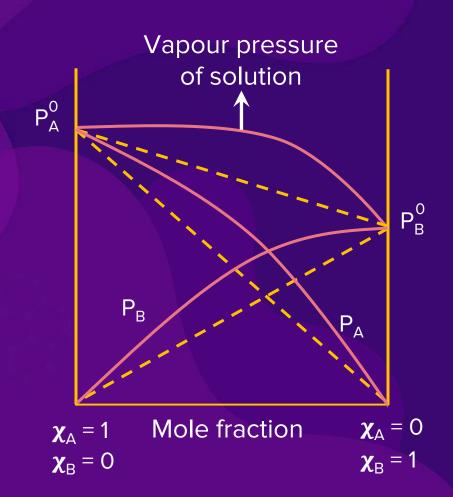


If the forces of attraction between **A**—**A**, **B**—**B** is stronger than A—**B**

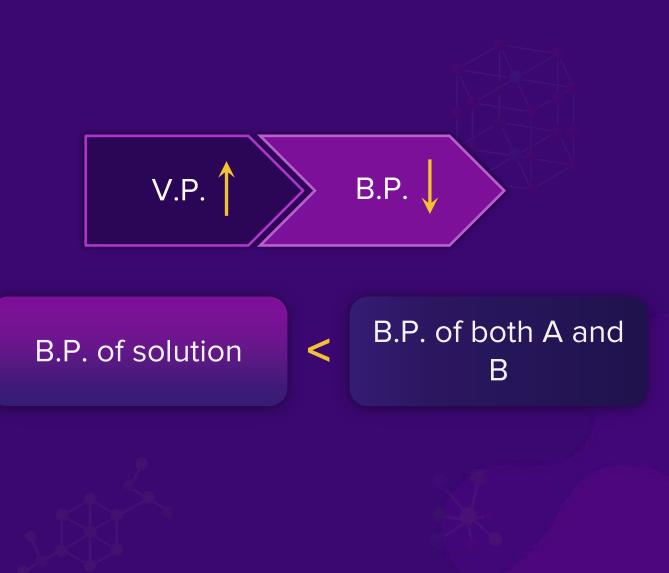
Partial pressure of each component A and B is **higher** than that calculated from Raoult's law.

Hence, the **total pressure** over the solution is **also higher** than the solutions, if were ideal.

Positive Deviation



Dashed lines represent vapour pressures and total pressure corresponding to **ideal solution.**



Characteristics of Positive Deviation

B

Raoult's law is **not obeyed**.

$$\Delta V_{mix} > 0 (1L + 1L > 2L)$$

2

Intermolecular forces between molecules of A and B are weaker than those in the pure liquids.

When the liquids are mixed, **less heat is evolved** when the new attractions are set up than was absorbed to break the original ones.

Characteristics of Positive Deviation



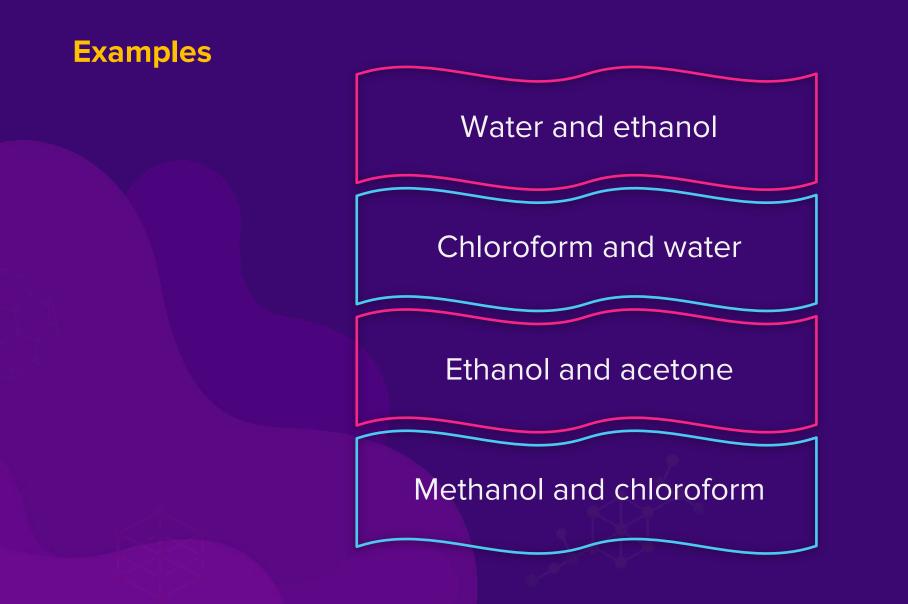
5
$$(\Delta_{mix}S)_{surr} = 0 \Rightarrow (\Delta_{mix}S)_{surr} = \frac{-q_{sys}}{T} < 0$$

(Δ_{mix}S)_{univ} > 0 ⇒ Mixing is a spontaneous process

6

4

Positive Deviation



X

Negative Deviation

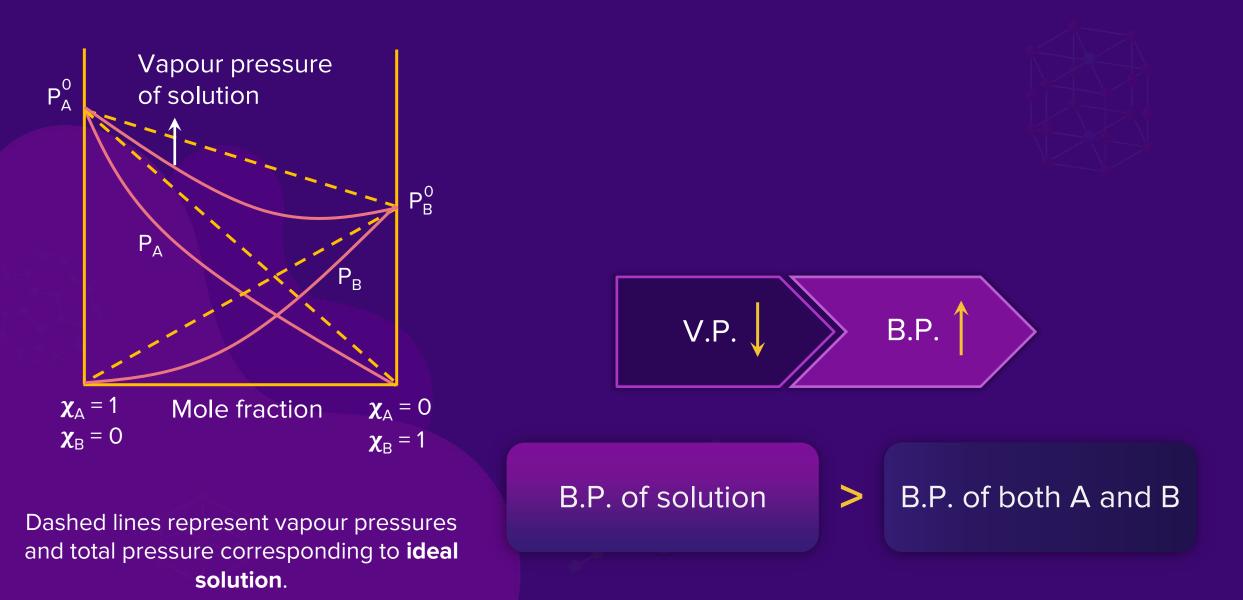
If the forces of attraction between **A**—**A**, **B**—**B** are weaker than A—**B**

Partial pressure of each component A and B is lower than that calculated from Raoult's law.

Hence, the **total pressure** over the solution is also **lower** than the solutions, if were ideal.

Negative Deviation





Characteristics of Negatie Deviation

3

Raoult's law is **not obeyed**.

$$\Delta V_{mix} < 0 (1L + 1L < 2L)$$

2

Intermolecular forces between molecules of A and B are stronger than those in the pure liquids. When the liquids are mixed, **more heat is evolved** when the new attractions are set up than was absorbed to break the original ones.

 $\Delta H_{mix} < 0$

Characteristics of Negatie Deviation





5
$$(\Delta_{mix}S)_{surr} = 0 \Rightarrow (\Delta_{mix}S)_{surr} = \frac{-q_{sys}}{T} > 0$$

(Δ_{mix}S)_{univ} > 0 ⇒ Mixing is a spontaneous process

6

4

Examples of Negative deviation

Chloroform and acetone

Chloroform and methyl acetate

H₂O and HCI

H₂O and HNO₃

Acetic acid and pyridine

Phenol and aniline



Comparing Ideal & Non-Ideal Solutions

Ideal solutions	Non-ideal solutions	
	Positive deviation	Negative deviation
$P_{T} = \boldsymbol{\chi}_{A} P_{A}^{O} + \boldsymbol{\chi}_{B} P_{B}^{O}$	$P_T > \chi_A P_A^0 + \chi_B P_B^0$	$P_{T} < \chi_{A}P_{A}^{0} + \chi_{B}P_{B}^{0}$
A-A & B-B molecular interaction are similar as A-B	A-A & B-B molecular interaction are stronger than A-B	A-A & B-B molecular interaction are weaker than A-B
$\Delta_{mix}H = 0$	Δ_{mix} H > 0	∆ _{mix} H < 0
$\Delta_{mix} V = 0$	$\Delta_{mix} V > 0$	$\Delta_{mix} V < 0$

Comparing Ideal & Non-Ideal Solutions

Ideal solutions	Non-ideal solutions	
	Positive deviation	Negative deviation
(Δ _{mix} S) _{sys} > 0	($\Delta_{mix}S)_{sys} > 0$	(Δ _{mix} S) _{sys} > 0
$(\Delta_{mix}S)_{surr} = 0$	(∆ _{mix} S) _{surr} < 0	(A _{mix} S) _{surr} > 0
(∆ _{mix} S) _{univ} > 0	(Δ _{mix} S) _{univ} > 0	(A _{mix} S) _{univ} > 0
(∆ _{mix} G) _{sys} < 0	(∆ _{mix} G) _{sys} < 0	(Δ _{mix} G) _{sys} < 0



The vapour pressure of the solution of two liquids A (P[°] = 80 *mm Hg*) and B (P[°] = 120 *mm Hg*) is found to be 100 mm Hg when $\chi_A = 0.4$. The result shows that:

RDS

- (a) Solution exhibits ideal behavior
- **(b)** Solution shows positive deviations
- (c) Solution shows negative deviations
- (d) Solution will show positive deviations for lower concentration and negative deviations for higher concentrations

Solution

Vapor pressure of solution as per Raoult's law should have been 104 *mm Hg* for it to become an ideal solution but it is 100 *mm Hg* as given in the question. Thus, solution shows negative deviation **Hence, option (c) is the correct answer.**



 P_A and P_B are the vapour pressures of pure liquid components, A and B, respectively of an ideal binary solution. If x_A represents the mole fraction of component A, the total pressure of the solution will be:

BOARDS

(a)
$$P_A + \chi_A (P_B - P_A)$$

(b) $P_A + \chi_A (P_A - P_B)$
(c) $P_B + \chi_A (P_B - P_A)$
(d) $P_B + \chi_A (P_A - P_B)$

Solution

$$P_{T} = \chi_{A}P_{A} + \chi_{B}P_{B}$$

$$\chi_{A} + \chi_{B} = 1$$

$$\Rightarrow \chi_{B} = 1 - \chi_{A}$$

$$P_{T} = \chi_{A}P_{A} + (1 - \chi_{A})P_{B}$$

$$P_{T} = \chi_{A}P_{A} + P_{B} - \chi_{A}P_{B}$$

$$\Rightarrow P_{T} = P_{B} + \chi_{A}(P_{A} - P_{B})$$

Hence, option (d) is the correct answer.



The vapour pressure of water depends upon:

ARDS

(a) Surface area of container

(b) Volume of container

(c) Temperature

(d) All of the above

Solution

The vapour pressure of water depends upon temperature. Hence, option (c) is the correct answer.



The mixture which shows **positive deviation** from Raoult's law is:

(a) Ethanol + Acetone

(b) Benzene + Toluene

(c) Acetone + Chloroform

(d) Chloroethane + Bromoethane

Solution

Benzene + Toluene is ideal solution.Acetone + Chloroform shows negative deviation.

Chloroethane + Bromoethane is ideal solution.

Hence, option (a) is the correct answer.





For an ideal solution, the correct option is:

BOARDS

(a) $\Delta_{mix} G = 0$ at constant T and P (b) $\Delta_{mix} S = 0$ at constant T and P (c) $\Delta_{mix} V \neq 0$ at constant T and P (d) $\Delta_{mix} H = 0$ at constant T and P

Solution

For ideal solution :

 $\Delta_{mix}G < 0 \text{ at constant T and P}$ $\Delta_{mix}S > 0 \text{ at constant T and P}$ $\Delta_{mix}V = 0 \text{ at constant T and P}$ $\Delta_{mix}H = 0 \text{ at constant T and P}$

Hence, option (d) is the correct answer.



Which of the following statements is **correct** regarding a solution of two components A and B exhibiting positive deviation from ideal behaviour?

(a) Intermolecular attractive forces between A-A and B-B are stronger than those between A-B

DARDS

(b) Δ_{mix} H = 0 at constant T and P

(c) $\Delta_{mix} V = 0$ at constant T and P

(d) Intermolecular attractive forces between A-A and B-B are equal to those between A-B

Solution

For a solution of two components A and B exhibiting positive deviation from ideal behaviour intermolecular attractive forces between A-A and B-B are stronger than those between A-B. Hence, option (a) is the correct answer.



Which condition is not satisfied by an ideal solution?

(a) $\Delta_{mix} V = 0$ (b) $\Delta_{mix} S = 0$ (c) Obey the Raoult's law (d) $\Delta_{mix} H = 0$

Solution

For ideal solution :

 $\Delta_{mix}G < 0 \text{ at constant T and P}$ $\Delta_{mix}S > 0 \text{ at constant T and P}$ $\Delta_{mix}V = 0 \text{ at constant T and P}$ $\Delta_{mix}H = 0 \text{ at constant T and P}$

Hence, option (b) is the correct answer.





ARDS

Azeotropic Mixtures

Very large deviations from ideality lead to a special class of mixtures known as azeotropes, azeotropic mixtures, or constant-boiling mixtures.

Azeotropic Mixtures

B

- Only non ideal solutions form azeotropes. Solutions do not have a constant boiling point.
- Composition of liquid A and vapour A becomes the same. Composition of liquid B and vapour B also becomes the same. So now the composition of liquid won't change even if it evaporates. Hence boiling point of liquid won't change.
- A liquid solution which evaporates without its change in composition is called azeotrope and are non ideal.



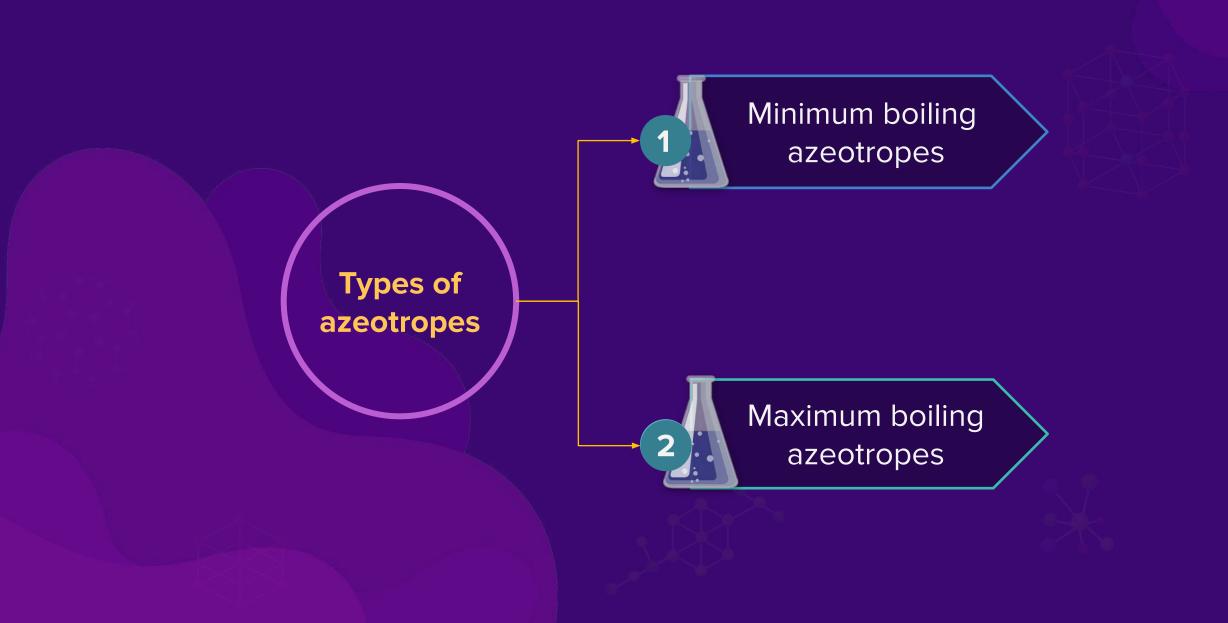
B

Liquid mixtures which boils at a constant temperature and can be distilled **without any change** in the composition

A boiling liquid mixture at the azeotropic composition produces vapours of exactly the same composition as that of the liquid. Composition of liquid mixtures at which distillation cannot separate the two liquids because the condensate has the same composition as that of the azeotropic liquid.









Non-ideal solutions showing large positive deviation from Raoult's law form minimum boiling azeotropes that boil at a temperature lower than the boiling points of its components 'A' and 'B'.

Examples:

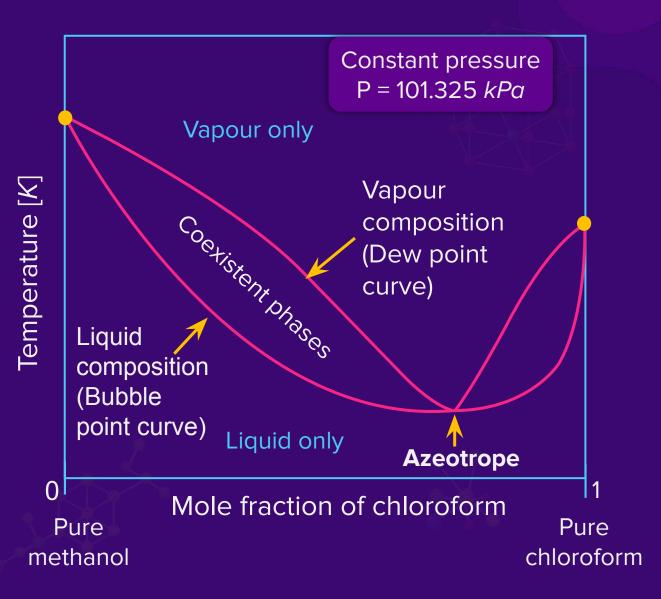
(i) Ethanol - water mixture containing ≈ 95% by volume of ethanol;
(ii) Chloroform - methanol mixture containing 87.4% chloroform and 12.6% methanol by mass

Temperature vs composition graph

The composition of the point where dew point and bubble point curves intersect is azeotropic composition.

At this point the composition of the components of the solution is same in both liquid and vapour phase.

Boiling point of the solution at this composition is lesser than the boiling points of either of the components.

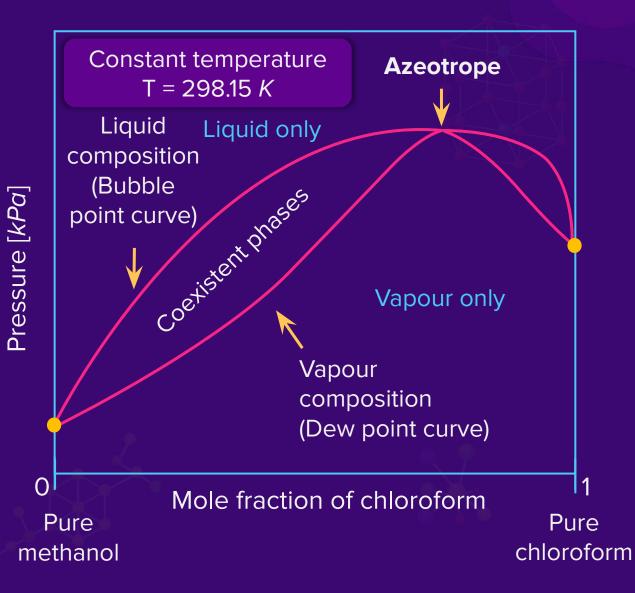


Pressure vs composition graph

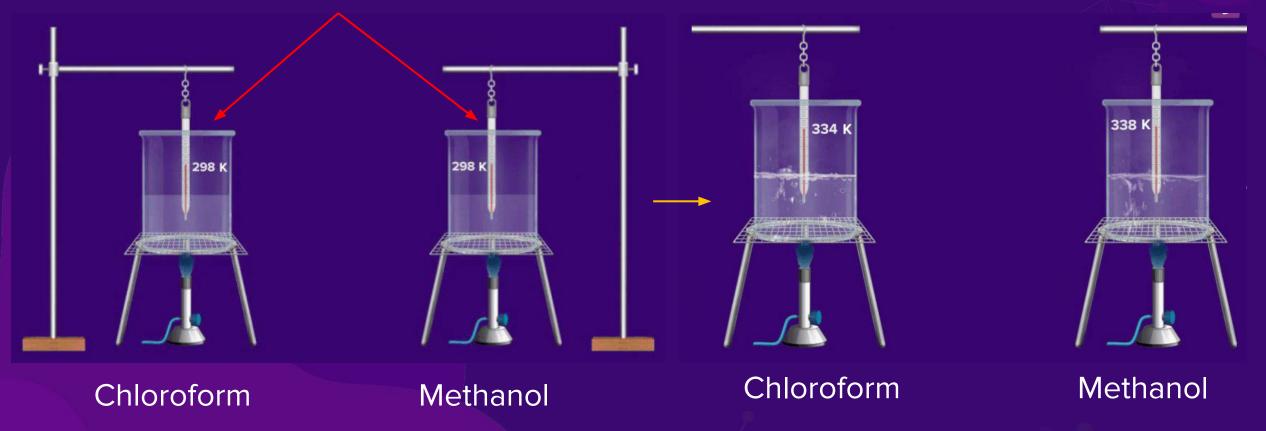
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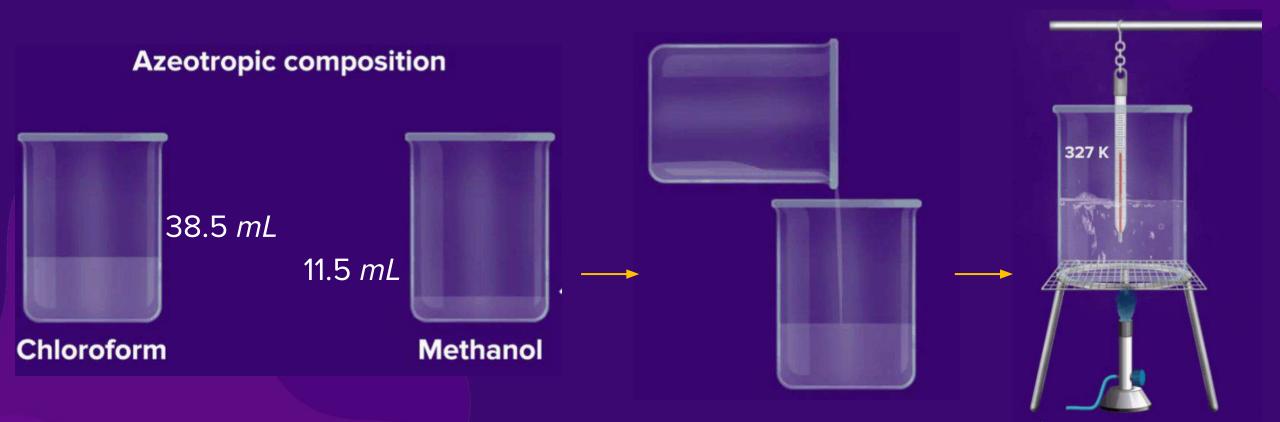
Vapour pressure of the solution at this composition is greater than the vapour pressures of the either of the components.



Room temperature



Both chloroform and methanol is taken at room temperature (298 K) and heated to their respective boiling points. Chloroform (B.P. = 334 K) and methanol (B.P. = 338 K)



Then we mix them in certain composition and then boil the mixture. We will see that this mixture boiled at 327 *K* that is at a lower temperature as compared to their individual boiling point. And this is only possible in **minimum boiling azeotropes.**

B

Maximum Boiling Azeotropes

Non-ideal solutions showing **large negative deviation** from Raoult's law form maximum boiling azeotropes that boil at a temperature **higher than the boiling points** of its individual components.

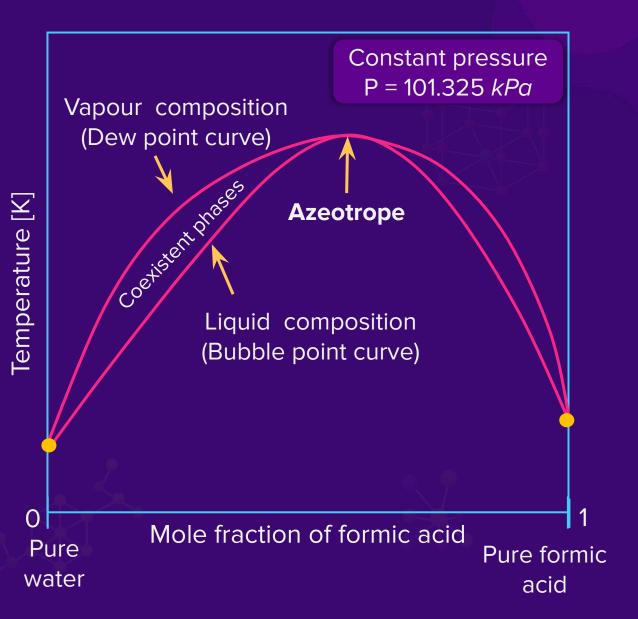
Examples:

(i) A mixture of HNO_3 and H_2O containing $\approx 68\%$ HNO_3 and 32% water by mass (ii) Formic acid - water mixture containing 77.6% formic acid (CH_2O_2) and 22.4% water by mass

Temperature vs composition graph

The composition of the point where dew point and bubble point curves intersect is azeotropic composition.

At this point the composition of the components of the solution is same in both liquid and vapour phase. Boiling point of the solution at this composition is higher than the boiling points of either of the components.



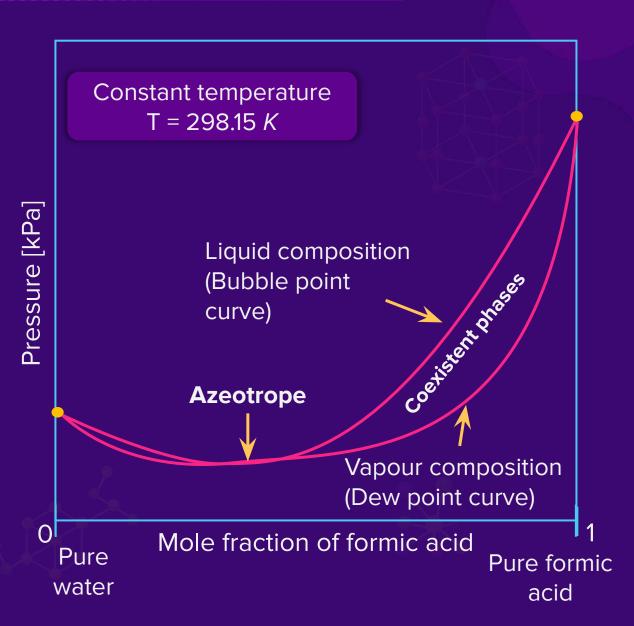
Pressure vs composition graph

The composition of the point where dew point and bubble point curves intersect is azeotropic composition.

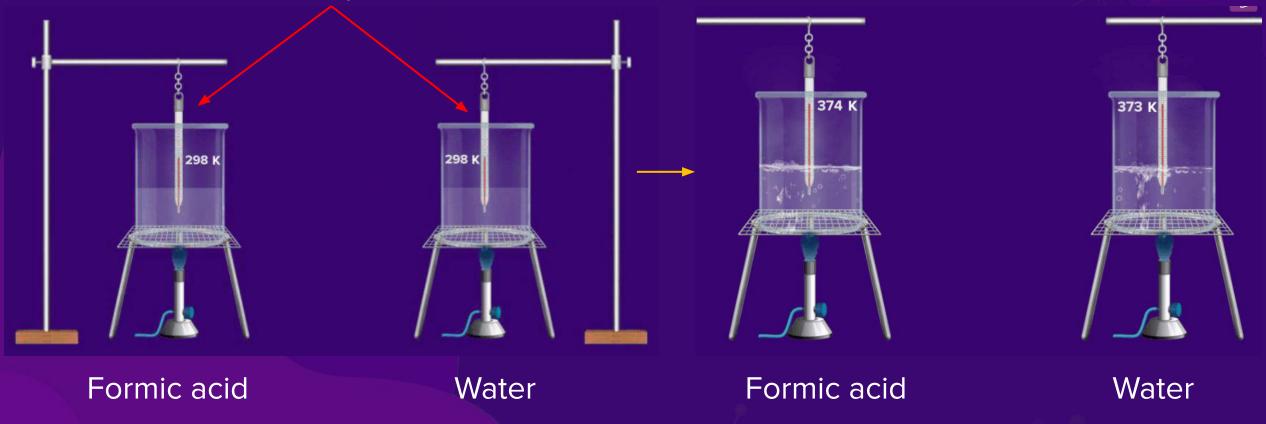
Vapour pressure of the solution at this composition is lesser than the vapour pressures of the either of the components.



An ideal solution does not boil at a constant temperature, whereas azeotrope does.

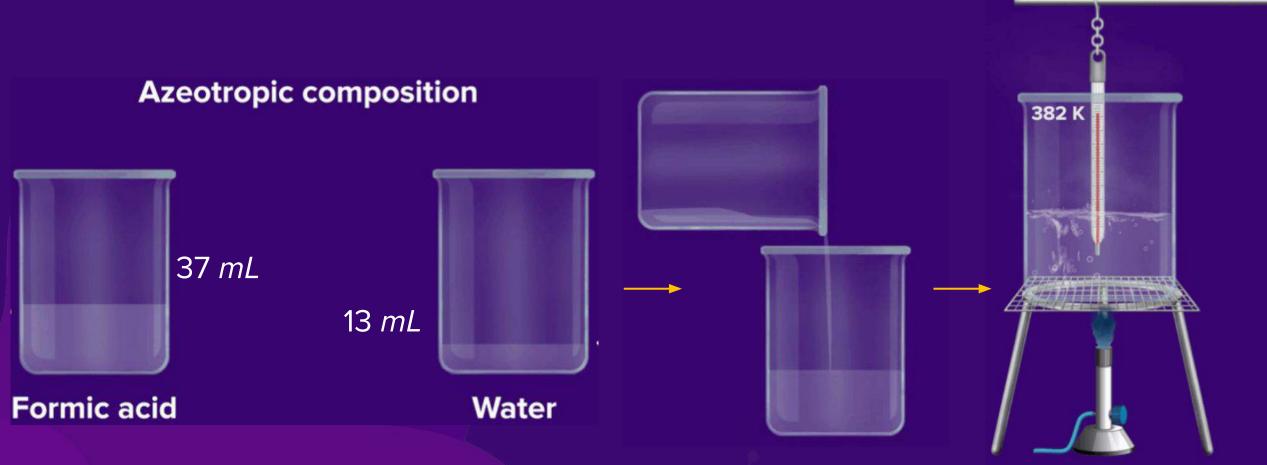


Room temperature



Both water and formic acid is taken at room temperature (298 K) and heated to their respective boiling points. Formic acid (B.P. = 374 K) and water (B.P. = 373 K)





Then we mix them in a certain composition and then boil the mixture. We will see that this mixture boiled at 382 *K* that is at a higher temperature as compared to their individual boiling point. And this is only possible in **maximum boiling azeotropes.**

An ideal solution does not boil at a constant temperature, whereas azeotrope does.



Which of the following azeotropic solutions has the boiling point more than the boiling point of the constituents A and B?

ARDS

(a) CH₃CH₂OH and CH₃COCH₃
(b) CS₂ and CH₃COCH₃
(c) CHCl₃ and CH₃COCH₃
(d) CH₃CHO and CS₂

Solution

The one which shows negative deviation will have more boiling point which is a mixture of chloroform and acetone. Hence, option (c) is the correct answer.



How many facts related to H₂O + HCI solution are correct? (a) It shows negative deviation

RDS

(b) It forms maximum boiling azeotropic mixture

(c) ΔS > 0

(d) All of these

Solution

(a) As $H_2O + HCI$ will have H-bonding so it will show negative deviation.

(b) All solutions showing negative deviation forms maximum boiling azeotropic mixture.

(c) On mixing, entropy always increases, hence $\Delta S > 0$.

Hence, option (d) is the correct answer.



Which is/are correct statement(s)?

B

BOARDS

- (a) When a mixture is more volatile than both pure components, there is positive deviation from Raoult's law
- (b) When the mixture is more volatile than both pure components, there is negative
 - deviation from Raoult's law
- (c) Ethanol and water form ideal solution
- (d) CHCl₃ and water form ideal solution

Solution

If the mixture is more volatile than both pure components then their vapour pressure will be higher than what we obtained from Raoult's law i.e. mixture will show positive deviation. Ethanol and water do not form ideal solution but form positive deviation. CHCl₃ and water do not form ideal solution. **Hence, option (a) is the correct answer.**



Benzene and Toluene form an ideal solution at room temperature. For this process, the false statement is:

(a) $\Delta H = 0$ (b) ΔS_{system} is positive (c) $\Delta S_{surroundings} = 0$ (d) ΔG is positive

Solution

- As they form ideal solution so $\Delta H = 0$.
- ΔS_{system} is positive.
- There is no effect on surrounding so $\Delta S_{surroundings} = 0$.
- ΔG for this process is negative as mixing is a spontaneous process.

Hence, option (d) is the correct answer.



A binary liquid solution is prepared by mixing n-heptane and ethanol. Which one of the following statement is correct regarding the behaviour of the solution?



The solution is non-ideal, showing +ve deviation from Raoult's law.

ARDS



The solution in non-ideal, showing -ve deviation from Raoult's law.



A binary liquid solution is prepared by mixing n-heptane and ethanol. Which one of the following statement is correct regarding the behaviour of the solution?



n-heptane shows +ve deviation while ethanol shows —ve deviation from Raoult's Law.



The solution formed is an ideal solution.

Hence, option (a) is the correct answer.



For an ideal solution of two components A and B, which of the following is true?

RDS



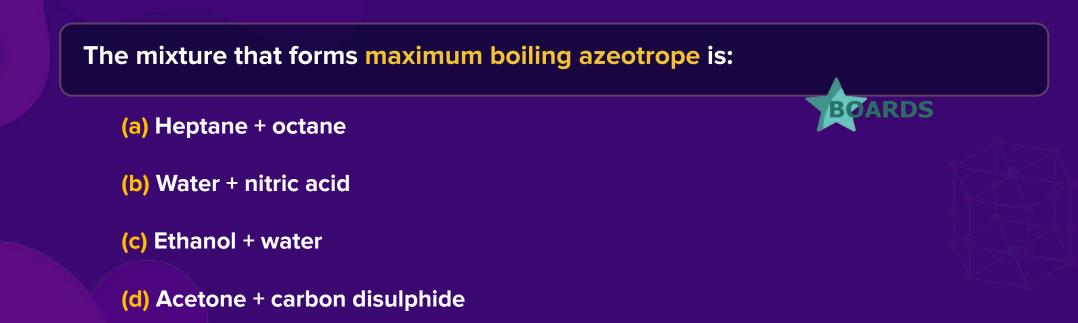
Solution

For an ideal solution, $\Delta_{mix} H = 0$

In ideal solutions, all the interactions are identical and therefore **option (d)** A–A, B–B, and A–B interactions are identical is the correct answer.

Hence, option (d) is the correct answer.





Solution

Maximum boiling azeotropes are those whose boiling point is more than their expected boiling point and show negative deviation.

(a) Heptane + octane, are alkanes and almost form ideal solutions.

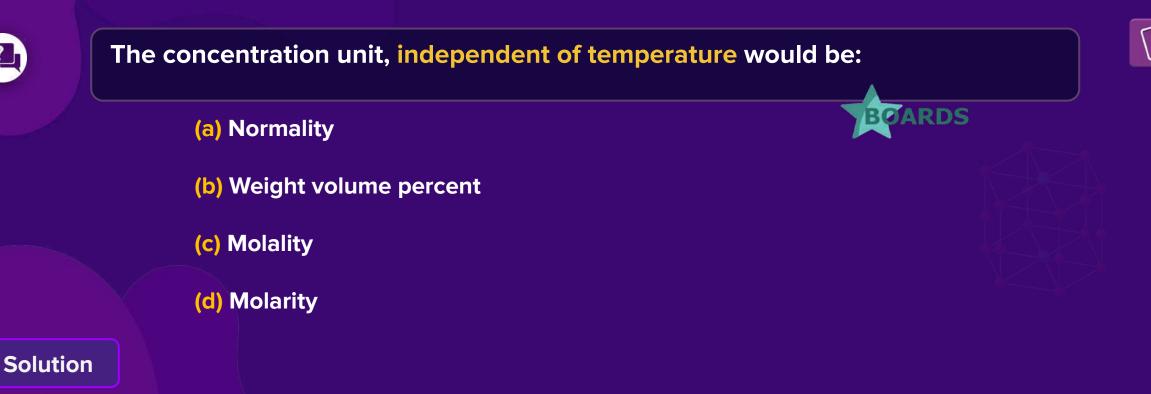
(b) Water + nitric acid, shows negative deviation. Solutions of water and acid always shows negative deviation.

(c) Ethanol + water, shows positive deviation. Solutions of water and alcohols except methanol always shows positive deviation.

(d) Acetone + carbon disulphide, shows positive deviation because carbon disulphide is non-polar and acetone is polar.

Hence, option (b) is the correct answer.





The concentration unit which is independent of temperature will also be volume independent.

(a) Normality is equivalents per liters of solution, so this is volume dependent.

(b) Weight volume percent is also volume dependent.

(c) Molality is moles of solutes per kg of solvent and this is volume independent and therefore will also be independent of temperature.

(d) Molarity is moles of solute per liters of solution, so this is volume dependent.

Hence, option (c) is the correct answer.



Assertion: One molal aqueous solution of glucose contains 180 g of glucose in 1 kg water. Reason: Solution containing one mole of solute in 1000 g of solvent is called one molal solution.

(a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion

(b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion

(c) If the Assertion is correct but Reason is incorrect

(d) If both the Assertion and Reason are incorrect



Solution

Assertion: Molar mass of Glucose($C_6H_{12}O_6$) = 180 g mol⁻¹

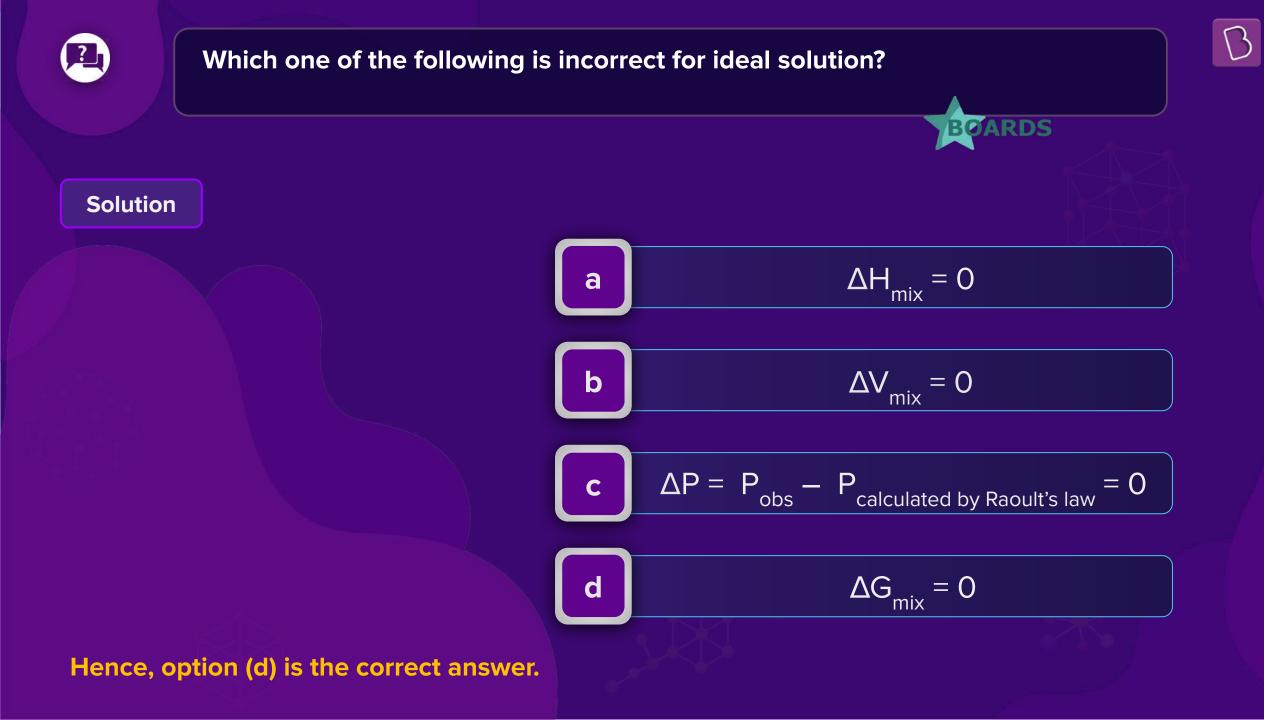
Given, mass of glucose = 180 g 180 Moles of glucose = $\frac{1}{180}$ = 1 mole 1 Molality = Moles of solute/solvent in kg = $\frac{1}{1}$ = 1 molal

Therefore, Assertion is true.

Reason: Solution containing one mole of solute in 1000 *g* of solvent is called one molal solution and this is also **true.**

Hence, option (a) is the correct answer.







Which of the following statements about the composition of the vapour over an ideal 1 : 1 molar mixture of benzene and toluene is correct? Assume that the temperature is constant at 25 °C. (Given, vapour pressure data at 25 °C, benzene = 12.8 kPa, toluene = 3.85 kPa)

(a) The vapour will contain equal amounts of benzene and toluene

(b) Not enough information is given to make a prediction

(c) The vapour will contain a higher percentage of benzene

(d) The vapour will contain a higher percentage of toluene

Solution

Moles of Benzene (n_B) = Moles of Toluene (n_T) = 1 Mole fraction of Benzene (x_B) = 0.5 and Mole fraction of Toluene (x_T) = 0.5 $P_B^0 = 12.8 \ kPa$ and $P_T^0 = 3.85 \ kPa$ Vapour pressure of benzene is more which means benzene is more volatile than toluene therefore vapour will contain more amounts of benzene. The vapour will contain a higher percentage of benzene because vapour pressure of benzene is more. **Hence, option (c) is the correct answer.**



A solution of acetone in ethanol:

(a) Obeys Raoult's law

(b) Shows a negative deviation from Raoult's law

(c) Shows a positive deviation from Raoult's law

(d) Behaves like a near ideal solution

Solution

Ethanol forms hydrogen bonds and acetone will interrupt the hydrogen bond between ethanol molecule and the extent of hydrogen bonding will decrease. Therefore, the solution will show positive deviation from Raoult's law.

Hence, option (c) is the correct answer.





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

(a) A–B attraction force is greater than A–A and B–B

(b) A–B attraction force is less than A–A and B–B

(c) A–B attraction force remains same as A–A and B–B

(d) Volume of solution is different from sum of volume of solute and solvent

BOARDS

Solution

In ideal solutions, all the interactions are identical and therefore option (c) A–A, B–B, and A–B interactions are identical is the correct answer.

Hence, option (c) is the correct answer.



All form ideal solution except:

(a) $C_6H_6 \& C_6H_5CH_3$ (b) n-Hexane & n-heptane (c) $C_6H_5CI \& C_6H_5Br$ (d) Phenol & aniline

Solution

(a) $C_6H_6 \& C_6H_5CH_3$, both are nonpolar and hence they will form ideal solution.

(b) n-Hexane & n-heptane, both are nonpolar and hence they will form ideal solution.

(c) $C_6H_5CI \& C_6H_5Br$ are almost of similar kind and hence they will form ideal solution.

(d) Phenol & aniline will form hydrogen bonding and will not form ideal solution and will show negative deviation.

Hence, option (d) is the correct answer.



ARDS



A liquid is kept in a closed vessel. If a glass plate (negligible mass) with a small hole is kept on top of the liquid surface, then the vapour pressure of the liquid in the vessel is:

ARDS

(a) More than what would be, if the glass plate were removed

(b) Same as what would be, if the glass plate were removed

(c) Less than what would be, if the glass plate were removed

(d) Cannot be predicted

Solution

Here vapour pressure of liquid depends only on temperature so here vapour pressure will remain same.

Hence, option (b) is the correct answer.



Choose the correct statement with respect to the vapour pressure of a liquid among the following:

DN

RDS

- (a) Increases linearly with increasing temperature
- (b) Increase non-linearly with increasing temperature
- (c) Decreases linearly with increasing temperature
- (d) Decreases non-linearly with increasing temperature

Solution

Vapour pressure of a liquid increases exponentially with increasing temperature. Hence, option (b) is the correct answer.



Low concentration of oxygen in blood and tissues of people living at higher altitude is due to:

(a) Low temperature

- (b) Low atmospheric pressure
- (c) High atmospheric pressure
- (d) Both low temperature & high pressure

Solution

At higher altitude the pressure is low but the human body temperature is same. As the partial pressure of oxygen is decrease at higher altitude the solubility of oxygen in blood will decrease.

Hence, option (b) is the correct answer.



Solubility of Solid in Liquid



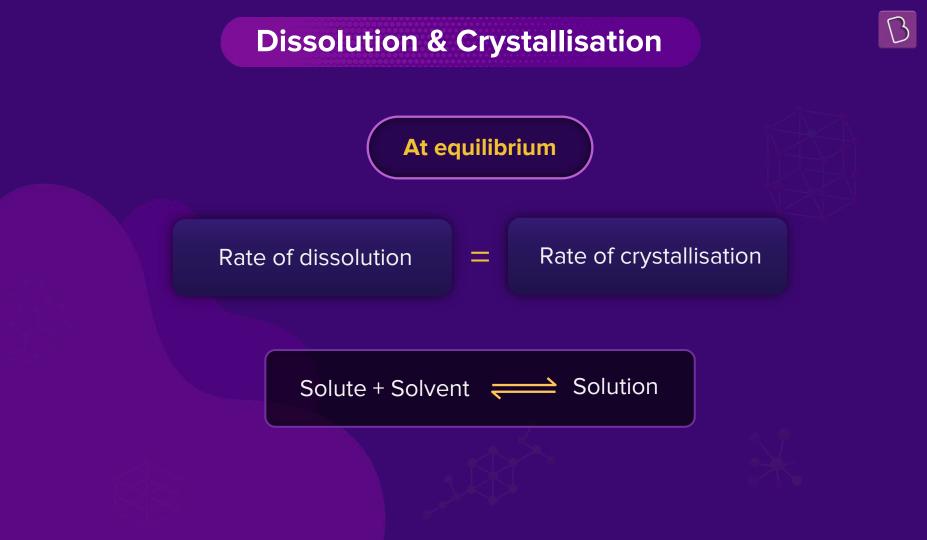


When a solid solute is added to the solvent, some **solute dissolves** and its **concentration increases** in the solution.

Crystallisation

B

Some solute particles in the solution collide with the other solid solute particles and get separated out of solution.







At this stage, the concentration of solute in solution will **remain constant** under the given temperature and pressure conditions

Such a solution is said to be **saturated** with the given solute.

Factors Affecting Solubility

Nature of the solvent & the solute

Ā

Temperature

Pressure

Nature of Solvent & Solute



Like dissolves like

Polar solutes dissolve in **polar solvents** and **non-polar solute** dissolve in **non-polar solvents**.

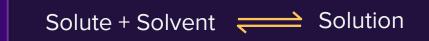




Sodium chloride **dissolves readily in water**, whereas naphthalene and anthracene do not.

Naphthalene and anthracene **dissolve readily in benzene** but sodium chloride do not.

Temperature





By Le Chatelier's principle,



Temperature





By Le Chatelier's principle,





B

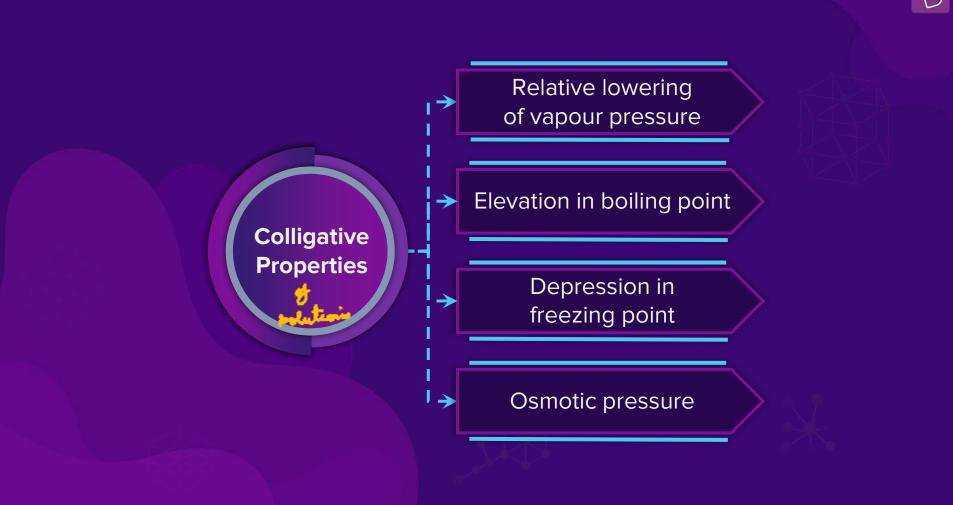
Pressure does not have any significant effect on solubility of solids in liquids.

Solids and liquids are highly incompressible and practically remain unaffected by changes in the pressure.

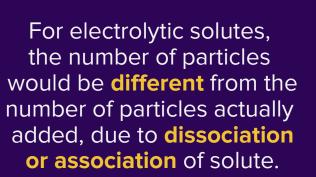
Colligative Properties

The properties of the solution that are **dependent only on the total number of solute particles** relative to solvent/solution

They are **not dependent on the nature of particle** i.e., shape, size, charge, etc.



If solute gets associated or dissociated in solution, then experimental/observed/actual value of colligative property will be **different** from theoretically predicted value.



NaCl (s) + $H_2O(I) \longrightarrow Na^+(aq) + Cl^-(aq)$

Example: On adding 1 mole of NaCl in excess water gives 1 mole of Na⁺ and 1 mole of Cl⁻ ions i.e. 2 moles of solute.

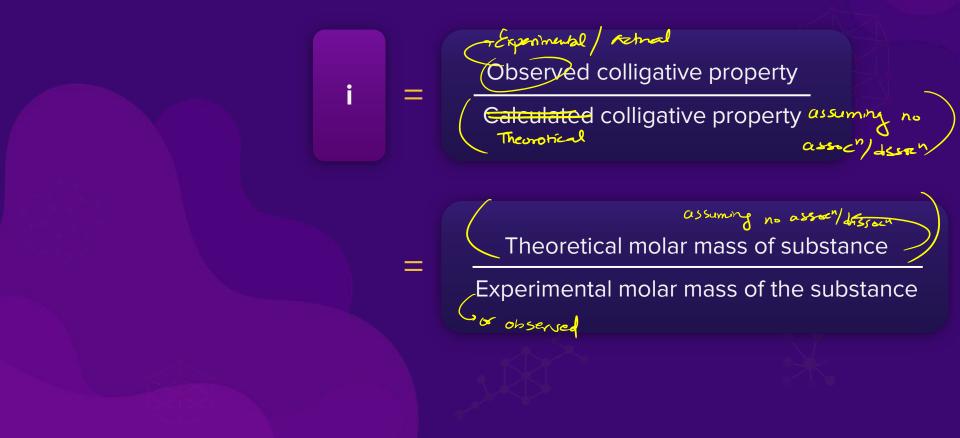
Abnormality in colligative property can be calculated in terms of van't-Hoff factor.

van't-Hoff Factor

The actual extent of dissociation/ association can be expressed with a correction factor known as van't Hoff factor (i).

van't–Hoff Factor (i)





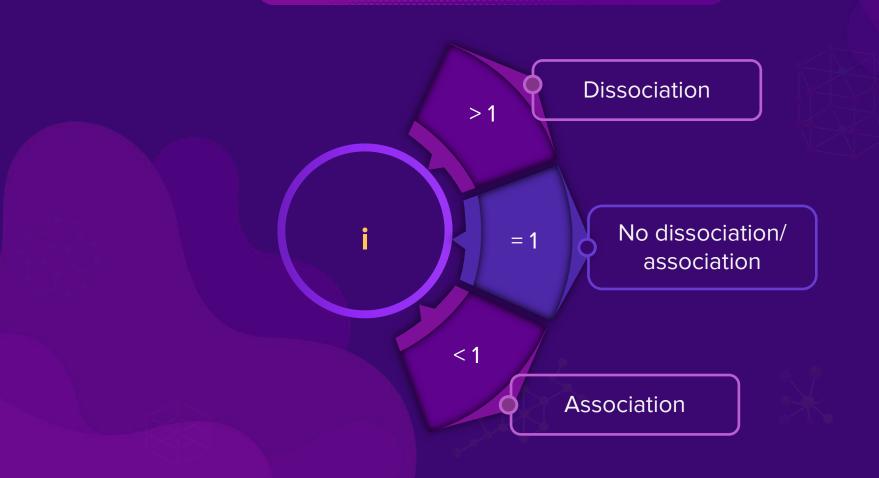


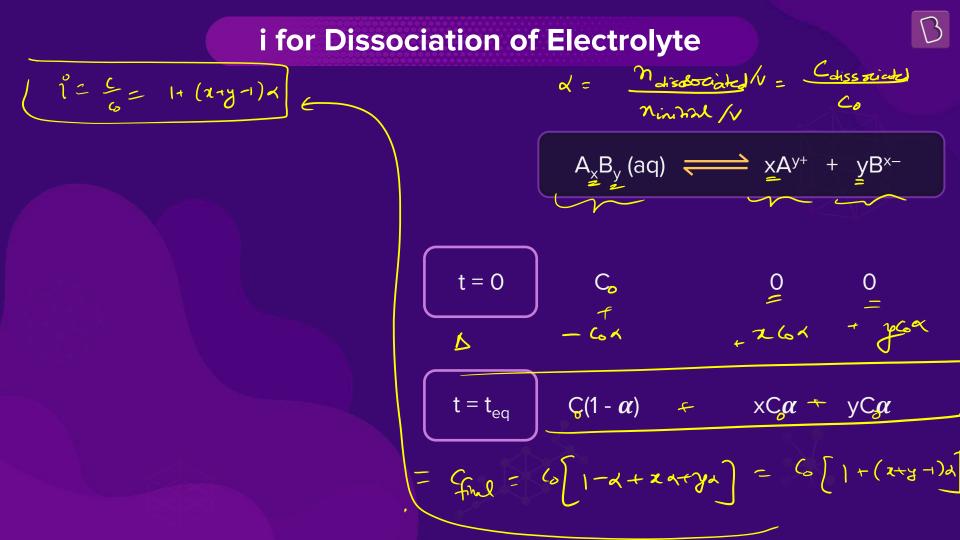
Moles of solute particles in solution after dissociation/ association

Moles of solute particles before association/dissociation

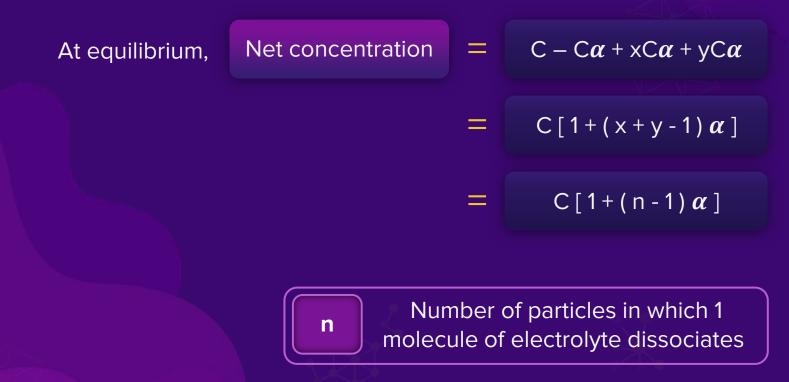




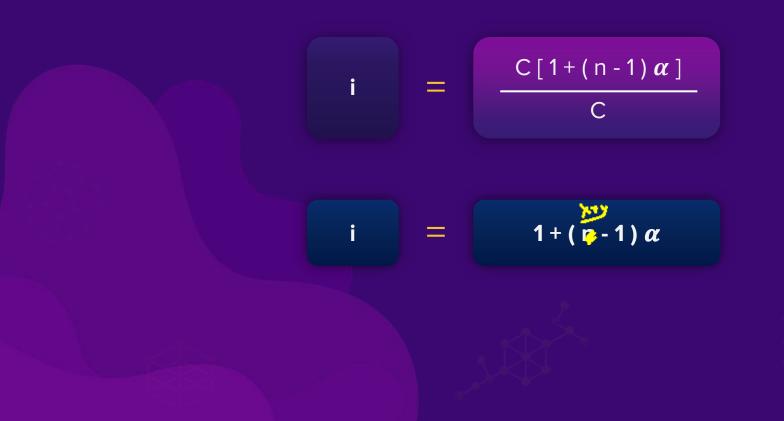




i for Dissociation of Electrolyte



i for Dissociation of Electrolyte











BaCl₂ (100% ionised)







Determine i (van't-Hoff factor) for:

- 1. $K_4[Fe(CN)_6]$ (75% ionisation)
- 2. KCI.MgCl_{2.}6H₂0(100% ionisation)



Answer- 1. i=4 Answer- 2. i=5

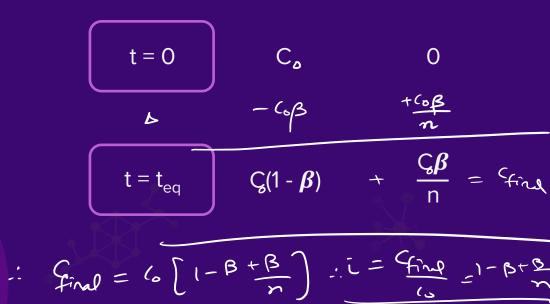
x=7576===75 +4× 0.75 i = 5/ <u>5</u> (an) +1(2 (an) + 100 (an) + 200 (an) HH+1+2 = 5 FR.CCN -> YET -+ Ky FRICONS 0 ini 26 ~4n.~ - sol 1 0-(1-24) 1/2 = no[1-1x + x + x] = no[1+x] ٠

i for Association of Electrolyte

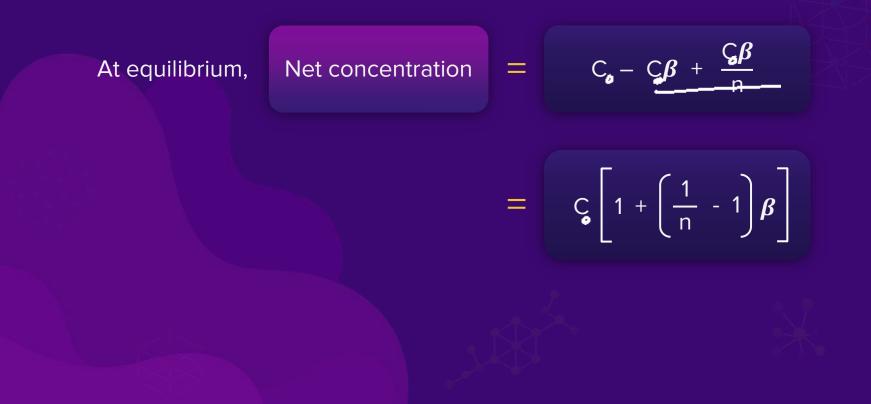


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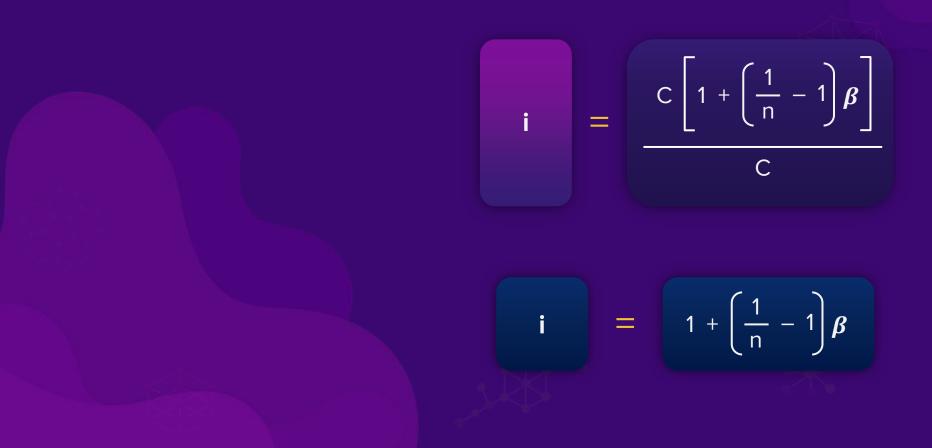


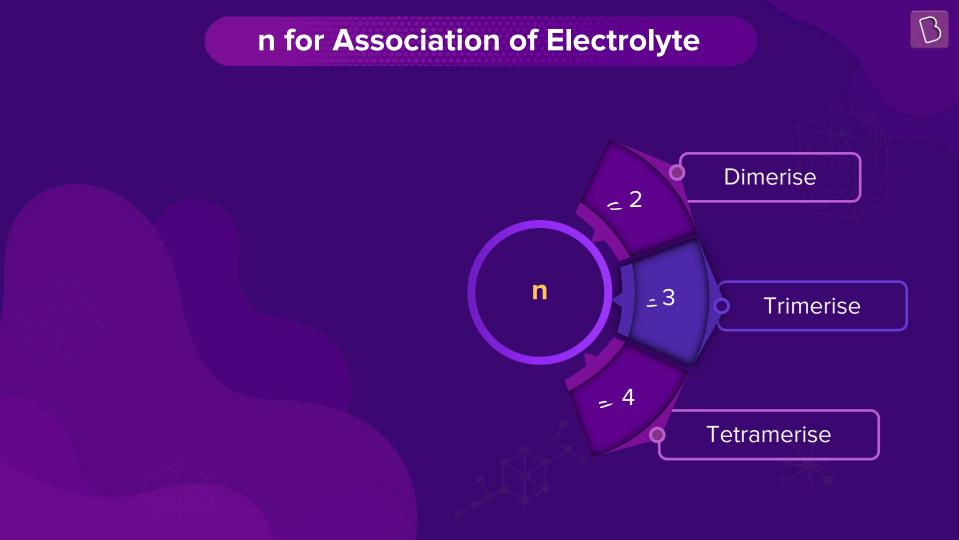


i for Association of Electrolyte



i for Association of Electrolyte









0.5

0.5

i

Dimerisation of C₆H₅COOH in benzene (100%)



An aqueous solution of a salt MX_2 at a certain temperature has a van't Hoff factor of 2. The degree of dissociation for this solution of the salt is:

$$m_{X_{2}} = m_{x}^{2} + 2x^{-1}$$

$$n_{0}(1-x) + n_{0}x + 2n_{0}x = n$$

$$n = n_{0}[1-a_{1}-a_{1}+2x]$$

$$a = 0.67$$

$$n = n_{0}[1+2x]$$

$$b = 0.33$$

$$\therefore c = n_{1} = 1+2a = 2$$

$$c = 0.80$$

$$\therefore 2a = 2-1$$

$$d = \frac{1}{2}$$

$$d = \frac{1}{2}$$

Solution

Hence, option d is the correct answer.



The van't Hoff factor for $0.1 \text{ M Ba}(\text{NO}_3)_2$ solution is 2.74.

B

The degree of dissociation is:

 $B_{a}(NO_{3})_{2} \longrightarrow B_{a}^{2}^{1} + 2N_{3}^{2}^{1}$ $n_{a}(1-a) \longrightarrow n_{a}d_{a} + 2n_{a}x = n_{f}$.: nf= no[1-a+a+2x] = no(1+2x) : i= m = 1+2x 91.3% a 2.74 = 1+2x 87% · 2 =), 74 100% С q - 1-77 d 74% = 0.87

Solution

Hence, option b is the correct answer.



van't Hoff factor :



Colligative Properties

Colligative Properties Relative lowering of vapour pressure

Elevation in boiling point

Depression in freezing point

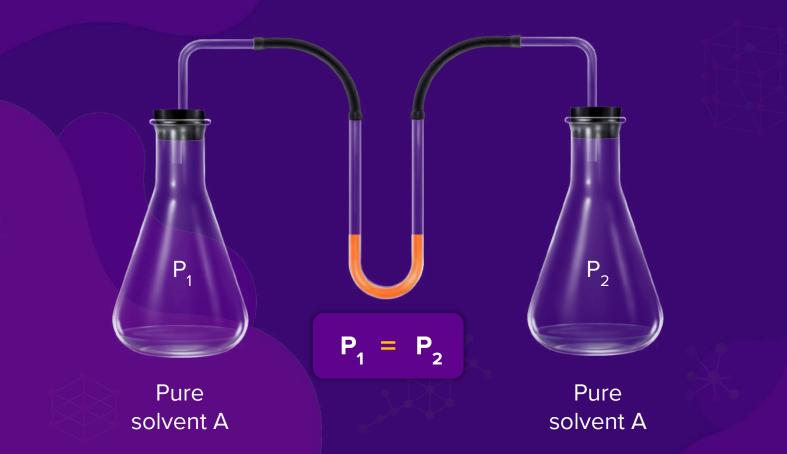
Osmotic pressure

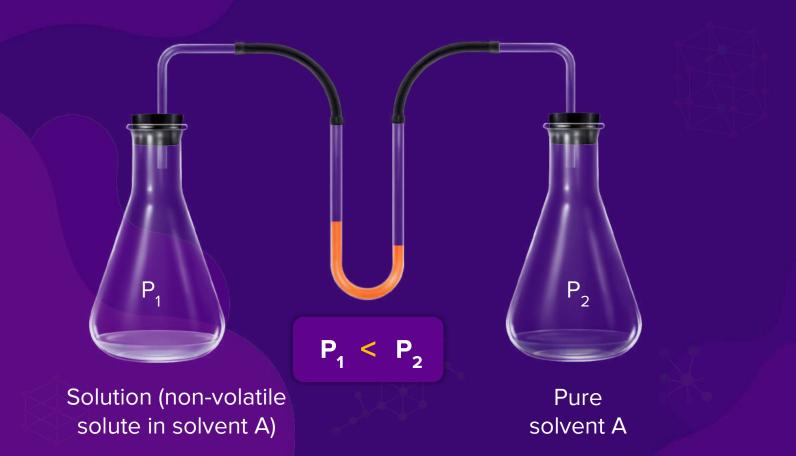
Relative Lowering of Vapour Pressure

V.P. of a solution containing a non-volatile solute (solid solute) is always found to be less than the V.P. of the pure solvent.



Relative Lowering of Vapour Pressure



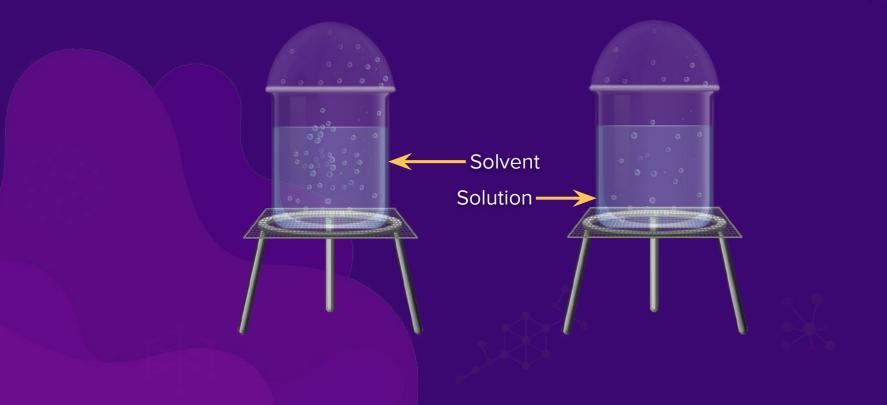


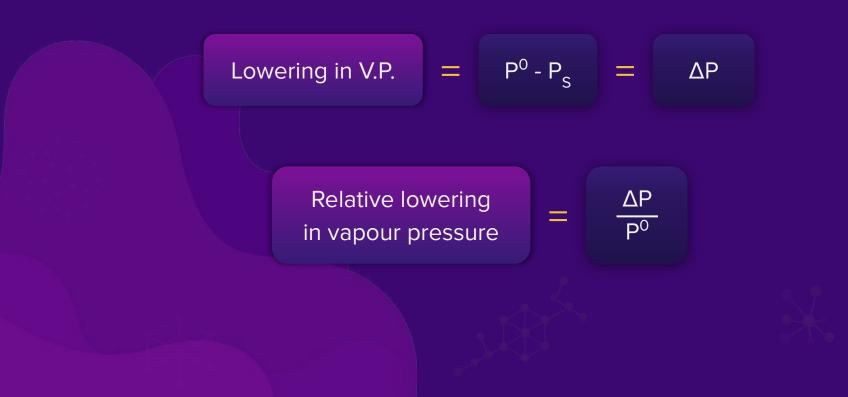
Reason

Some of the solute molecules will **occupy** some surface area of the solution.

> Tendency of the solvent particles to go into the vapour phase **slightly decreases**.

> > Hence, $P^{0} > P_{s}$, where P^{0} is V.P. of the pure solvent and P_{s} is the V.P. of the solution.



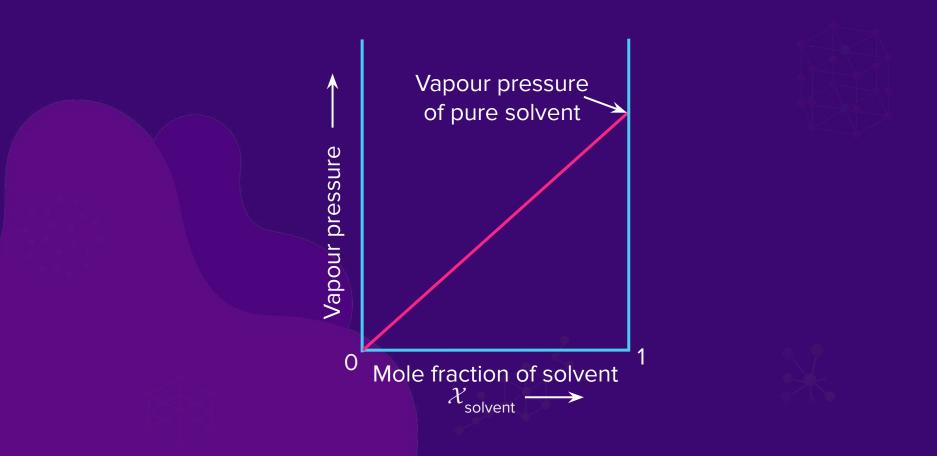




Relative lowering of vapour pressure is a colligative property whereas, lowering in vapour pressure is not.

Raoult's Law (For non-volatile solutes)

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**.



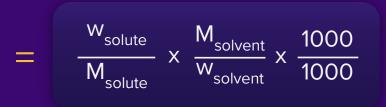
$$P_{s} = \mathcal{X}_{solvent} P^{0} = (1 - \mathcal{X}_{solute}) P^{0}$$



n = Number of moles of non-volatile soluteN = Number of moles of solvent in the solution

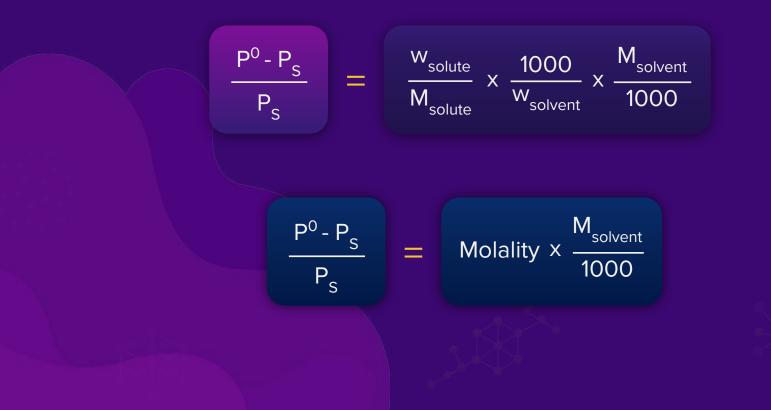
$$\frac{P^{0}}{P^{0} - P_{s}} = \frac{n + N}{n} = 1 + \frac{N}{n}$$
$$\frac{N}{n} = \frac{P^{0}}{P^{0} - P_{s}} - 1 = \frac{P_{s}}{P^{0} - P_{s}}$$
$$\frac{P^{0} - P_{s}}{P_{s}} = \frac{n}{N}$$

$$\frac{P^{0} - P_{s}}{P_{s}} = \frac{W_{solute}}{M_{solute}} \times \frac{M_{solvent}}{W_{solvent}}$$



w = Weight of speciesM = Molar mass of species





If solute gets associated or dissociated

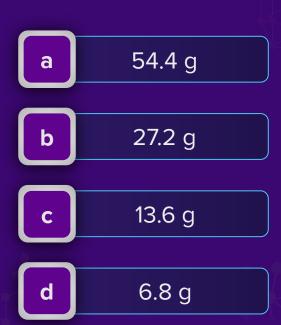
$$\frac{P^{0} - P_{s}}{P^{0}} = \frac{i.n}{i.n + N}$$

$$\frac{P^{0} - P_{s}}{P_{s}} = \frac{i.n}{N} = ix \text{ Molality } x \frac{M_{solvent}}{1000}$$



The weight of urea which must be dissolved in 400 g of water. Therefore, the final solution has vapour pressure 2% less than the vapour pressure of pure water is:

Solution



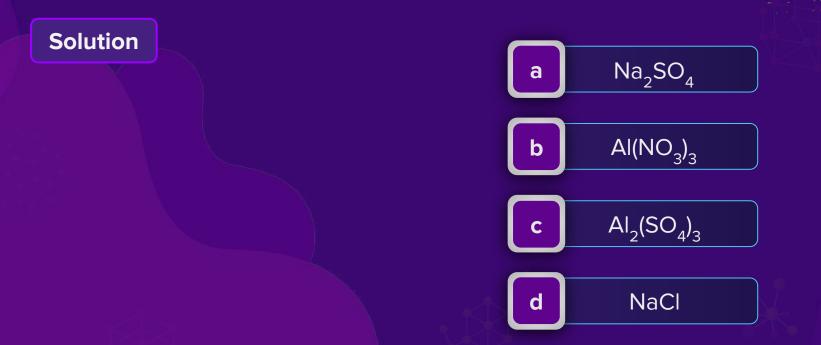
1)

Hence, option (b) is the correct answer.



Which of the following salts has the same value of van't Hoff factor (i) as that of $K_3[Fe(CN)_6]$?

U



Hence, option (b) is the correct answer.



The van't Hoff factor (i) for a dilute aqueous solution of the strong electrolyte barium hydroxide is:





JARDS







Hence, option (d) is the correct answer.



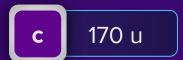
The vapour pressure of pure benzene at a certain temperature is 0.850 bar. A non-volatile, non-electrolyte solid weighing 0.5 g is added to 39.0 g of benzene (molar mass 78 g mol⁻¹). The vapour pressure of the solution then is 0.845 bar. What is the approximate value of molecular mass of the solid substance?

Solution

a

58 u



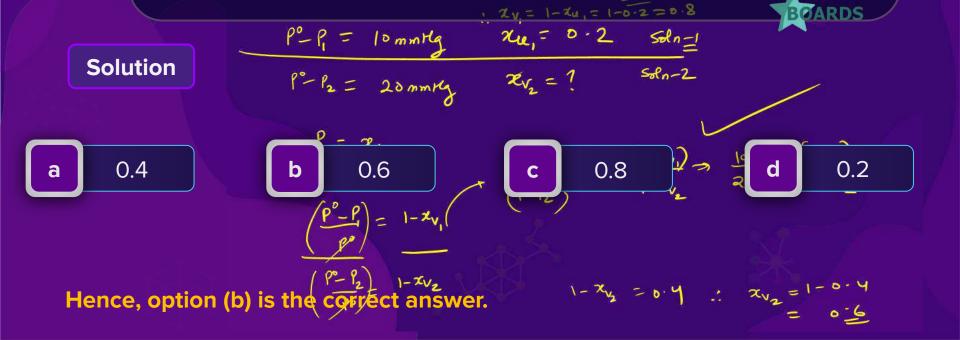




Hence, option (c) is the correct answer.

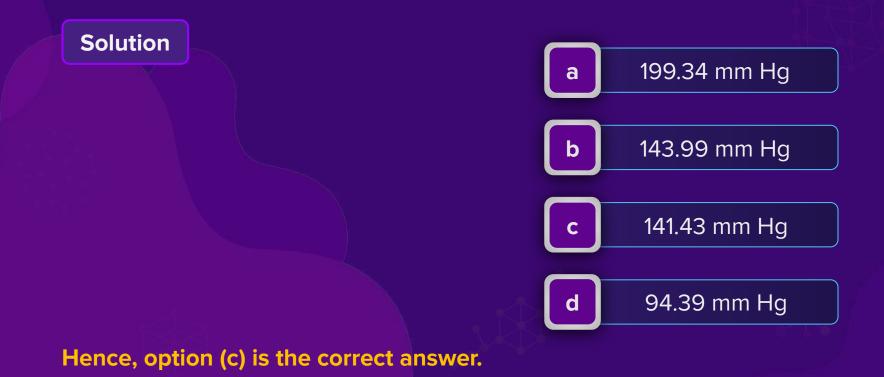


The vapour pressure of a solvent decreased by 10 *mm* of mercury when a non-volatile solute was added to the solvent. The mole fraction of the solute in the solution is 0.2 . What should be the mole fraction of the solvent if the decrease in the vapour pressure is to be 20 *mm* of mercury?





The vapour pressure of CCl_4 at 25 °C is 143 mm Hg. If 0.5 g of a non-volatile solute (mol. weight = 65) is dissolved in 100 g CCl_4 , the vapour pressure of the solution will be:





a

С

The relative lowering of the vapour pressure is equal to the ratio between the number of:



Solute molecules to the solvent molecules.



d

Solute molecules to the total molecules in the solution.

Solvent molecules to the total molecules in the solution.

Solvent molecules to the total number of ions of the solute.





Relative lowering of vapour pressure for dilute solutions:

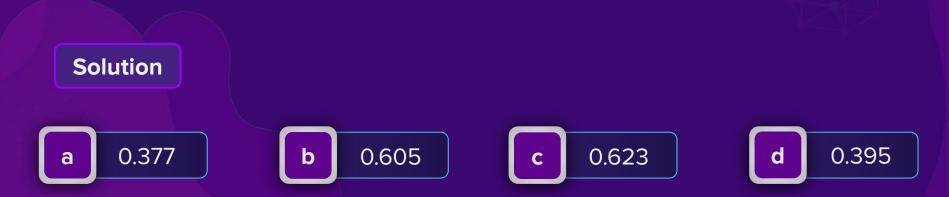


So, relative lowering of the vapour pressure is equal to the ratio between the number of solute molecules to the total molecules in the solution

Hence, option (b) is the correct answer.



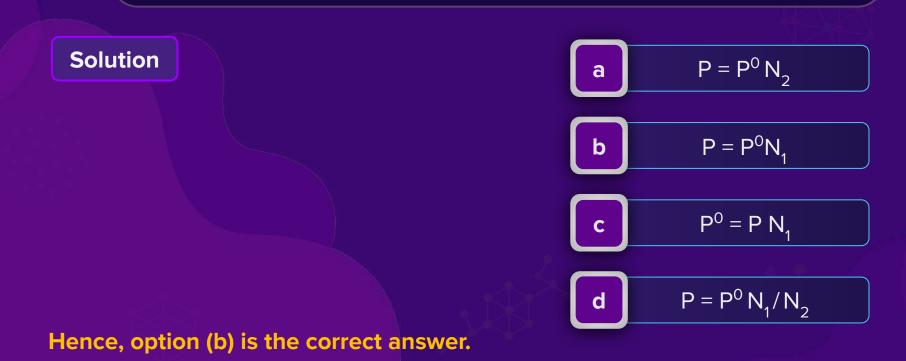
The vapour pressure of pure benzene, C_6H_6 at 50 °C is 268 Torr. How many moles of non-volatile solute per moles of benzene is required to prepare a solution of benzene having a vapour pressure of 167 Torr at 50 °C?



Hence, option (b) is the correct answer.



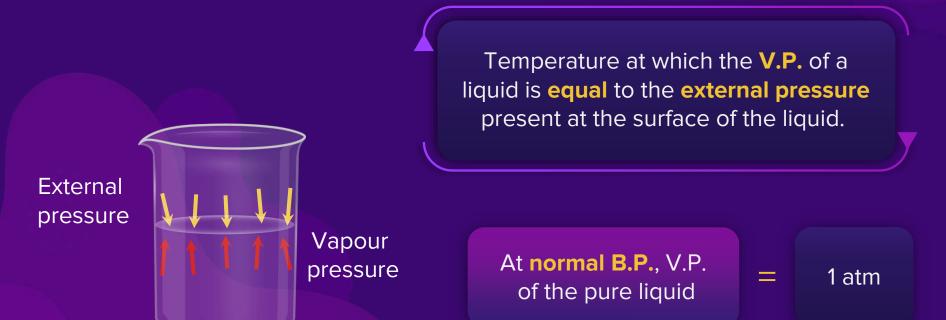
If P^0 and P are the vapour pressures of a solvent and its solution respectively and N_1 and N_2 are the mole fractions of the solvent and non-volatile solute respectively, then correct relation is:



Colligative Properties Elevation in boiling point

Depression in freezing point

Osmotic pressure



In a pressure cooker pressure increases , hence boiling point of water increases and now rice is cooked in more heat as water boils at higher temperature. So now rice will cook faster.

When a **non-volatile solute is added** into a volatile liquid to form solution, V.P. decreases.

The solution need to be **heated to a higher temperature** to boil it, so that V.P. becomes equal to external pressure.

For example,

Vapour pressure of an aqueous solution of sucrose is less than 1.013 bar at 373.15 K. I INºC

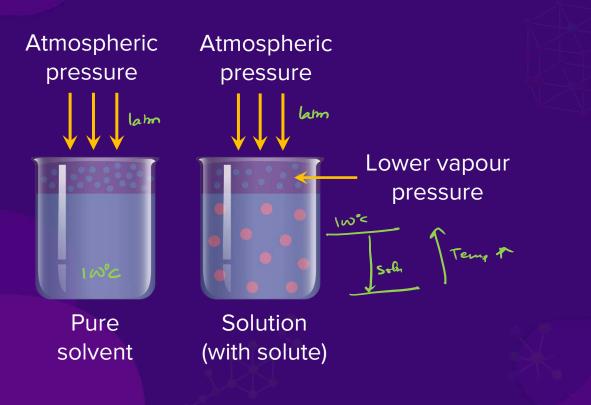
- ano

To make this solution boil, its vapour pressure must be increased to 1.013 bar by raising the temperature above the boiling temperature of the pure solvent (water).

The boiling point of a solution

Thus,

The boiling point of the pure solvent



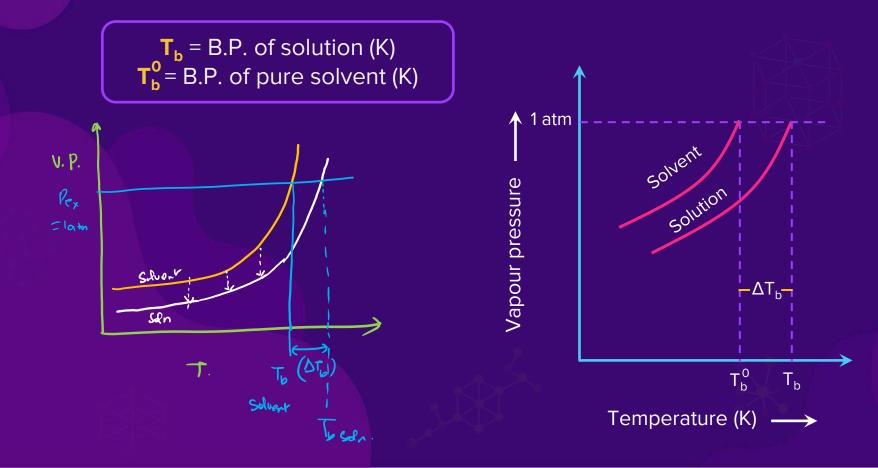


Water

+ Water



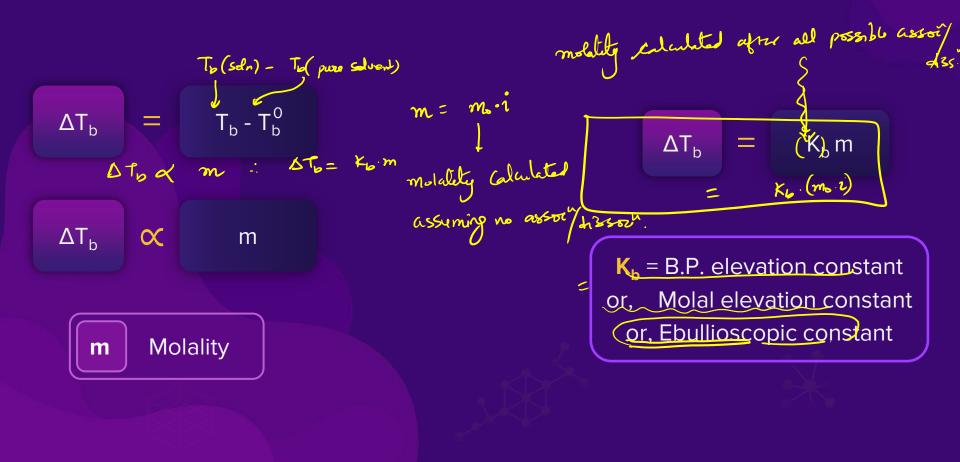
Hence, we can say that because of the addition of non-volatile solute the boiling point of solution increases



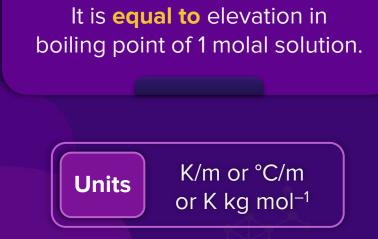
V.P. of solution

Hence, to make the V.P. equal to P_{ext}, we have to heat the solution by a greater amount in comparison to pure solvent.

V.P. of pure solvent

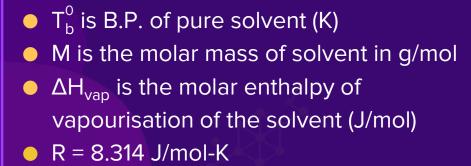


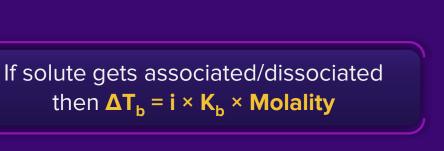
K_b





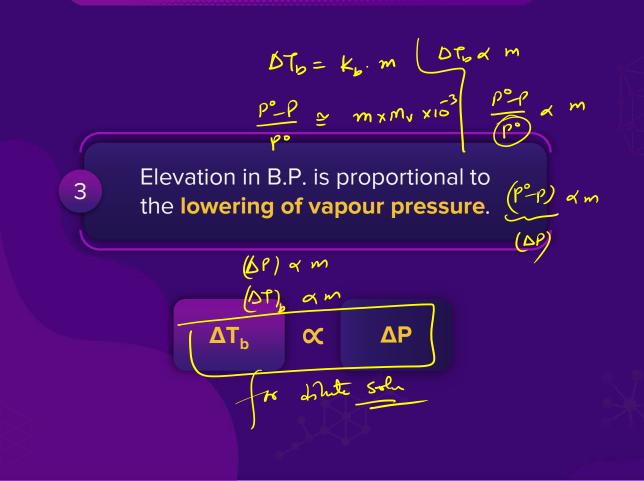


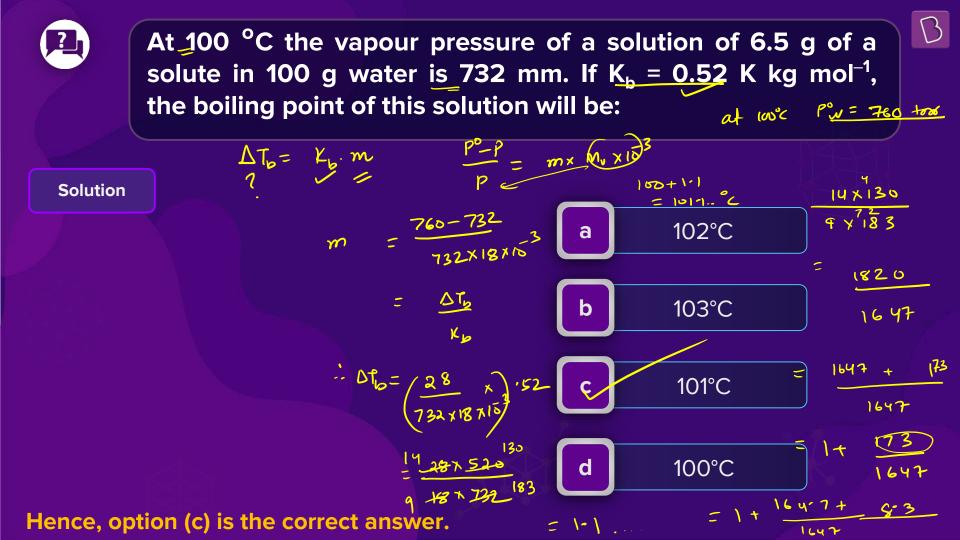




 $\rm K_{\rm b}$ is the property of solvent

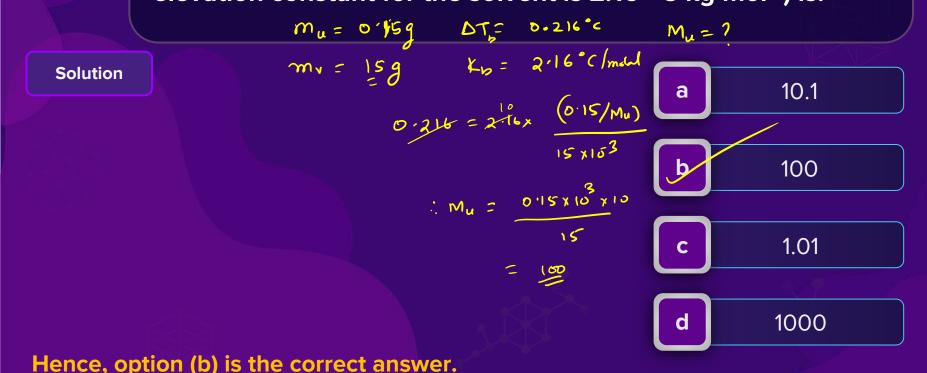
2







If 0.15 g of a solute, dissolved in 15 g of solvent, is boiled at a temperature higher by 0.216° C, than that of the pure solvent. The molecular weight of the substance (Molal elevation constant for the solvent is 2.16 °C kg mol⁻¹) is:



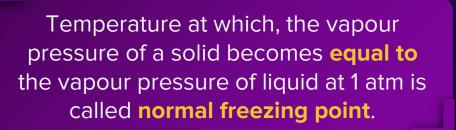
Relative lowering of vapour pressure

Colligative Properties Elevation in boiling point

Depression in freezing point

Osmotic pressure

Freezing Point (F.P.)



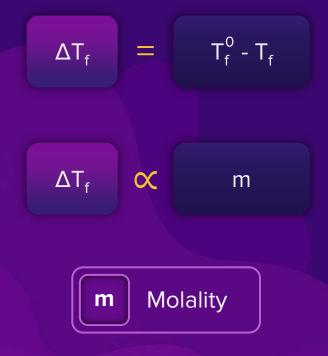


When a non-volatile solute is dissolved in the solvent, the **V.P. of the solvent** in the solution **decreases**.

V.P. of solid and liquid solvent will become equal at a **lower temperature**, i.e., F.P. of solution is **lower than that of a pure solvent.**

ΔT_f

The difference between F.P. of a pure solvent T_f^0 and F.P. of its solution $T_f^{.}$



$$\Delta T_{f} = K_{f} m$$

K_f = F.P. depression constant
or molal depression constant
or cryoscopic constant.

It is **equal to** the depression in freezing point of 1 molal solution.

K_f





- T_f^0 is F.P. of pure solvent (K)
- M is the molar mass of solvent in g/mol
- ΔH_{fus} is the molar enthalpy of fusion of the solvent (J/mol)
- R = 8.314 J/mol-K



Depression in freezing point is proportional to the lowering of vapour pressure i.e. $\Delta T_f \propto \Delta P$

If solute gets associated/dissociated then $\Delta T_f = i \times K_f \times Molality$

2

3

At freezing point or below it, only solvent molecules will freeze & not solute molecules.

Colligative Properties



Colligative Properties

Relative lowering in vapour pressure

 $\frac{\mathbf{P}^{\mathbf{o}} - \mathbf{P}_{\mathbf{s}}}{\mathbf{P}_{\mathbf{s}}} = \frac{\mathbf{n}_{\mathbf{u}}}{\mathbf{n}_{\mathbf{v}}} = \mathbf{m} \times \mathbf{M}_{\mathbf{v}} \times 10^{-3}$

Where, m = molality, $M_v = mass of solvent$

Depression in freezing point

 $\Delta T_{f} = K_{f} \times m$ $K_{f} = \frac{RT_{f} \circ {}^{2} M}{1000 \times \Delta H_{fus}}$

• Elevation in boiling point

 $\Delta T_{b} = K_{b} \times m$

$$K_{b} = \frac{RT_{b}^{o 2} M}{1000 \times \Delta H_{var}}$$

Applications of Depression in Freezing Point

Salting roads in winter to reduce the freezing point of water.

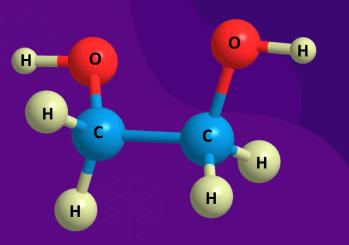
Roads are salted in the winter to reduce the freezing point of water, so that the removal of ice from roads and footpaths becomes easy. Water normally freezes at $0^{\circ}C$. On adding salt (i.e., a solute), the freezing point of water is reduced to, say around, $-3 \ ^{\circ}C$ (this value is taken for understanding purpose).



Thus, the ice formed will melt at any temperature above $-3 \circ C$. Hence, the snow on the road can be easily removed as it will start to melt when the temperature is higher than $-3 \circ C$.

Applications of Depression in Freezing Point

Ethylene glycol prevents our car's engine from freezing in the winter and acts as a coolant to reduce overheating in the summer.



Ethylene glycol is a chemical commonly used in many commercial and industrial applications including antifreeze and coolant.

The freezing point depression constant (K_f) of benzene is 5.12 K kg mol⁻¹. The freezing point depression for the solution of molality 0.078 m containing a non-electrolyte solute in benzene is (rounded off upto two decimal places).

Kg = 5-12 K.g. mol BOARDS

0.2 K

0.40 K

0.80 K

0.60 K

a

С

d

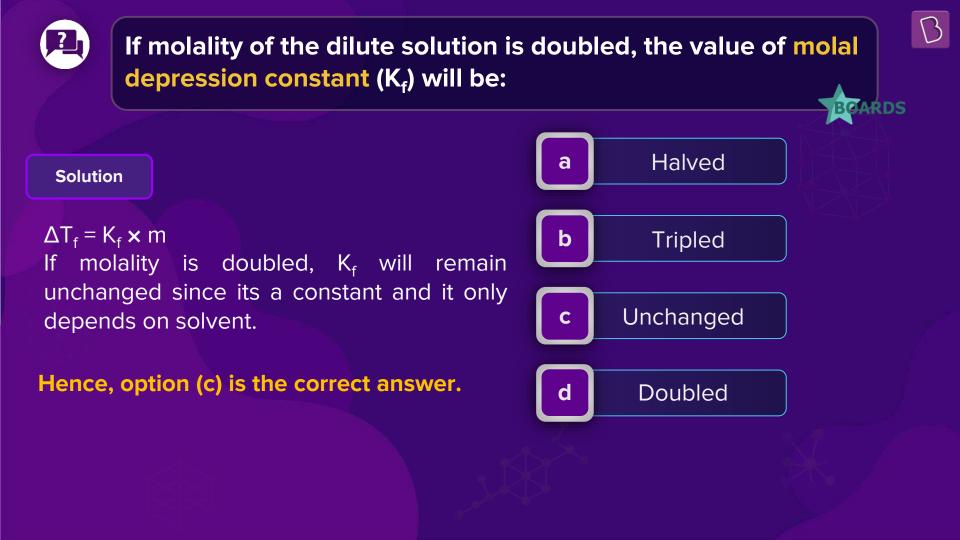
Solution

Hence, option (b) is the correct answer.

m. K

= 5.12 × 0.078

~ 5 x 0.080 ~ 0.4



A solution of sucrose (molar mass = 342 g mol⁻¹) has been prepared by dissolving 68.5 g of sucrose in 1000 g of water. The freezing point of the solution obtained will be $(K_f \text{ for water} = 1.86 \text{ K kg mol}^{-1})^{-1}$ 10 = -1 68.59 moles of solute -342 g/mg Kgm = 1.86x 68.5 Solution - Tr (sila) - Tsolvent 1 = 0.5 - 0.372°C 3 - 1333 = 1.86×68.5 342 - - - 25 - 0.520°C b · Tr (soln)= - 1.86x 68.5 5 = .20 + 0.372°C - 1666 ≈ -1.86 2× 102 Hence, option (a) is the - 1414 · 3913 × 1000 correct answer. 0.570°C - 372

Relative lowering of vapour pressure

Colligative Properties

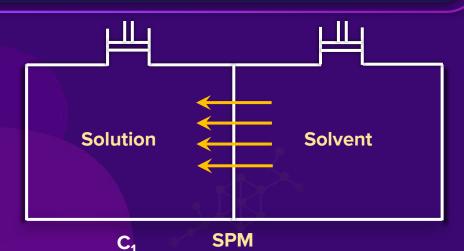
Elevation in boiling point

Depression in freezing point

Osmotic pressure



The spontaneous flow of solvent particles from solvent side to solution side, or from solution of low concentration side to solution of high concentration side through a semi-permeable membrane (SPM).







- A membrane, which allows only solvent particles to pass through it is known as a semipermeable membrane.
- The submicroscopic holes or pores present in the membrane are designed in such a way that only solvent particles can be passed through these pores.
- The transfer of bigger solute molecules through SPM is hindered.

Illustration of SPM:

Blue coloured particles represent solvent molecules and the red coloured particles represent the solute molecules in the figure shown. Since the solvent molecules are smaller than the solute molecules, they can pass through the holes in SPM. The solute particles being bigger in size, cannot pass through the holes in SPM.

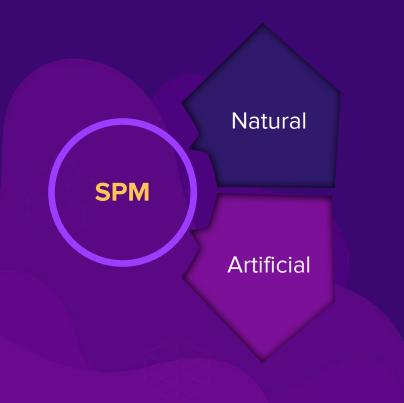




Solvent particles can pass through a semipermeable membrane, but solute particles cannot pass through a semipermeable membrane.

Osmosis

Semi-permeable Membrane (SPM)



Natural : Animal/plant cell membrane formed just below the outer skins. Artificial SPM : $Cu_2[Fe(CN)_6]$ & Silicate of Ni, Fe, Co can act as SPM.

Example of Osmosis

B

A raw mango placed in a concentrated salt solution loses water & shrivel into pickle.

People taking a lot of salt, experience
 ii water retention in tissue cells. This results
 in puffiness or swelling called edema.

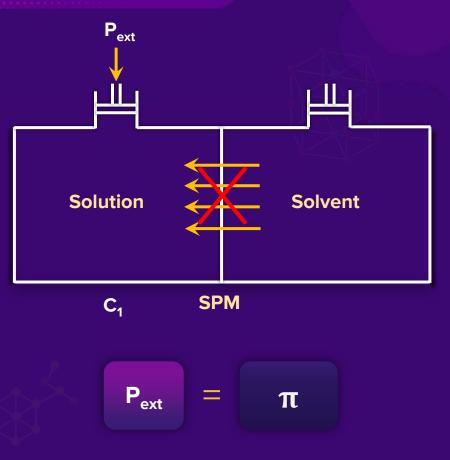


Osmotic Pressure (\pi)



The external pressure that must be applied on the solution side to just stop the process of osmosis.

If solvent and solution are in contact by SPM then osmosis will take place. Now in order to avoid this osmosis P_{ext} is applied on the solution side. The flow of solvent molecules will not take place and hence osmosis will stop.



The extra pressure that must be applied to the solution which is in contact with its pure solvent through a semi-permeable membrane in order to just stop osmosis. This is called the **osmotic pressure** (π) of that solution.

- Osmotic pressure is a colligative property as it depends on the number of solute molecules and not on their identity or nature.
- The osmotic pressure has been found to depend on concentration of the solution and temperature.

For dilute solutions, it has been found experimentally that osmotic pressure is proportional to the molarity, C of the solution at a given temperature T. Thus,

 $\pi \propto C$ (molarity) and $\pi \propto T$



B

Hence,

π = CRT

Osmotic Pressure (π)

Where, π = Osmotic pressure, C = Concentration (*mol* L⁻¹), R = Universal gas constant (*L* atm mol⁻¹ K⁻¹) and T = Temperature (K)

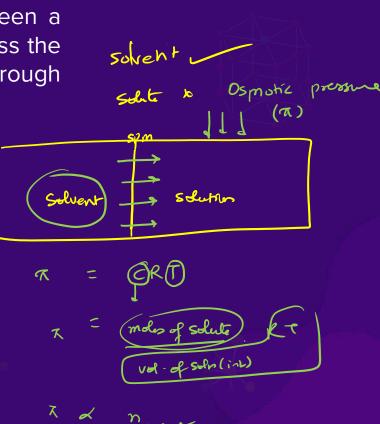
Concentration can be expressed as C = n/V, where n is the number of moles of the solute and V is the volume of the solution. Substituting C = n/V in the equation for osmotic pressure,

$$\pi = \frac{n}{V} RT$$

Osmotic Pressure (\pi)

When a semi-permeable membrane is placed between a solution and solvent, solvent particles can move across the membrane but solute particles can not pass through membrane.

Osmosis : The spontaneous flow of solvent 4 celli genra particles from solvent side to solution side, or from solution of low concentration side to solution of high concentration side through a semipermeable membrane (SPM) **Osmotic Pressure** (π) : The extra pressure that must be applied to the solution which is in contact with its pure solvent through a semipermeable membrane in order to just stop osmosis. This is called the **osmotic pressure** (π) of that solution



van't – Hoff Formula

If **more than one** type of solute particles are present.

$$C_{T} = C_{1} + C_{2} + C_{3} + \dots$$

$$\frac{n_1 + n_2 + n_3 + \dots}{V}$$

$$\pi$$
 = C_TRT



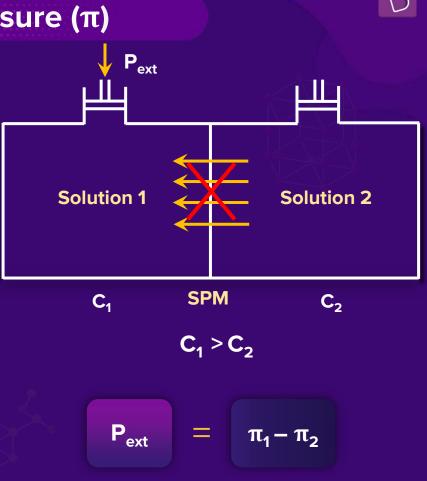




Osmotic Pressure (\pi)

If two solutions of concentration $C_1 \& C_2$ are kept separated by SPM, and $C_1 > C_2$, then the **solvent particle movement** take place from **lower to higher** concentration.

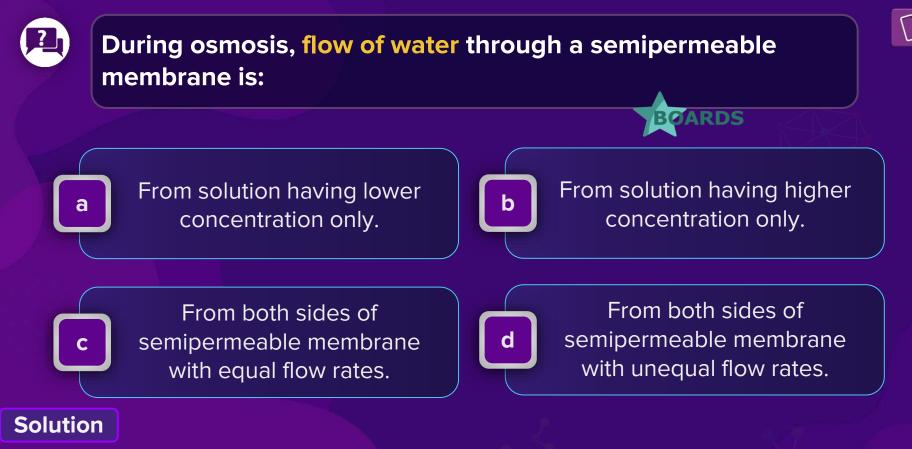
So, an **extra pressure** is applied on the higher concentration side to **stop osmosis**.



Osmotic Pressure (π)

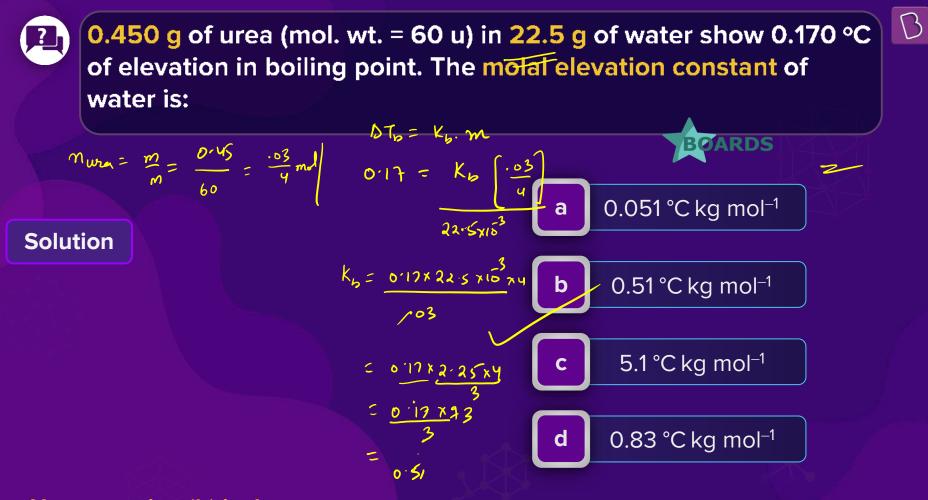
If solute gets associated or dissociated then $\Pi = i \times CRT$

Osmotic pressure of very dilute solutions is also **quite significant**. So, its **measurement in lab is very easy**.

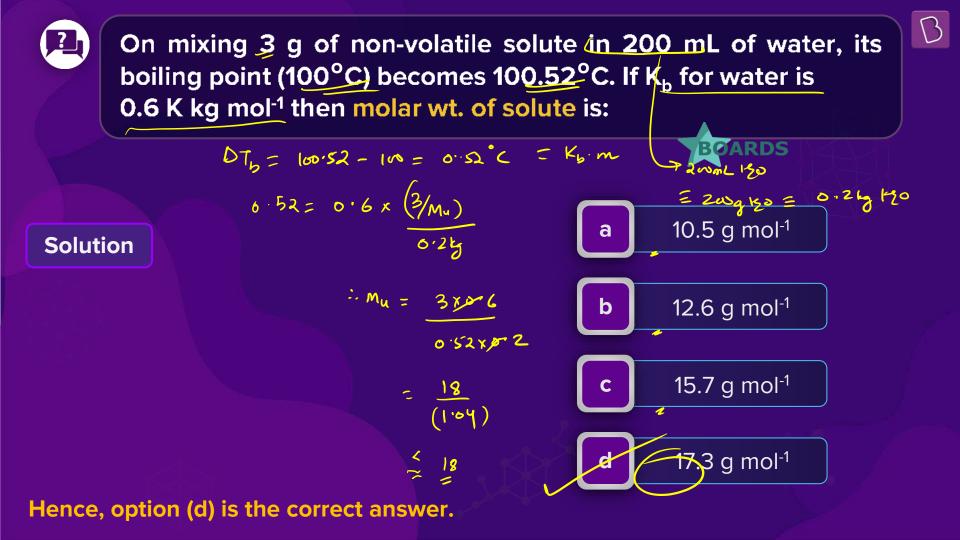


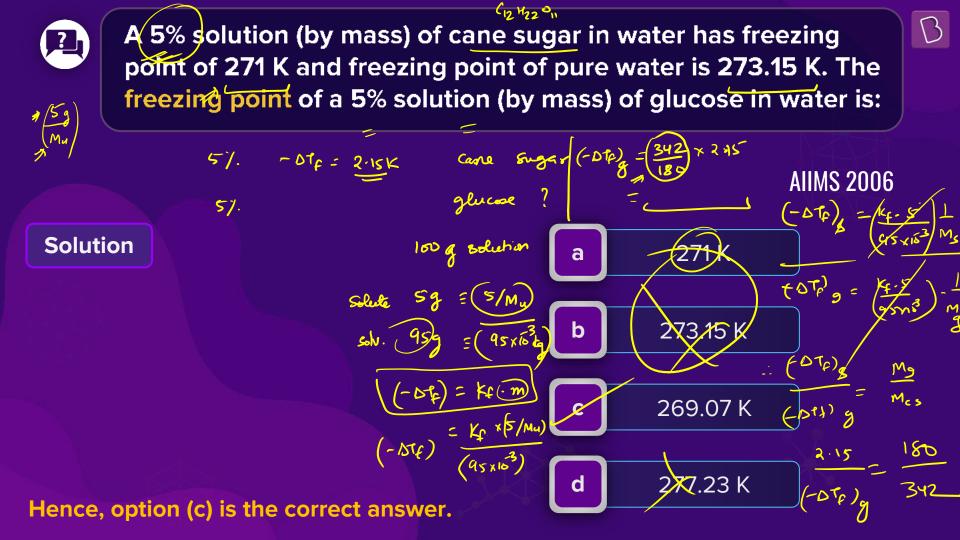
During osmosis, flow is from both sides of semipermeable membrane with unequal flow rates.

Hence, option (d) is the correct answer.



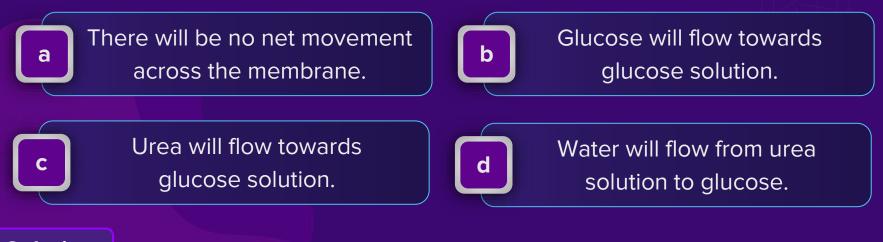
Hence, option (b) is the correct answer.







If 0.1 M solution of glucose and 0.1 M solution of urea are placed on two sides of the semipermeable membrane to equal heights, then it will be correct to say that:



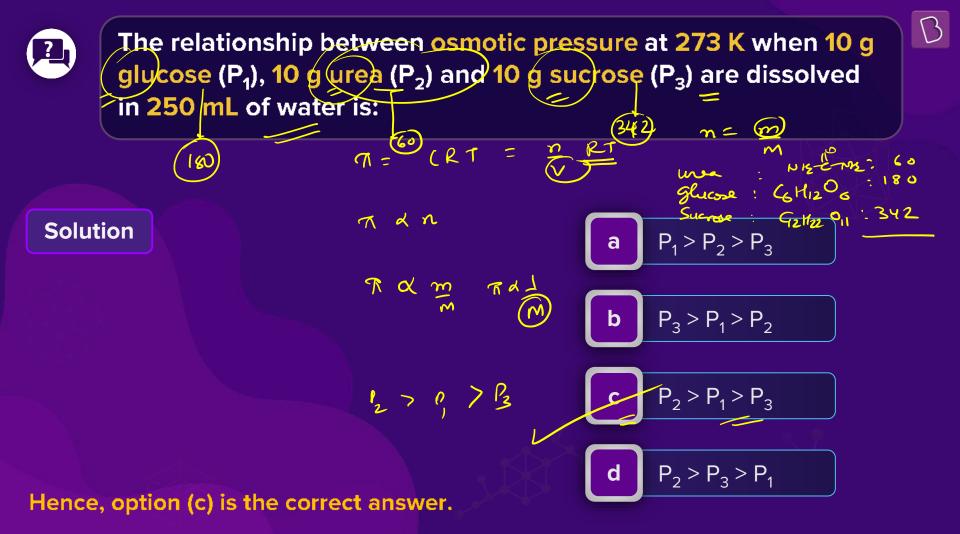
Solution

 π = CRT ; Since , concentration is same (Isotonic solution), so π will be same and there will be no net movement across the membrane. Hence, option (a) is the correct answer.



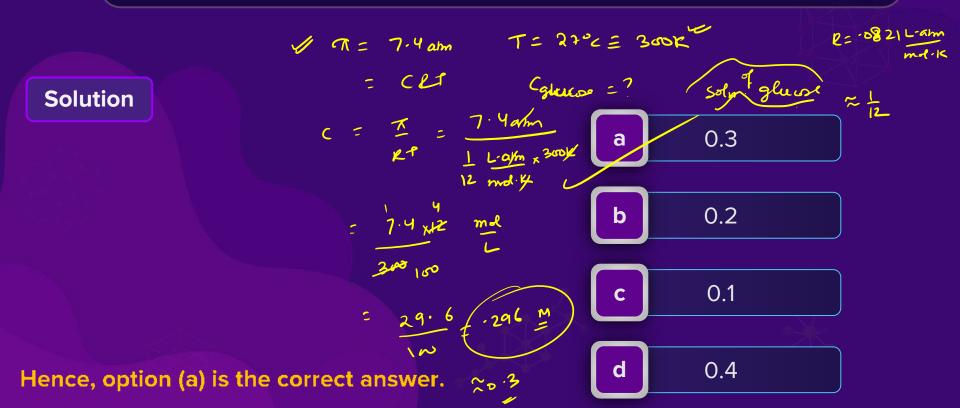
O. IM glucose orbition at 27°C (305K) Find to osmitic promise (A). Given: $R = 0.0821 \frac{1-ahm}{md.K} \approx \frac{1}{12} \frac{1.ahm}{mot.K}$ Solution $\pi = CRP$ = 0.1 mol x 12 K-am x 300 K K 12 mol-K $=\frac{30}{12}$ alm = (2.5ahm)







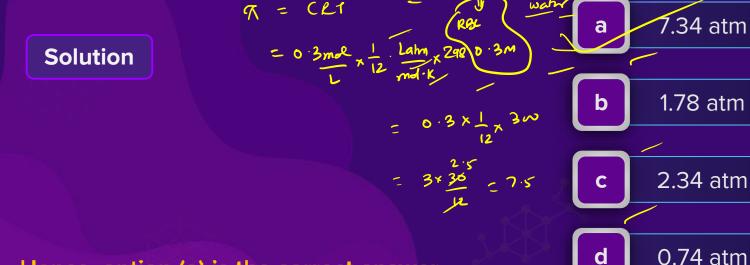
Osmotic pressure of blood is 7.40 atm at 27 °C. Number of moles of glucose to be used per litre for an intravenous injection that is to have the same osmotic pressure as blood is:





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

- - 05



Hence, option (a) is the correct answer.



Isotonic, Hypotonic, & Hypertonic Solutions







B

Based on the difference in osmotic pressure

Isotonic solution

Hypotonic solution

2

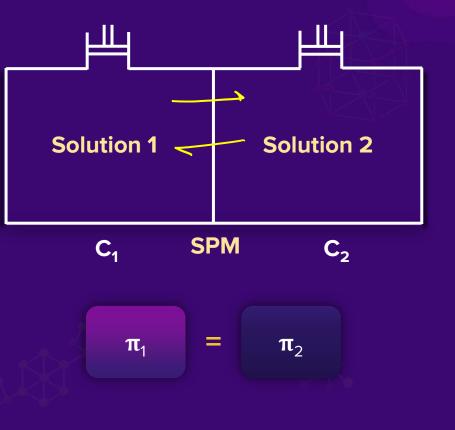
3

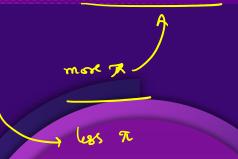
Hypertonic solution



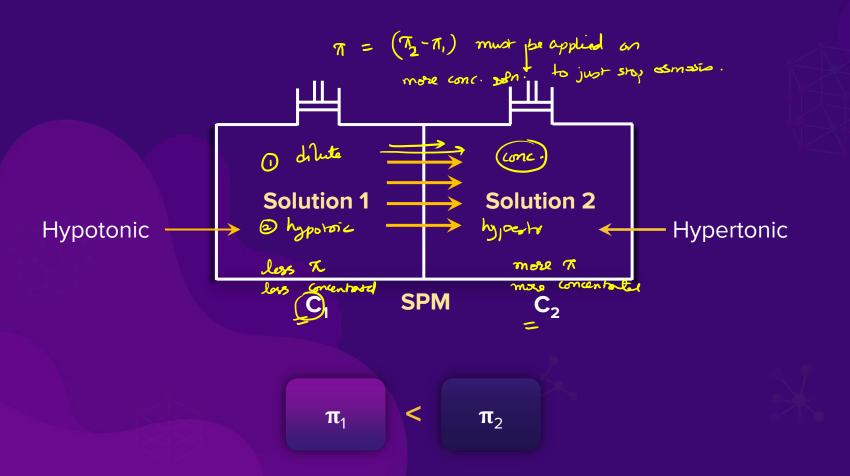
Isotonic Solution

Two solutions having same osmotic pressure are considered as isotonic solution.

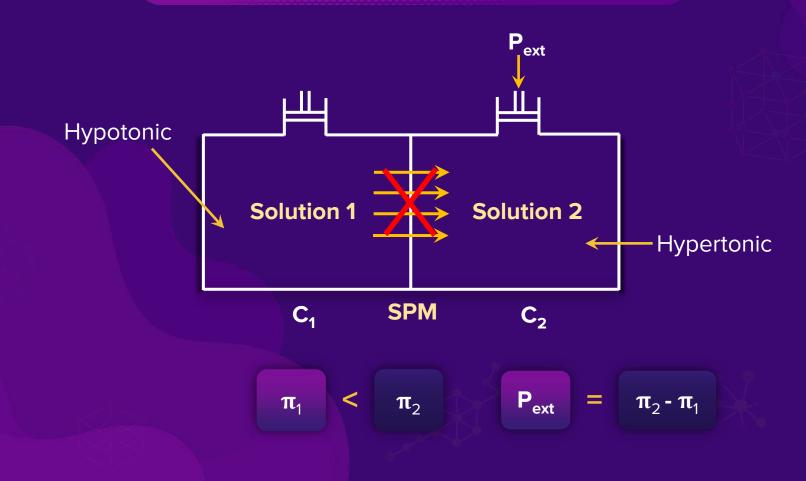




If two solutions '1' and '2' are such that $\pi_2 > \pi_1$, then '2' is called hypertonic solution and '1' is called hypotonic solution.



Pressure is applied on the hypertonic solution to stop the flow of solvent particles.



Types of Solutions

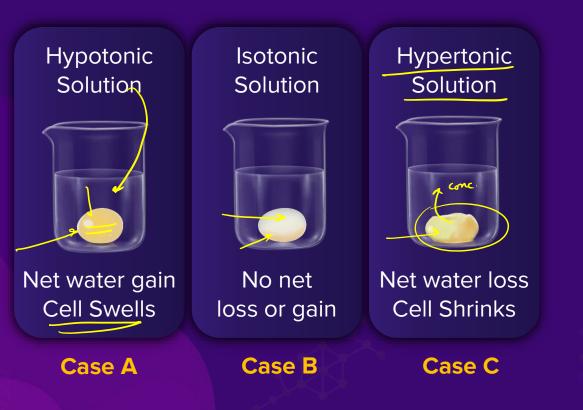


Illustration of hypotonic, hypertonic, and isotonic solutions

The white shell of an egg is carefully removed so that a semipermeable membrane is obtained on the egg.

- When this egg is placed in a solution of low concentration like corn syrup/vinegar/any solute, then the water flows into the egg and the egg swells. This solution is known as a hypotonic solution as shown in case A.
- When this egg is placed in a solution with equal concentration like water, no net loss or gain of water occurs. This solution is known as an isotonic solution, as shown in **case B**.
- When this egg is placed in a solution with higher concentration like boric acid, water will flow out of the egg, and the egg will shrink. Such a solution is known as a hypertonic solution as in **case C**.

Types of Solutions



Plasmolysis

When the cell is placed in a solution having its osmotic pressure greater than that of the cell sap, **water passes out of the cell** due to osmosis.

Consequently, the **cell material shrinks** gradually. The gradual shrinking of the cell material is called **plasmolysis**.





Why do mangoes **shrivel** into pickle in concentrated salt solution?

Because water from mangoes flow to concentrated salt solution because of osmosis.



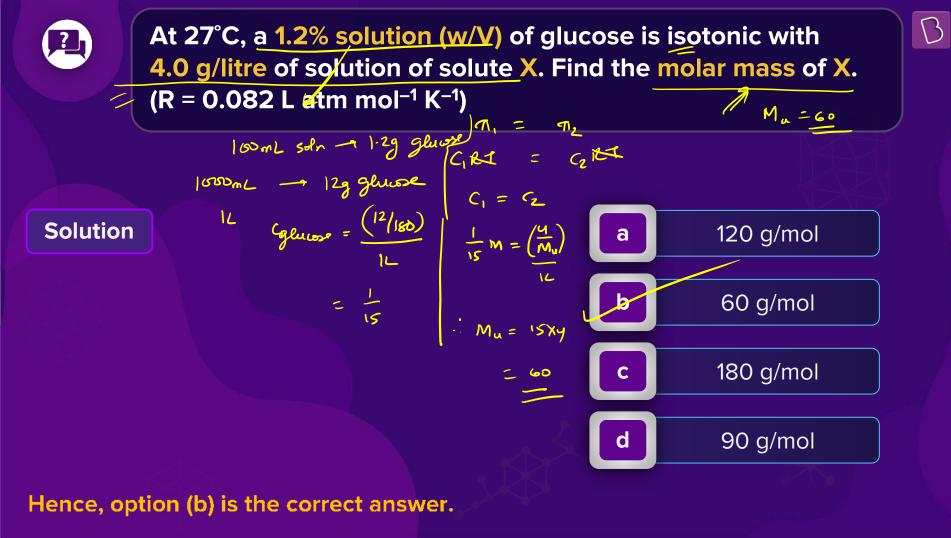
Reverse Osmosis (R.O.)



If the **pressure applied** on the solution side is **more than the osmotic pressure** of the solution, then the solvent particles will move from **solution to solvent side**.

P_{ext} > π

- In R.O. filters high pressure is applied on the impure water so only pure water flows through SPM and collected.
- Used in desalination of sea-water.



Application of Osmotic Pressure

Determination of **molecular mass** of the solute.



• w is mass of solute

a.

- V is volume of the solution
- \bullet **I** is osmotic pressure of the solution
- T is temperature
- R is universal gas constant



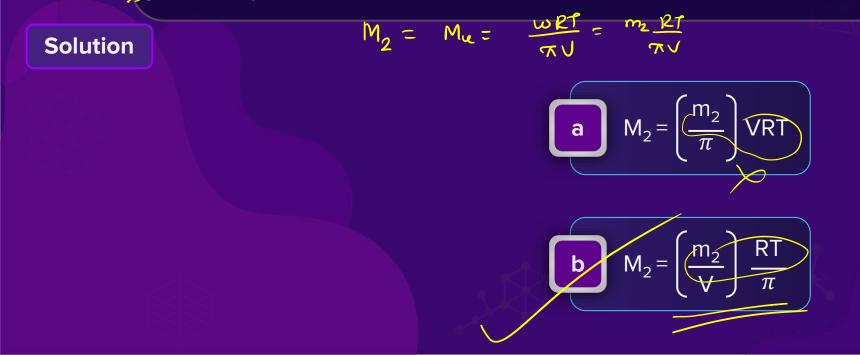
Application of Osmotic Pressure

Widely used to **determine molar masses** of proteins and other biomolecules, as they are generally not stable at higher temperatures

This method has the advantage over other methods as pressure measurement is around the **room temperature**.

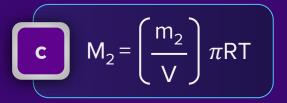


A solution contains non-volatile solute of molecular mass M_2 . Which of the following can be used to calculate the molecular mass of solute in terms of osmotic pressure? (m₂ = mass of solute, V = volume of solution, π = osmotic pressure)





A solution contains non-volatile solute of molecular mass M_2 . Which of the following can be used to calculate the molecular mass of solute in terms of osmotic pressure? (m_2 = mass of solute, V = volume of solution, π = osmotic pressure)

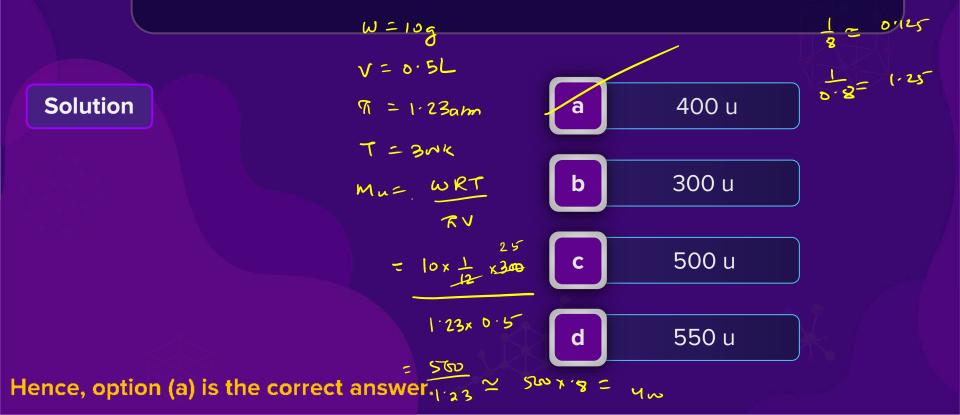


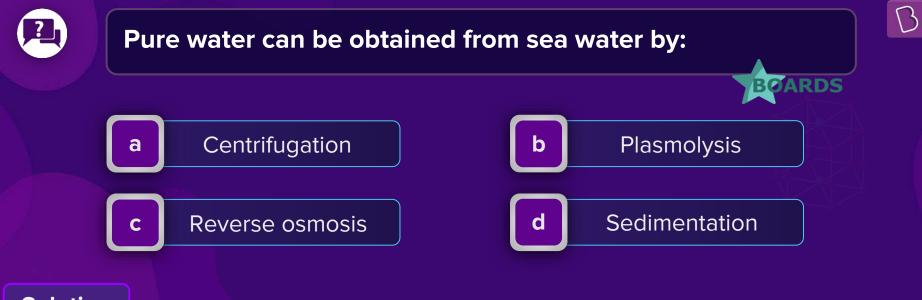
d
$$M_2 = \left(\frac{m_2}{V}\right) \frac{\pi}{RT}$$

Hence, option (b) is the correct answer.



If 10 g of an unknown substance (non-electrolytic) is dissolved to make 500 mL of solution, then osmotic pressure at 300 K is observed to be 1.23 atm. Find molecular weight of solute. 15





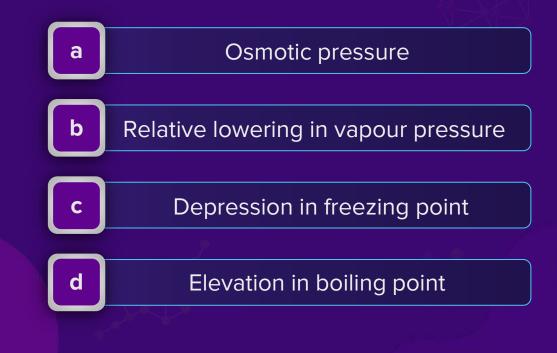
Solution

Reverse osmosis is used in desalination of seawater. Salts are removed by passing seawater through SPM.

Hence, option (c) is the correct answer.



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



B

Solution

Osmotic pressure is widely used to determine molar masses of proteins and other biomolecules, as they are generally not stable at higher temperatures. This method has the advantage over other methods as pressure measurement is around the room temperature.

Hence, option (a) is the correct answer.

Application of Osmotic Pressure

b. Dialysis

Artificial kidney **removes waste** products from blood through osmosis.

 In dialysis selectively permeable membrane is used and it allows solvent as well as small solute particles but it does not allow big solute particles to pass through it such as RBC (red blood cells) and WBC (white blood cells). Dissolved impurities from blood such as urea can be passed through SPM and removed.