Welcome to

Aakash + BYJU'S LIVE

Solutions and colligative properties

Solution

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

By convention

Solvent - Constituent present in the **largest** amount.

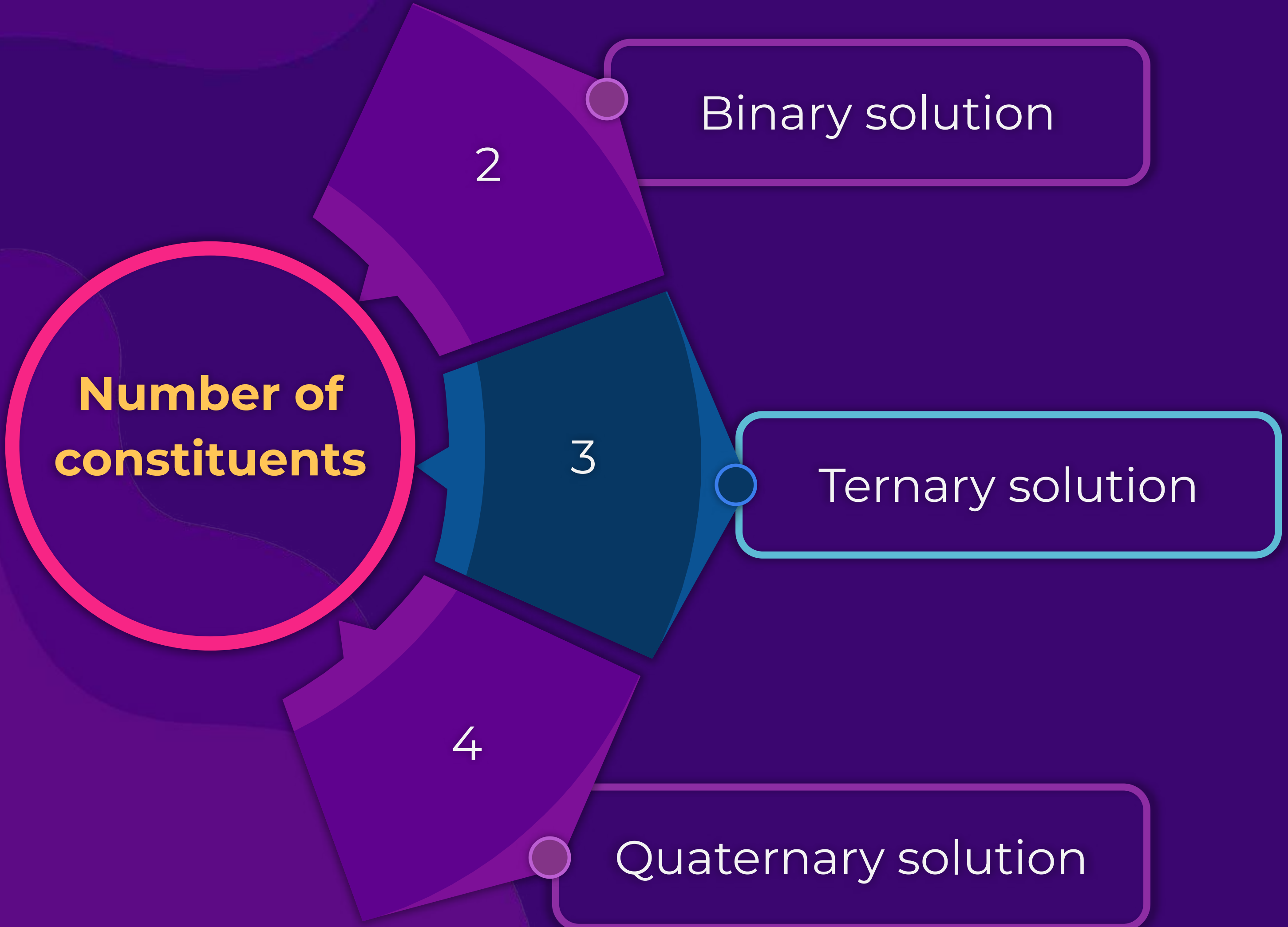
Solute - Constituents present in **relatively small** amounts.

Note

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.

Solvent determines the **physical state** in which the solution exists.

Types of solutions



Number of constituents

2 Binary solution

3 Ternary solution

4 Quaternary solution

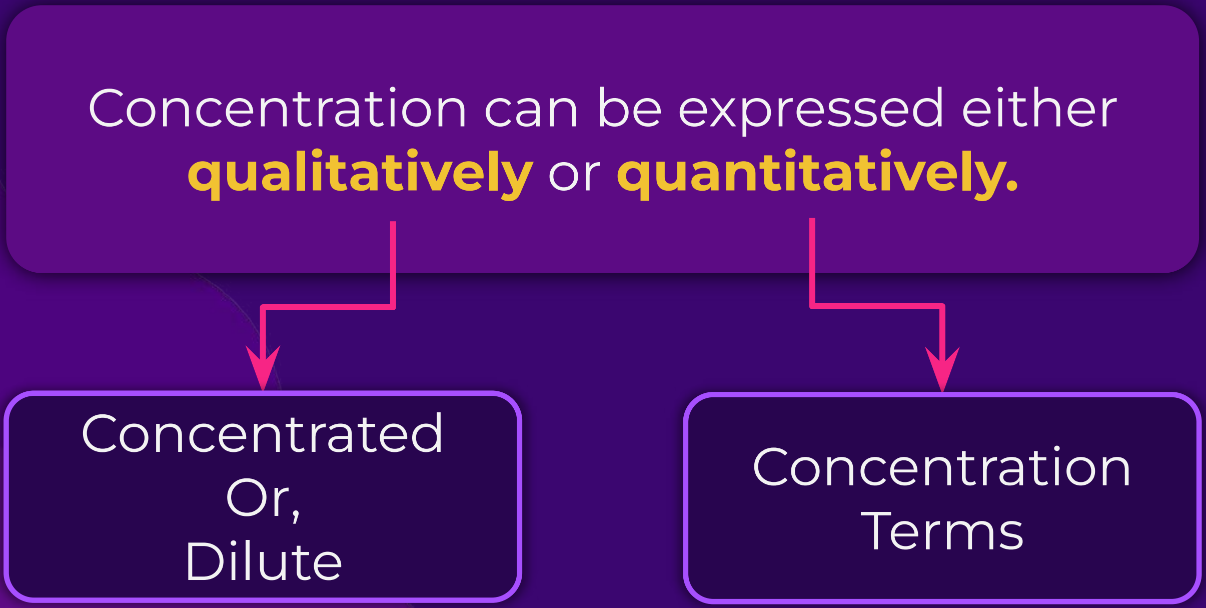
Liquid solutions

Gas in liquid
e.g., carbonated drinks

Liquid in liquid
e.g., alcohol and water

Solid in liquid
e.g., salt in water

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



Concentration can be expressed either **qualitatively** or **quantitatively.**

Concentrated
Or,
Dilute

Concentration
Terms

Percentage Concentration Terms

% w/w	**% w/V**	**% V/V**
Amount of **solute** in grams dissolved **per 100 g** of solution.	Amount of **solute** in grams dissolved **per 100 mL** of solution.	Volume of a **solute (in mL)** dissolved **per 100 mL** of solution.
$\% \text{ w/w} = \frac{\text{Weight of solute (g)}}{\text{Weight of solution (g)}} \times 100$	$\% \text{ w/V} = \frac{\text{weight of solute (g)}}{\text{Volume of solution (mL)}} \times 100$	$\% \text{ V/V} = \frac{\text{volume of solute (mL)}}{\text{Volume of solution (mL)}} \times 100$

Other Concentration Terms

- Strength (S)
- Molarity (M)
- Molality (m)
- Normality (N)
- ppm
- Mole fraction (χ)

Strength (S)

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

$$\text{Strength (S)} = \frac{\text{Weight of solute (g)}}{\text{Volume of solution (L)}}$$

Molarity (M)

Number of **moles** of **solute** per litre of solution.

$$M = \frac{\text{No. of moles of solute (n)}}{\text{Volume of solution (L)}}$$

Molality (m)

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

$$m = \frac{\text{No. of moles of solute (n)}}{\text{Mass of solvent (kg)}}$$

Normality (N)

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

$$\textbf{Normality} = \frac{\text{Number of gram equivalents of solute}}{\text{Volume of solution (L)}}$$

$$\textbf{Number of gram equivalents} = \frac{\text{Mass of the species}}{\text{Gram equivalent mass}}$$

$$= \frac{\text{Mass of the species}}{\dfrac{\text{Molar mass}}{\text{n - factor}}}$$

‘n’ - factor

- For oxidising/ reducing agents
- For acid / base
- For salt

For Oxidising/Reducing Agents

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

$$5e^- + 8H^+ + MnO_4^- \longrightarrow Mn^{2+} + H_2O$$

n-factor = 5

For Acid/Base and Salts

Number of moles of **H^+** ions displaced/OH^- ions displaced per mole of acid/base.

For simple salts, n-factor is a total **charge on cations** or a total **charge on anions.**

Example: H_2SO_4

n-factor = 2

Example: NaOH

n-factor = 1

Example: $Al_2(SO_4)_3$

n-factor = charge on the cation
= 2 × 3 = 6

Parts per Million (ppm)

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

$$\text{ppm (w/w)} = \frac{\text{Weight of solute (g)}}{\text{Weight of solution (g)}} \times 10^6$$

$$\text{ppm (w/V)} = \frac{\text{Weight of solute (g)}}{\text{Volume of solution (mL)}} \times 10^6$$

$$\text{ppm (moles/moles)} = \frac{\text{Moles of solute}}{\text{Moles of solution}} \times 10^6$$

Mole Fraction (χ)

Ratio of the **number of moles** of a **particular component** to the **total number of moles** of all the components.

For a binary solution,

$$\chi_{\text{solute}} = \frac{\text{Moles of solute}}{\text{Total moles in solutions}} = \frac{n}{n + N}$$

$$\chi_{\text{solvent}} = \frac{\text{Moles of solvent}}{\text{Total moles in solutions}} = \frac{N}{n + N}$$

$$\chi_{\text{solute}} + \chi_{\text{solvent}} = 1$$

Based on the amount of the solute dissolved

Unsaturated

It is a solution in which **more amount** of solute **can be dissolved** at a particular temperature.

Saturated

A solution in which no more solute **can be dissolved** at a particular temperature.

Supersaturated

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

Solubility

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:

1. **Nature** of the solute and solvent
2. **Temperature**
3. **Pressure**

1. Nature of Solvent & Gas

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

E.g., **HCl** is highly soluble in **water.**

Like dissolves like

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

2. Effect of Temperature

Generally,

Dissolution of gas in liquid is **exothermic**

Temperature ↑

Solubility ↓

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 waters rather than in warm waters.

3. Effect of Pressure (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.

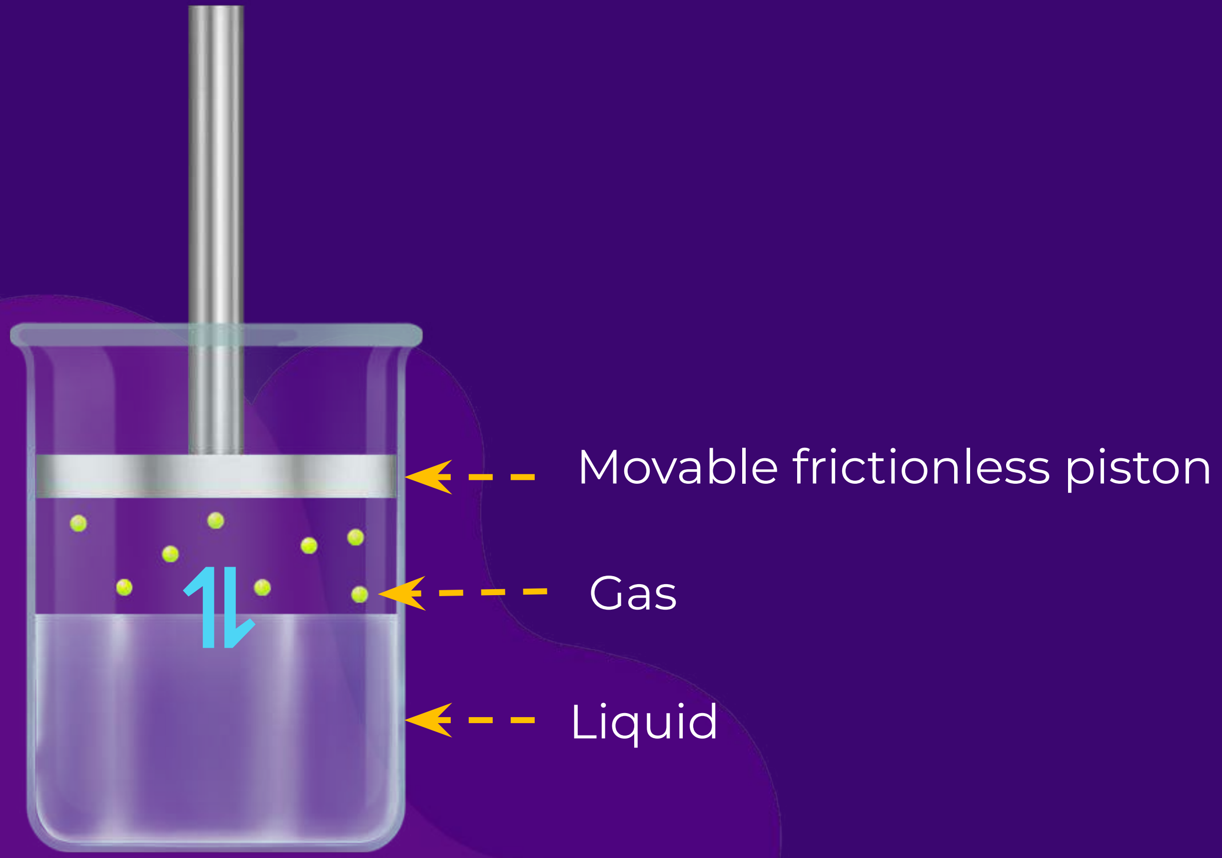
$$\mathcal{X} \propto P$$

$$P = K_H \mathcal{X}$$

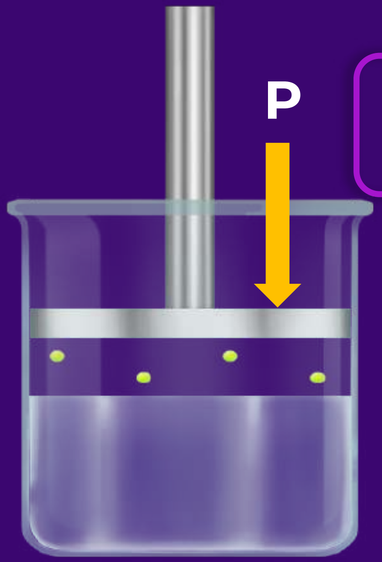
P is the **partial pressure** of gas in equilibrium with the solution.

K_H is Henry's law **constant.**

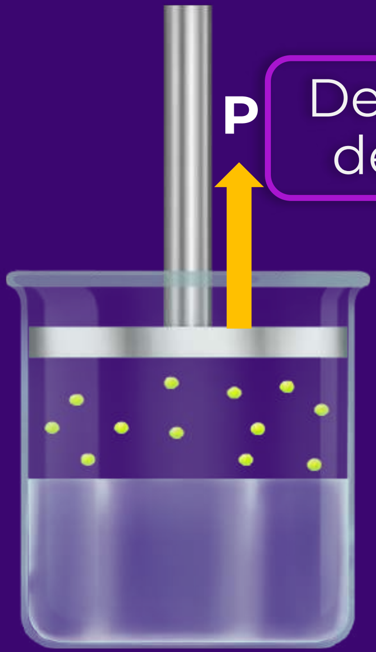
$\mathcal{X}$ is the **mole fraction** of the unreacted gas in the solution.



Gas is in equilibrium with the liquid solution



Increase in pressure increases solubility



Decrease in pressure decreases solubility

Characteristics of Henry’s Law Constant

a Same unit as that of **pressure**: **torr or bar**

b Different gases have **different K_H** for the **same solvent**.

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

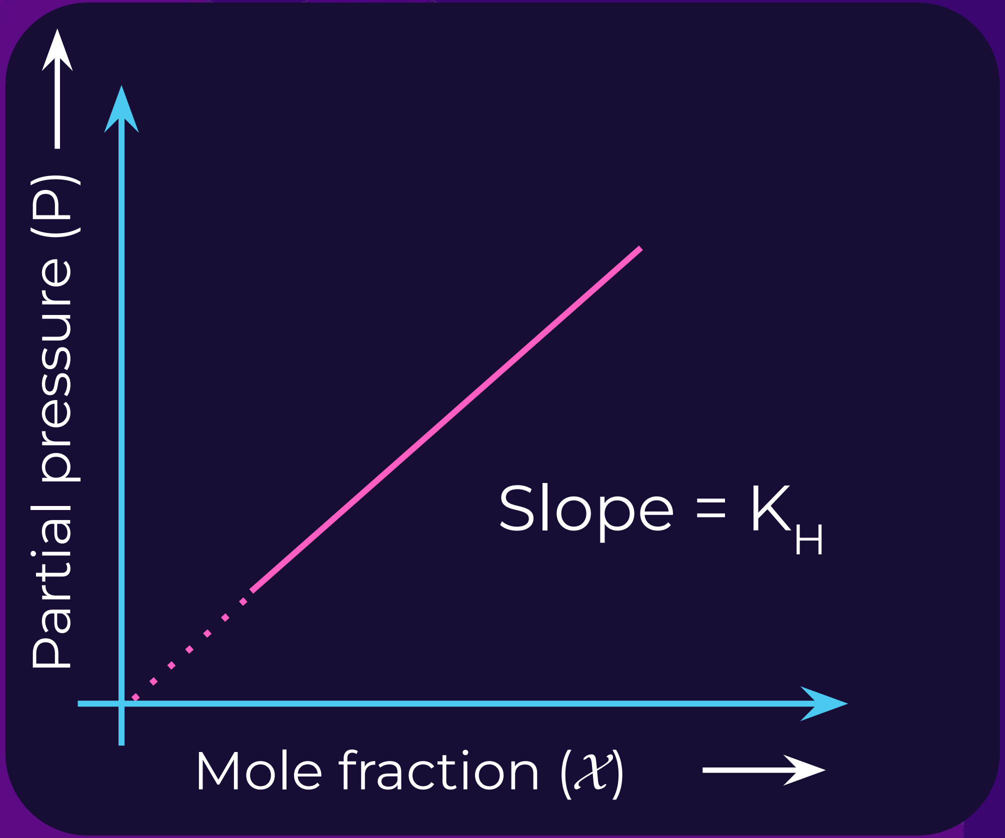
d K_H value **increases** with increase in **temperature**.

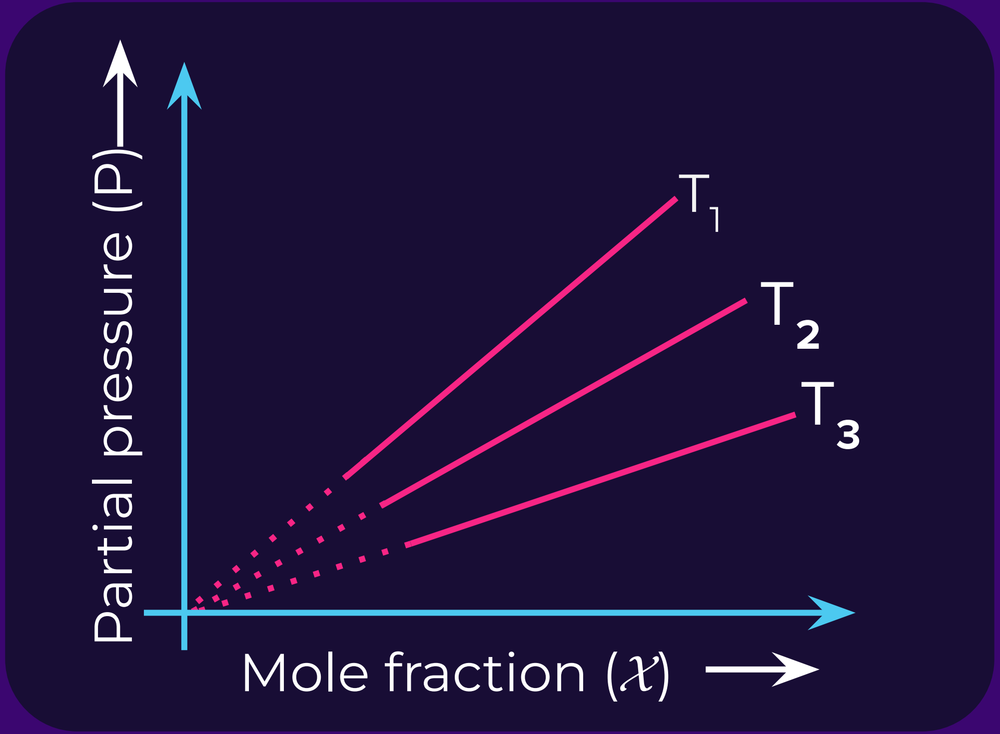
e **Higher** the value of K_H of a gas, **lower** will be its **solubility.**

Since, $x = \dfrac{P}{K_H}$

Graphical Analysis (Henry's Isotherm)

Plot of P vs $\mathcal{X}$ is a straight line passing through the origin with **slope equal to K_H**.





$T_1 > T_2 > T_3$

$K_{H_1} > K_{H_2} > K_{H_3}$

Note

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.

Application of Henry’s Law

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

(b) At high altitudes, the partial pressure of **oxygen is less** than that at the ground level.

(c) **Scuba diving tanks** are diluted with helium.

Low blood oxygen level causes **anoxia**.

Application of Henry's Law

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

Increased pressure increases solubility of atmosphere gases in the blood which are released when the diver comes towards the surface. 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:

1. Pressure of the gas is **not too high**.
2. Temperature is **not too low**.
3. The gas should **not undergo** any **chemical reaction** with the solvent.
4. The gas should **not undergo dissociation** in solution.

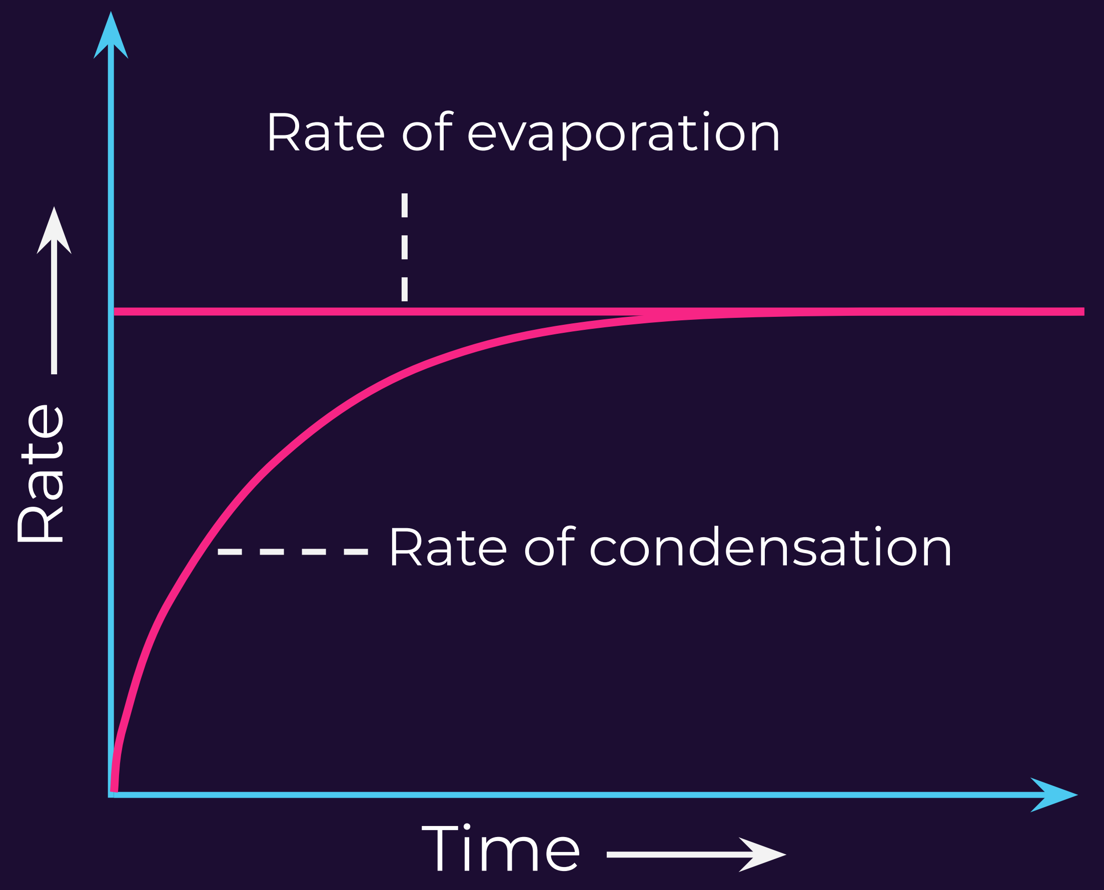
Vapour Pressure

Evaporation of a Liquid in a Closed Container

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.

Evaporation and Condensation



An **equilibrium is set up rapidly** 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

$H_2O\,(l) \rightleftharpoons H_2O\,(g)$

$K_p = P_{eq}\,(H_2O\,(g))$

K_p = V.P.

Vapour Pressure of Solution

Vapour Pressure

Pressure exerted by the vapour of solvent 'A' and solute 'B' in **equilibrium** with the liquid phase.

(a) Vapour pressure of a liquid **does not** depend on:

1 **Amount** of liquid taken

2 **Surface area** of the liquid

3 **Volume** or shape of the container

Vapour Pressure of Solution

(b) It depends upon the **nature** of the liquid

Intermolecular attractive forces ↓ **Vapour pressure** ↑ **Boiling point** ↓

Loosely held molecules escape more easily into the vapour phase.

Boiling Point

Temperature at which the **vapour pressure** of a liquid is **equal** to the **external pressure**.

At normal b.p., the vapour pressure of the pure liquid = 1 atm

Vapour Pressure of Solution

(c) Temperature

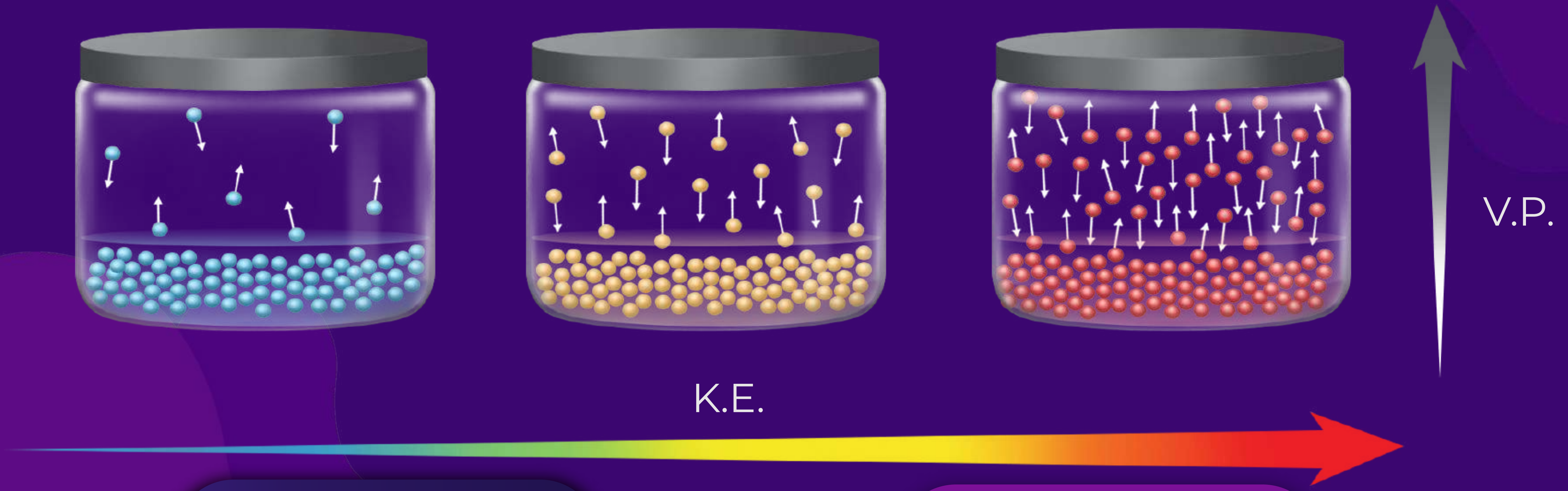
Temperature ↑

Vapour pressure ↑

More molecules from the liquid have **enough K.E.** to escape from the surface of the liquid.

Temperature at which the **vapour pressure** of a liquid is **equal** to the **external pressure**.

At normal b.p., the vapour pressure of the pure liquid = 1 atm



Temperature ↑

K.E. of particles ↑

As the **temperature** of a liquid increases, the kinetic energy of its molecules also increases. As the kinetic energy of the molecules increases, the number of molecules transitioning into a **vapor** also increases, thereby increasing the **vapor pressure**. In the first container (extreme left) the temperature is lowest and in the third one (extreme right) the temperature is maximum, consequently the number of molecules shown in the container is also maximum.

Temperature

$H_2O\ (l) \rightleftharpoons H_2O\ (g)$

$\Delta H > 0$

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

Raoult's Law

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

$P_A \propto x_A$

$P_A = x_A P_A^\circ$

P_A	Partial vapour pressure of component 'A'
x_A	Mole fraction of component 'A' in solution
P_A°	Vapour pressure of pure component 'A' at a given temperature

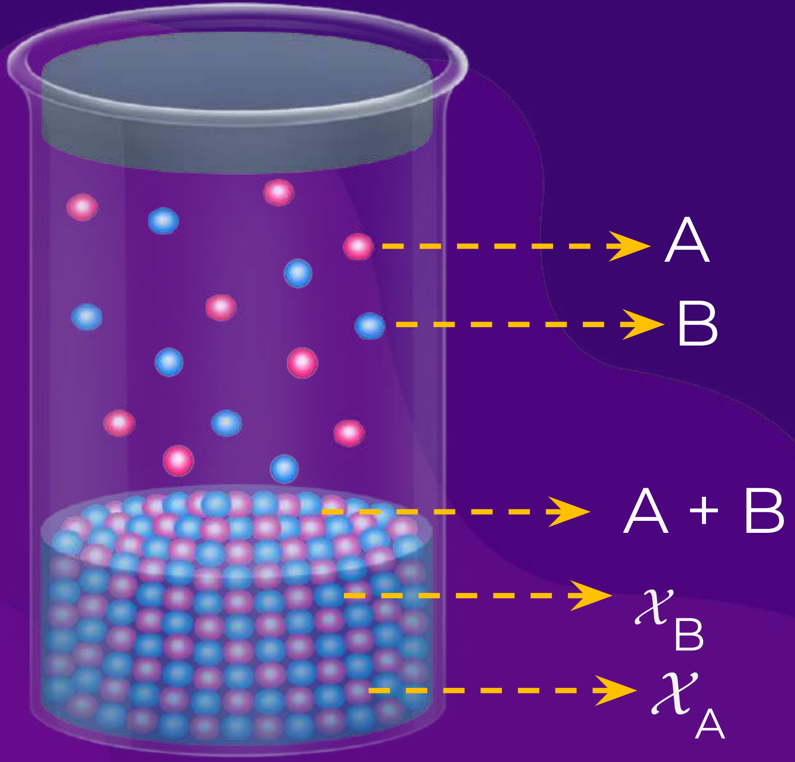
For Binary Solutions of A & B

$P_A = \chi_A P_A^o$

$P_B = \chi_B P_B^o$

$P_T = P_A + P_B$

$P_T = \chi_A P_A^o + \chi_B P_B^o$



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

Relation between Total Pressure vs Mole Fraction

$$P_T = \chi_A P_A^o + \chi_B P_B^o$$

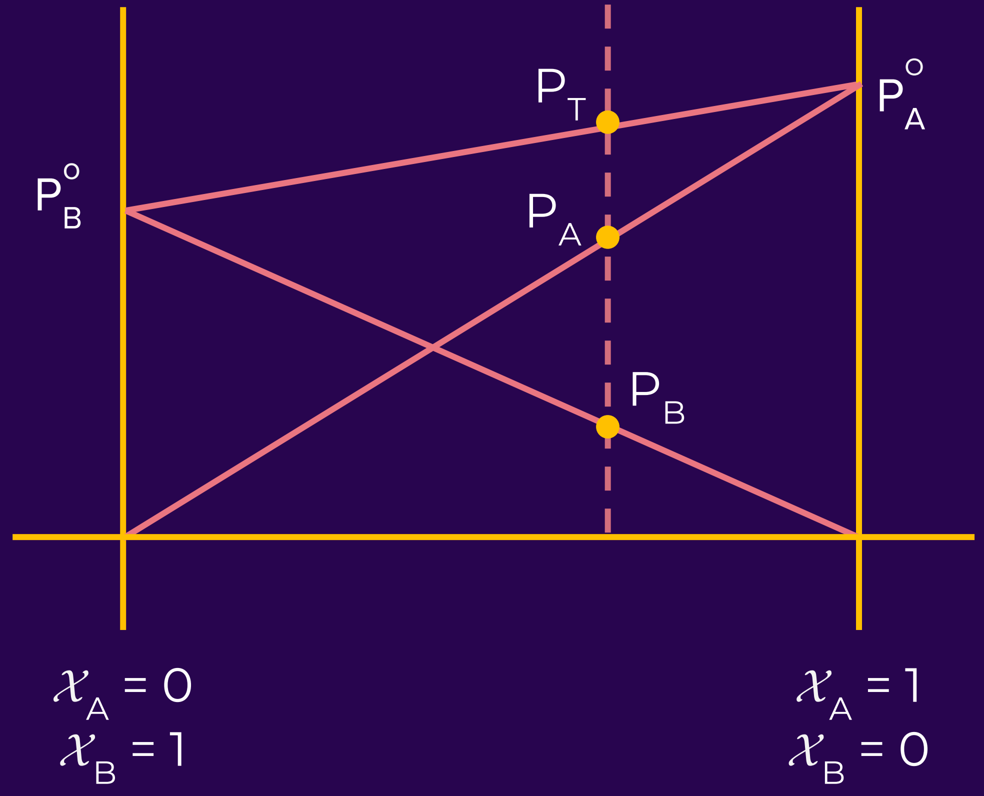
$$\chi_A + \chi_B = 1$$

$$P_T = (P_A^o - P_B^o)\chi_A + P_B^o$$

This represents equation of a **straight line** of P_T vs χ_A

If $P_A^o > P_B^o$ → A is more volatile than B

b.p. of A < b.p. of B



Composition of Vapour Phase

y_A Mole fraction of A in vapour phase above the solution

y_B Mole fraction of B in vapour phase above the solution

$$P_A = y_A P_T$$

Dalton's Law

$$P_A = x_A P_A^{\circ}$$

Raoult's Law

Similarly,

$$P_B = y_B P_T = x_B P_B^{\circ}$$

P_T in Terms of Composition of Vapour Phase

$$x_A + x_B = 1$$

$$\frac{y_A P_T}{P^o_A} + \frac{y_B P_T}{P^o_B} = 1$$

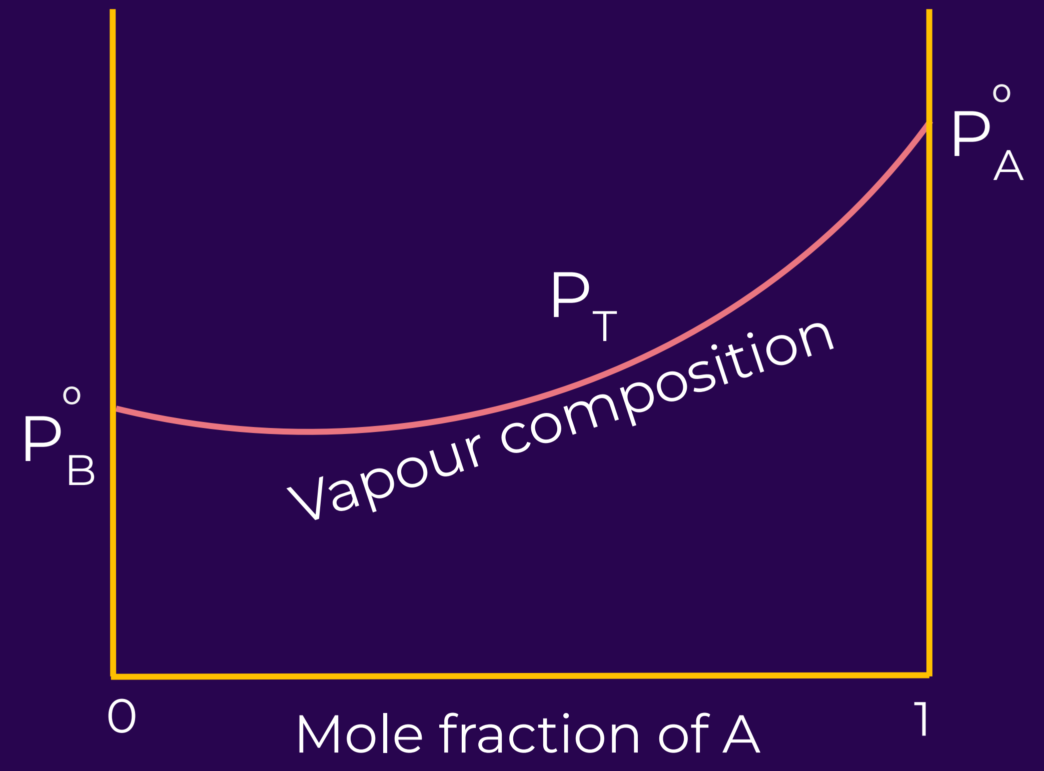
$$\Rightarrow \frac{1}{P_T} = \frac{y_A}{P^o_A} + \frac{y_B}{P^o_B}$$

$$\frac{1}{P_T} = \frac{y_A}{P^o_A} + \frac{y_B}{P^o_B}$$

$$= \frac{y_A}{P^o_A} + \frac{1 - y_A}{P^o_B}$$

$$P_T = \frac{P^o_A P^o_B}{P^o_A + (P^o_B - P^o_A)\, y_A}$$

P_T in Terms of Composition of Vapour Phase

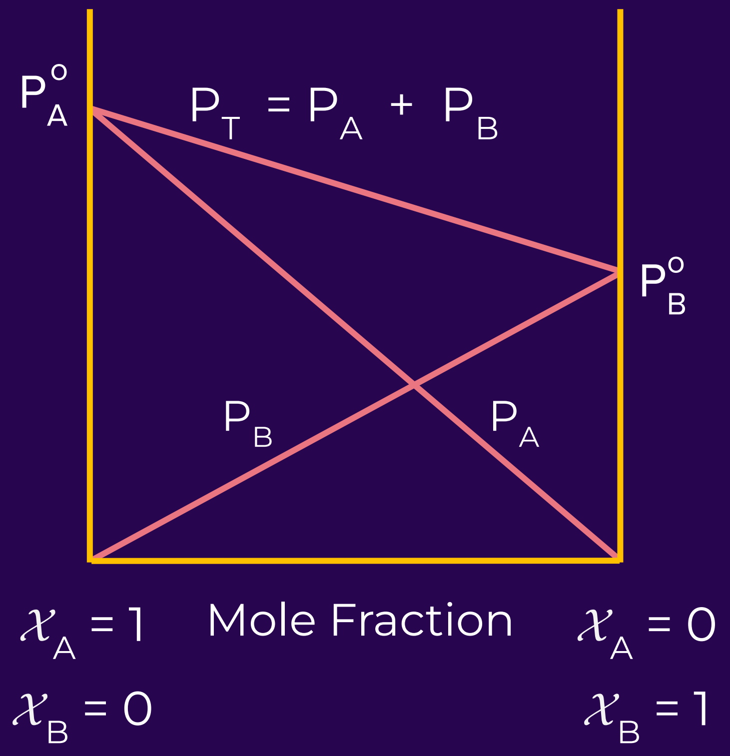


Did You Know?

Compositions of the liquid and vapour that are in **mutual equilibrium** are **not necessarily the same**.

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

Characteristics of ideal solution



(i) Ideal Solutions **obey Raoult's law** over the entire range of concentration

(ii) If the forces of attraction between **A—A, B—B is similar to A—B**, then A and B will form ideal solution.

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

(iv) **$\Delta_{mix}V = 0$**, (1L + 1L = 2L) i.e., there should not be a change in volume on mixing.

Characteristics of ideal solution

(v)

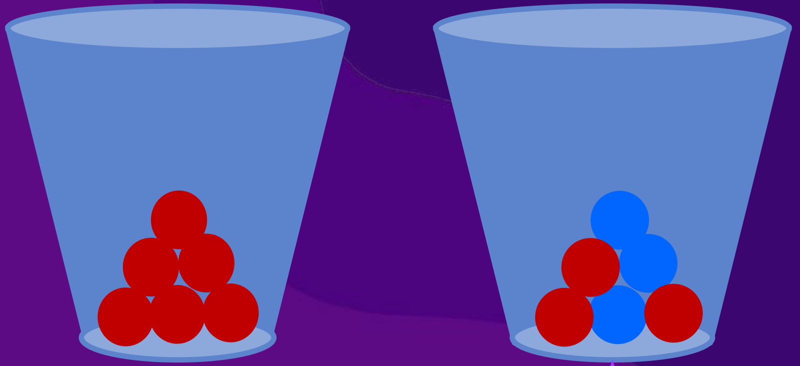
$(\Delta_{mix}S)_{sys} > 0 \Rightarrow$ randomness increases on mixing.

(vi)

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

(vii)

$(\Delta_{mix}S)_{univ} > 0 \Rightarrow$ Mixing is a spontaneous process



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

Examples

n-Hexane and n-Heptane

Benzene and Toluene

Ethyl bromide and Ethyl iodide

Chlorobenzene and Bromobenzene

Non-Ideal Solution

Solutions that **do not obey Raoult's law** over the entire range of concentration

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

Characteristics:

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

2 $\Delta H_{mix} \neq 0$

3 $\Delta V_{mix} \neq 0$

Non-ideal Solutions

- Positive deviation from Raoult’s Law
- Negative deviation from Raoult’s Law

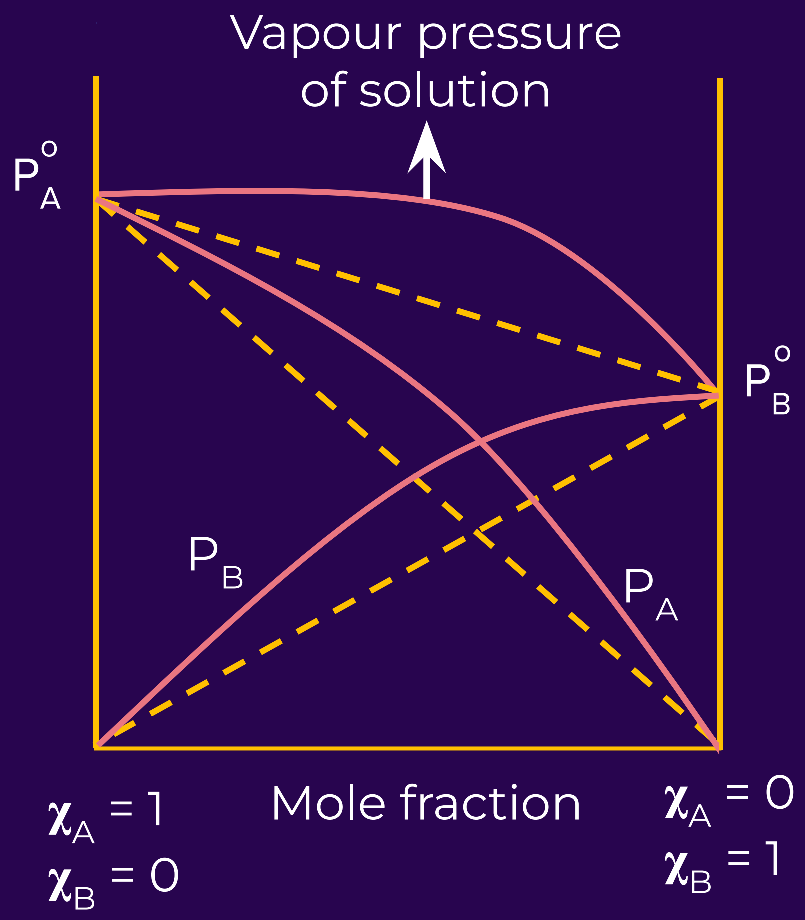
Non-Ideal with Positive Deviation

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.

Non-Ideal with Positive Deviation



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

V.P. ↑ B.P. ↓

b.p. of solution < b.p. of both A and B

Characteristics

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

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

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

3 $\Delta H_{mix} > 0$

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

4 $(\Delta_{mix}S)_{sys} > 0 \Rightarrow$ randomness increases on mixing.

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

6 $(\Delta_{mix}S)_{univ} > 0 \Rightarrow$ Mixing is a spontaneous process

Examples

Water and ethanol

Chloroform and water

Ethanol and acetone

Methanol and chloroform

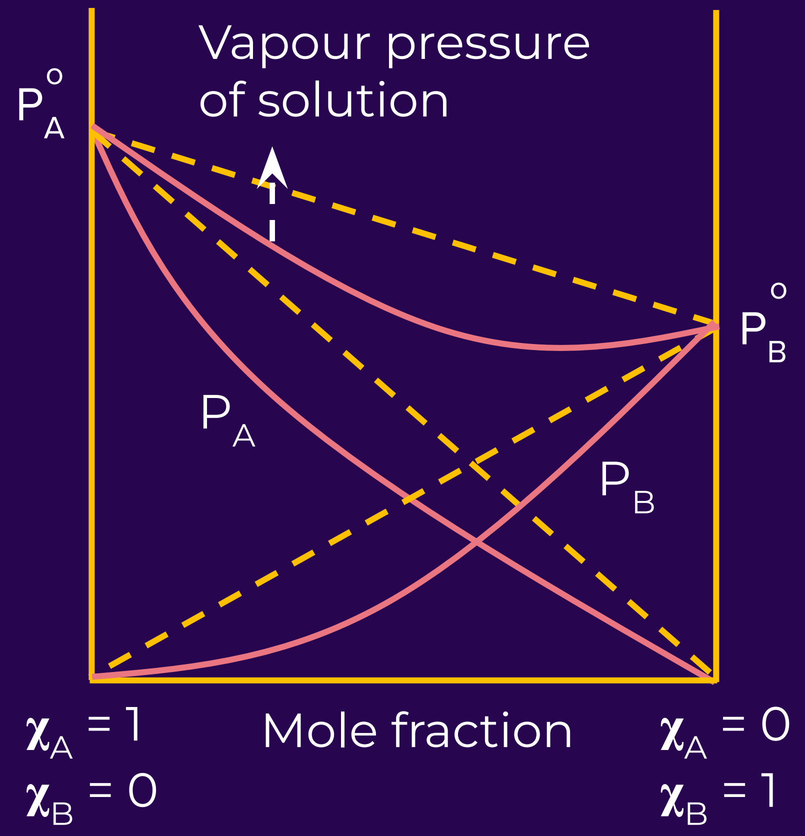
Non-Ideal with Negative Deviation

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.

Non-Ideal with Negative Deviation



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

V.P. ↓ B.P. ↑

B.P. of solution > B.P. of both A and B

Characteristics

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

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

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

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

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Examples

- Chloroform and acetone
- Chloroform and methyl acetate
- H_2O and HCl
- H_2O and HNO_3
- Acetic acid and pyridine
- Phenol and aniline

Comparing Ideal & Non-Ideal Solutions

Ideal solutions	**Non-ideal solutions**	
	Positive deviation	Negative deviation
$P_T = \chi_A P_A^o + \chi_B P_B^o$	$P_T > \chi_A P_A^o + \chi_B P_B^o$	$P_T < \chi_A P_A^o + \chi_B P_B^o$
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
$\Delta_{mix}H = 0$	$\Delta_{mix}H > 0$	$\Delta_{mix}H < 0$
$\Delta_{mix}V = 0$	$\Delta_{mix}V > 0$	$\Delta_{mix}V < 0$

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

Azeotropic Mixtures

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

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.

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.

Azeotropes are of two types:

1. **Maximum boiling azeotropes**
2. **Minimum boiling azeotropes**

Minimum Boiling Azeotropes

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'.

Ethanol - water mixture containing ≈ 95% by volume of ethanol

Chloroform - methanol mixture containing 87.4% chloroform and 12.6% methanol by weight

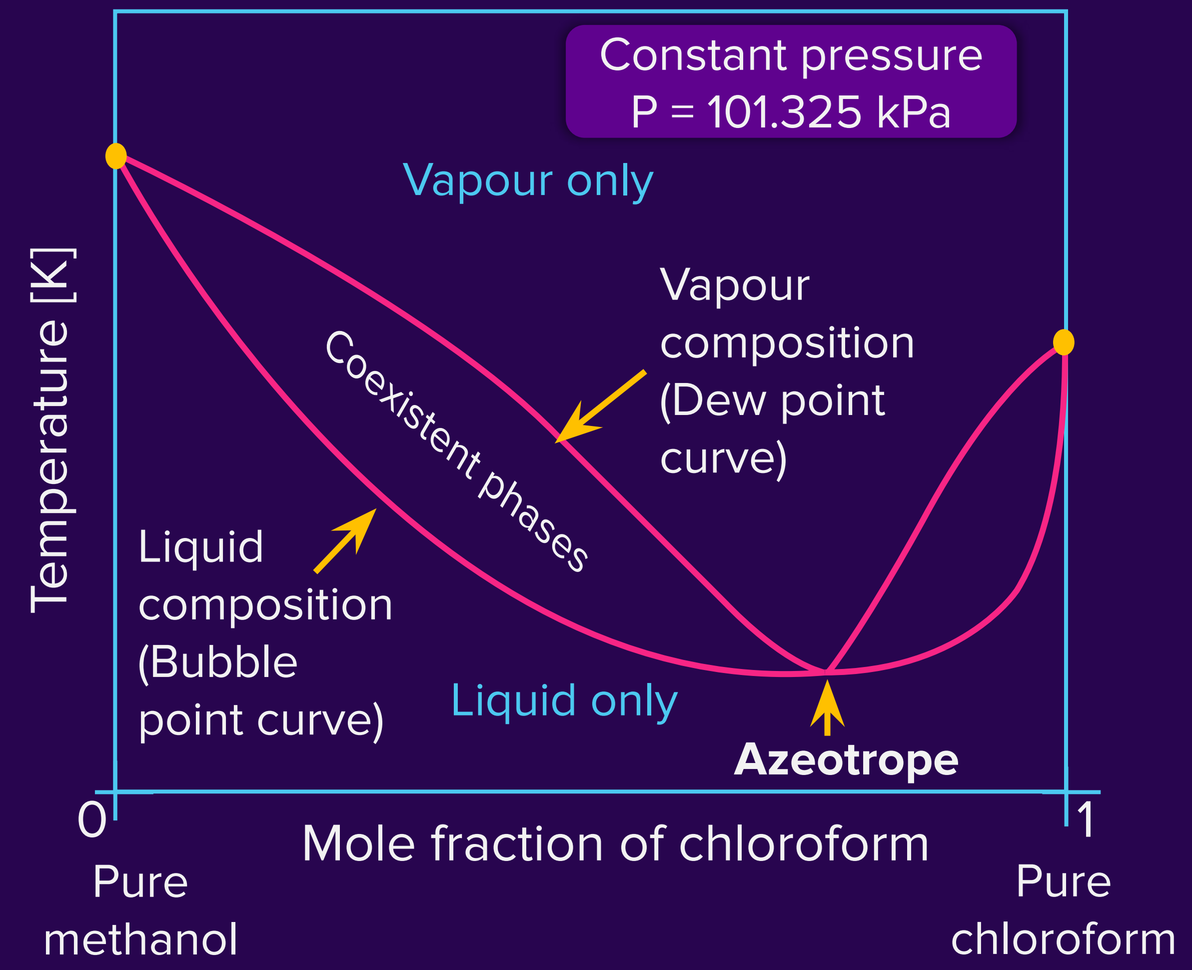
Minimum Boiling Azeotropes

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 components 'A' and 'B'.

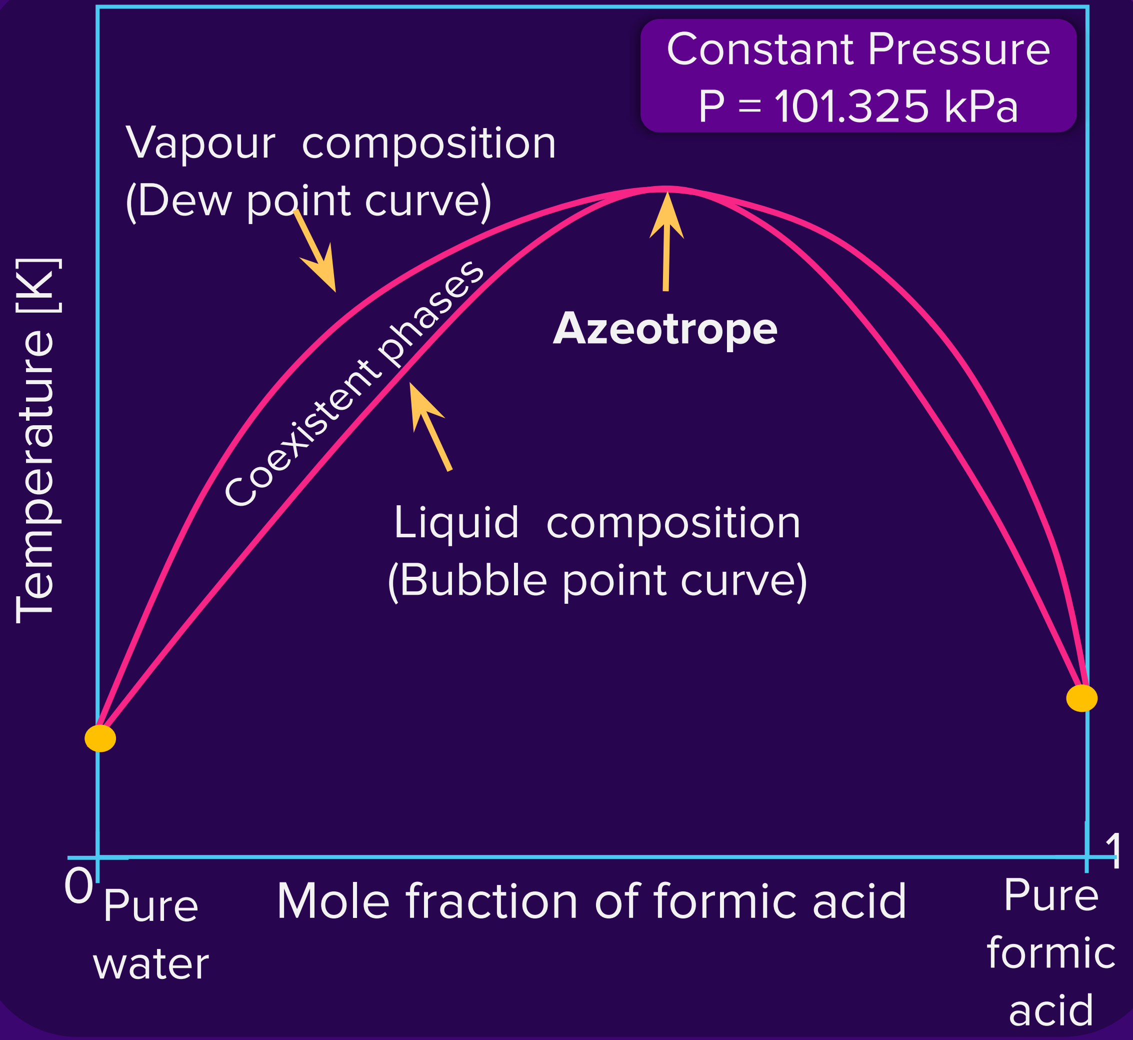
A mixture of HNO_3 and H_2O containing ≈68% HNO_3 and 32% water by mass

Formic acid - water mixture containing 77.6% formic acid and 22.4% water by mass.

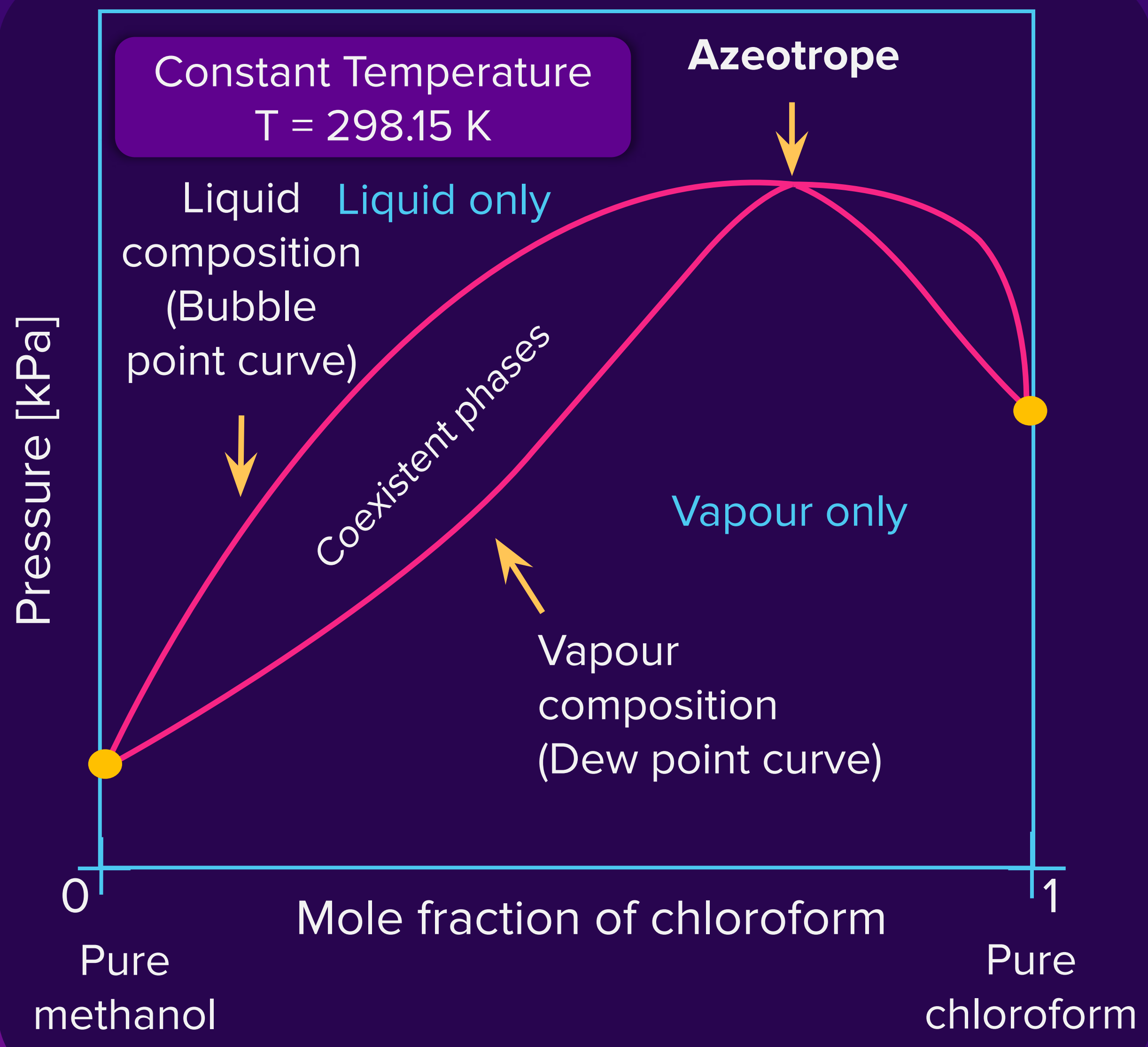
Minimum Boiling Azeotropes



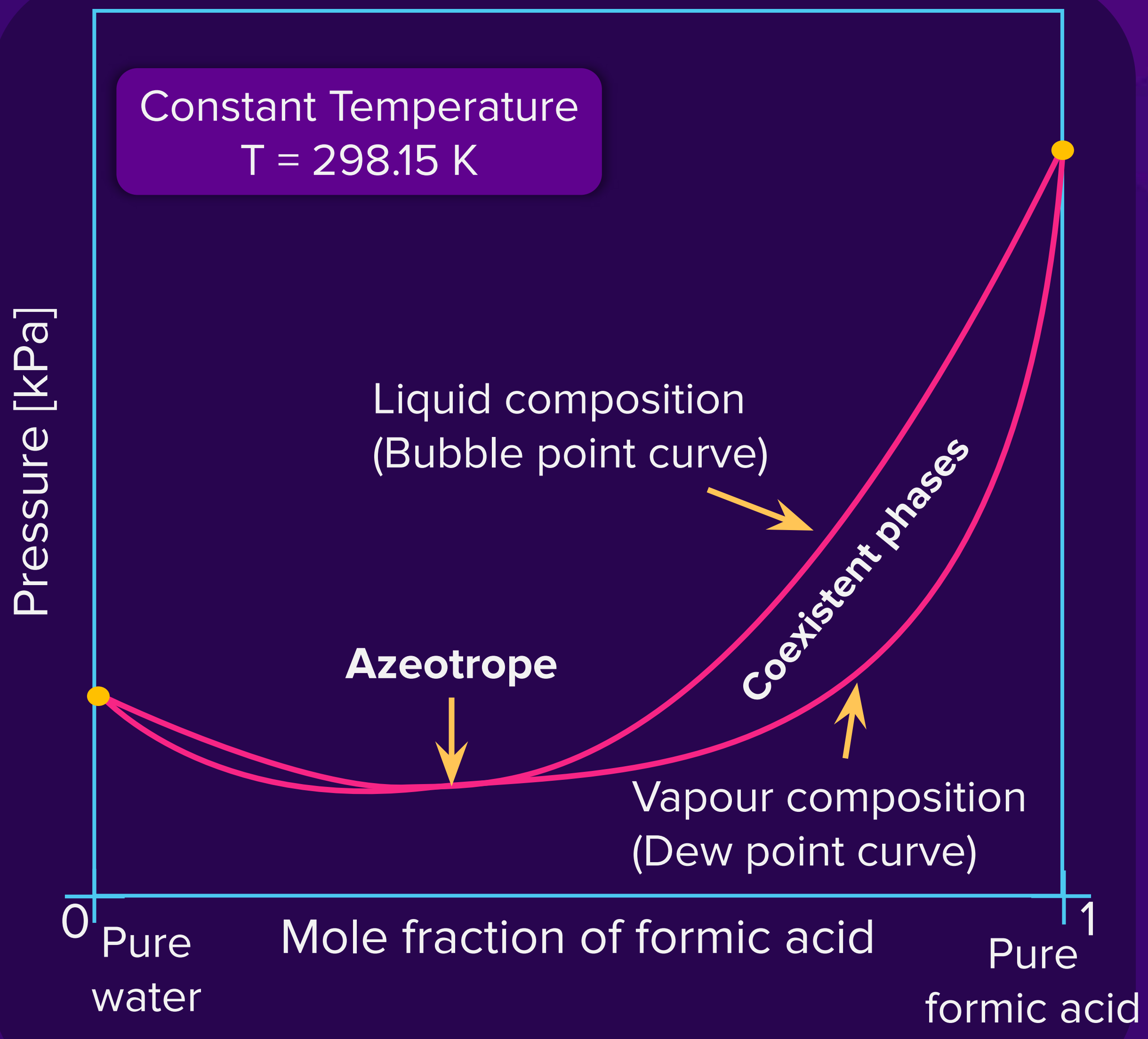
Maximum Boiling Azeotropes



Minimum Boiling Azeotropes



Maximum Boiling Azeotropes



Dissolution & Crystallisation

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

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

At equilibrium

Rate of dissolution = Rate of crystallisation

$$\text{Solute + Solvent} \rightleftharpoons \text{Solution}$$

Equilibrium

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 of Solid in liquid

- Nature of the solvent & the solute
- Temperature
- Pressure

1. Nature of Solvent & Solute

Like dissolves like

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

2. Effect of Temperature

Solute + Solvent $\rightleftharpoons$ Solution

If dissolution is **exothermic**

$\Delta H < 0$

By Le Chatelier's principle,

T ↑ Solubility ↓

Solute + Solvent $\rightleftharpoons$ Solution

If dissolution is **endothermic**

$\Delta H > 0$

By Le Chatelier's principle,

T ↑ Solubility ↑

3. Effect Of Pressure

Pressure **does not have any significant effect on the 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 are known as colligative properties.

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

Colligative Properties

- Relative lowering of the vapour pressure
- Elevation in the boiling point
- Depression in the freezing point
- Osmotic pressure

Abnormal Colligative Property

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

For electrolytic solutes, the number of particles would be **different** from the number of particles actually added due to **dissociation or association** of the solute.

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

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

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.

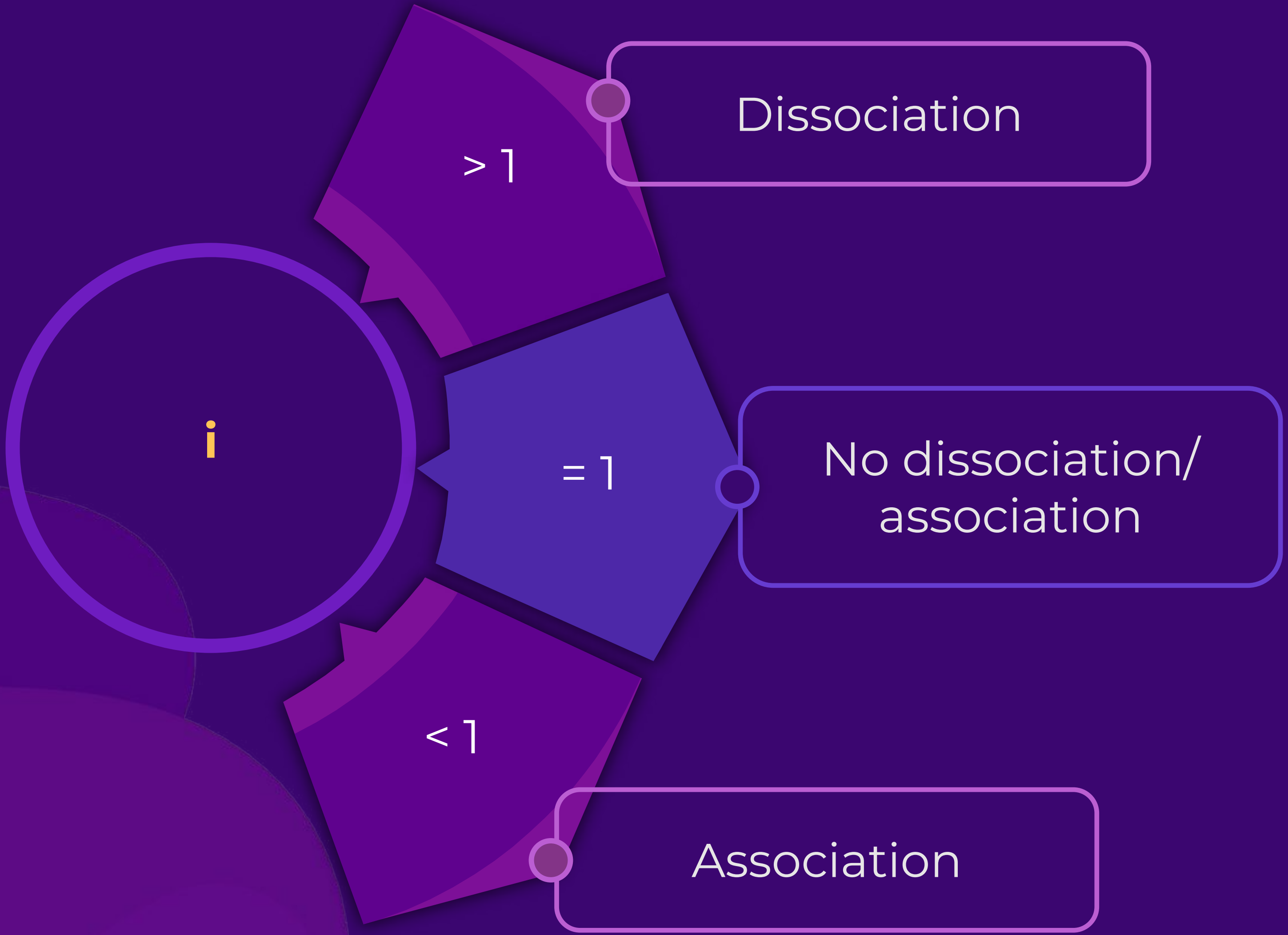
van’t Hoff Factor (i)

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

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

$$i = \frac{\text{Moles of solute particles in solution after dissociation/ association}}{\text{Moles of solute particles before association/dissociation}}$$

van’t–Hoff Factor (i)



i

> 1

Dissociation

= 1

No dissociation/ association

< 1

Association

i for Dissociation of Electrolyte

$$A_xB_y\,(aq) \rightleftharpoons xA^{y+} + yB^{x-}$$

$t = 0$	C	0	0
$t = t_{eq}$	$C(1 - \alpha)$	$xC\alpha$	$yC\alpha$

At equilibrium, Net concentration $= C - C\alpha + xC\alpha + yC\alpha$

$$= C[1 + (x + y - 1)\alpha] = C[1 + (n - 1)\alpha]$$

n Number of particles in which 1 molecule of electrolyte dissociates

i for Dissociation of Electrolyte

$$i = \frac{C[1+(n-1)\alpha]}{C}$$

$$i = 1+(n-1)\alpha$$

Examples

NaCl (100% ionised) $i = 2$

$BaCl_2$ (100% ionised) $i = 3$

i for Association of Electrolyte

$$nA \rightleftharpoons A_n$$

	nA	A_n
t = 0	C	0
t = teq	$C(1 - \beta)$	$\frac{C\beta}{n}$

At equilibrium,

Net concentration $= C - C\beta + \frac{C\beta}{n}$

$$= C\left[1 + \left(\frac{1}{n} - 1\right)\beta\right]$$

i for Association of Electrolyte

$$i = \frac{C\left[1 + \left(\frac{1}{n} - 1\right)\beta\right]}{C}$$

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

Examples

Dimerisation of CH_3COOH in benzene (100 %) $i = 0.5$

Dimerisation of C_6H_5COOH in benzene (100 %) $i = 0.5$

Colligative Properties

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

1. Relative Lowering of Vapour Pressure (RLVP)

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**.

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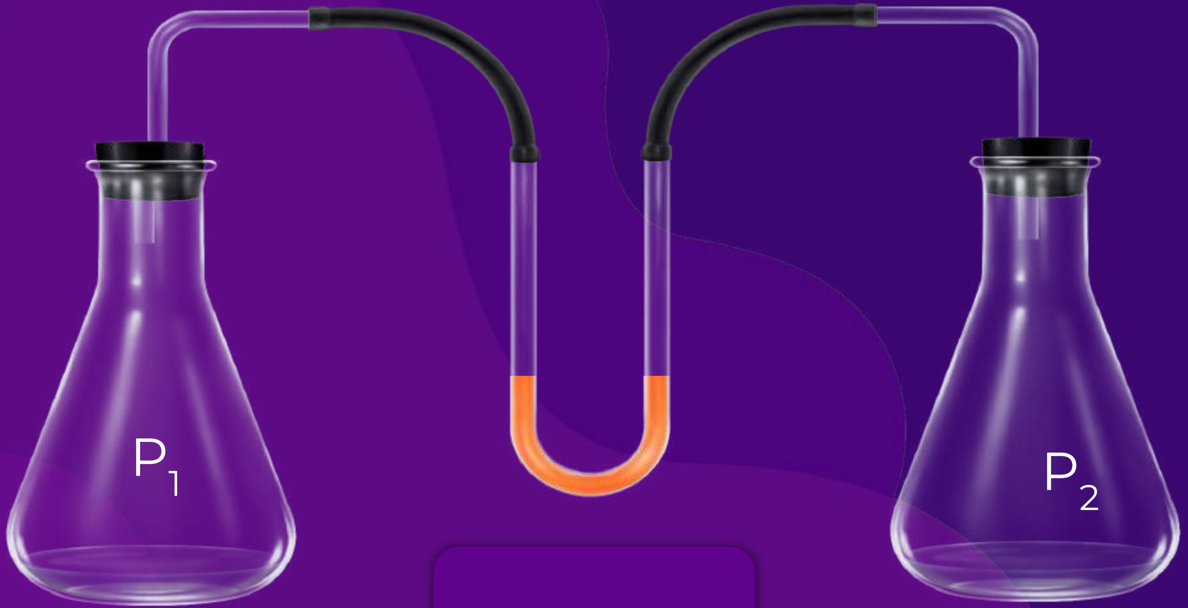
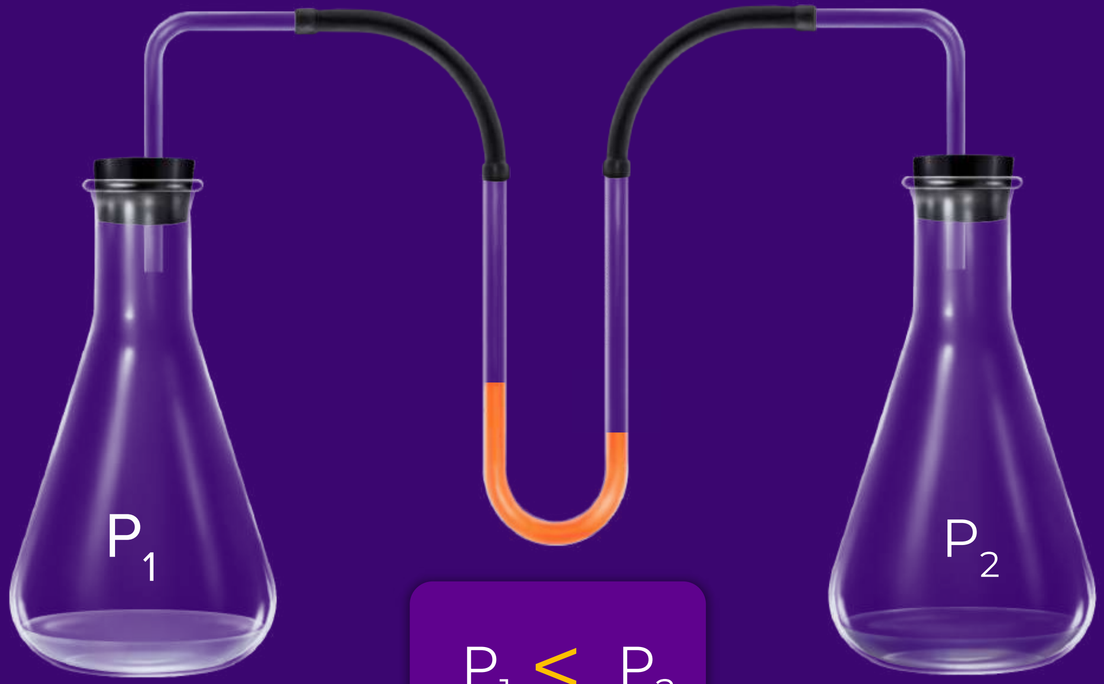


Pure solvent A

$P_1 = P_2$

Pure solvent A



Solution (non-volatile solute in solvent A)

$P_1 < P_2$

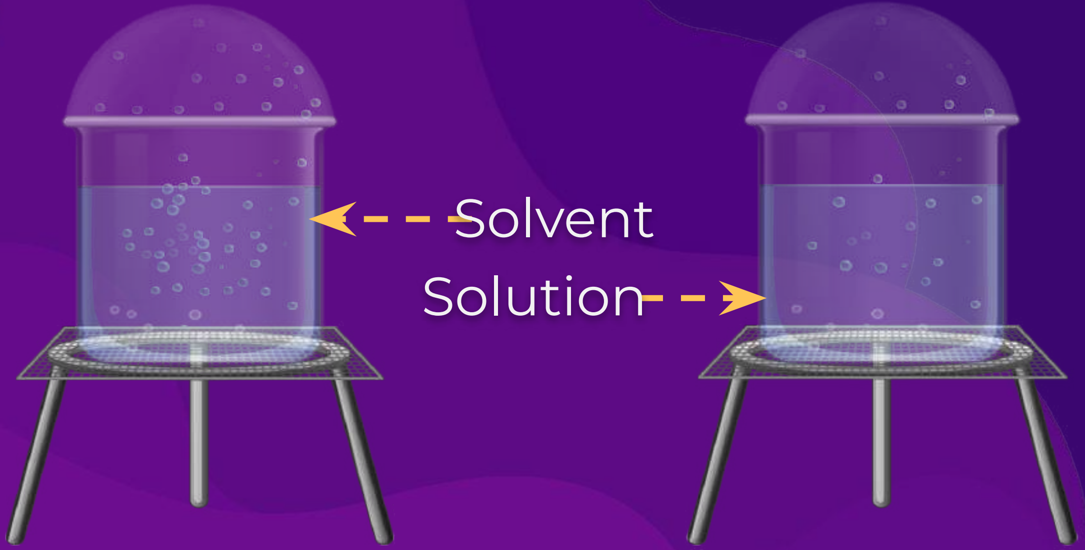
Pure solvent A

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, $\mathbf{P^0 > P_S}$, where P^0 is V.P. of the pure solvent and P_S is the V.P. of the solution.



1. Relative Lowering of Vapour Pressure

Lowering in V.P. $= P^o - P_s = \Delta P$

Relative lowering in vapour pressure $= \dfrac{\Delta P}{P^o}$

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

Note

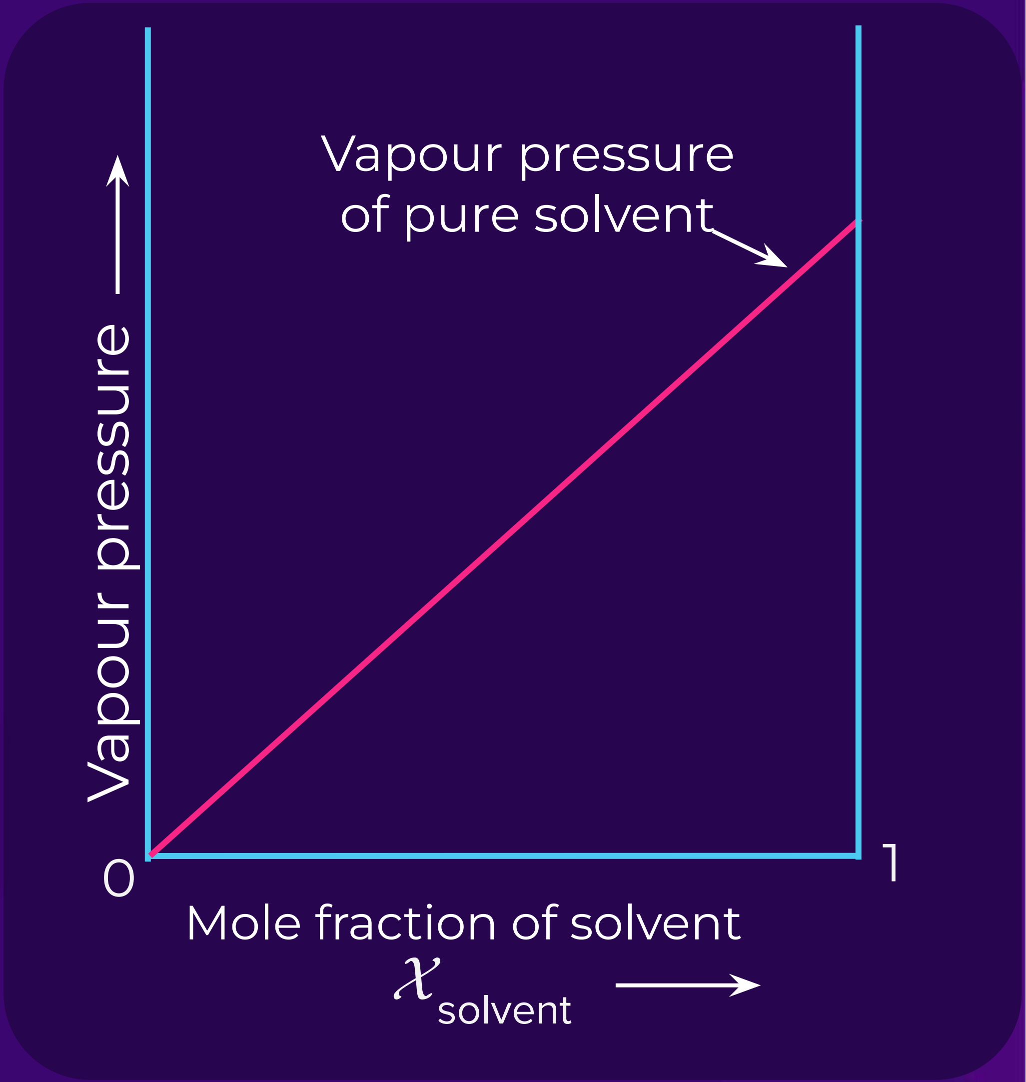
Raoult's Law (For non–volatile solutes)

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**.

$$P_S = \mathcal{X}_{solvent}\, P^o = (1 - \mathcal{X}_{solute})\, P^o$$

$$\textbf{RLVP} = \frac{P^o - P_S}{P^o} = \mathcal{X}_{solute} = \frac{n}{n + N}$$

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



1. Relative Lowering of Vapour Pressure

$$\frac{P^{o}}{P^{o} - P_{S}} = \frac{n + N}{n} = 1 + \frac{N}{n}$$

$$\frac{P^{o} - P_{S}}{P_{S}} = \frac{w_{solute}}{M_{solute}} \times \frac{M_{solvent}}{w_{solvent}}$$

$$\frac{N}{n} = \frac{P^{o}}{P^{o} - P_{S}} - 1 = \frac{P_{S}}{P^{o} - P_{S}}$$

$$= \frac{W_{solute}}{M_{solute}} \times \frac{M_{solvent}}{W_{solvent}} \times \frac{1000}{1000}$$

$$\frac{P^{o} - P_{S}}{P_{S}} = \frac{n}{N}$$

w = Weight of species
M = Molar mass of species

1. Relative Lowering of Vapour Pressure

$$\frac{P^{o} - P_{S}}{P_{S}} = \frac{W_{solute}}{M_{solute}} \times \frac{1000}{W_{solvent}} \times \frac{M_{solvent}}{1000}$$

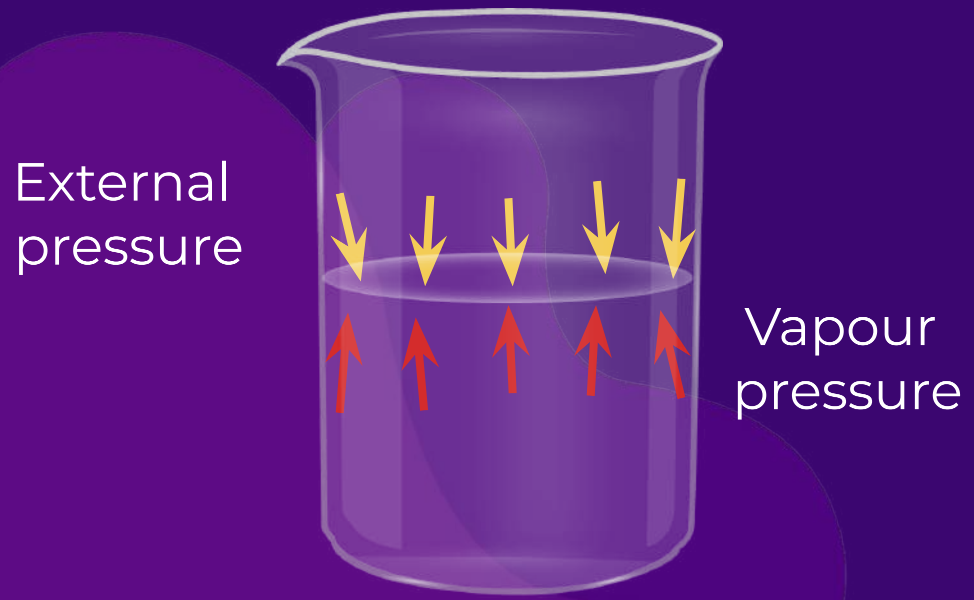
$$\frac{P^{o} - P_{S}}{P_{S}} = \text{Molality} \times \frac{M_{solvent}}{1000}$$

If the solute gets **associated or dissociated**

$$\frac{P^{o} - P_{S}}{P^{o}} = \frac{i \times n}{i \times n + N}$$

$$\frac{P^{o} - P_{S}}{P_{S}} = \frac{i \times n}{N} = i \times \text{Molality} \times \frac{M_{solvent}}{1000}$$

Boiling Point



Temperature at which the **V.P.** of a liquid is **equal** to the **external pressure** present at the surface of the liquid.

At **normal B.P.**, V.P. of the pure liquid = 1 atm

2. Elevation in Boiling Point

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.

2. Elevation in Boiling Point

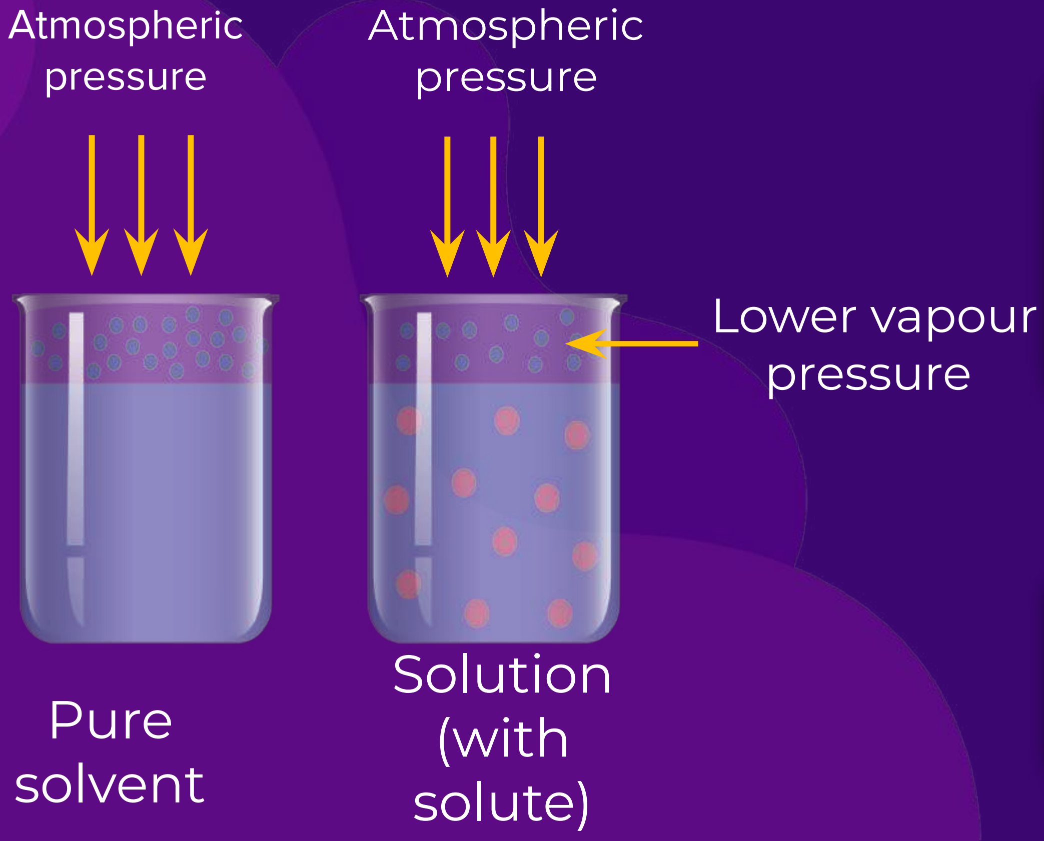
For example,

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

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).

Thus,

The boiling point of a solution **>** The boiling point of the pure solvent



Atmospheric pressure

Atmospheric pressure

Lower vapour pressure

Pure solvent

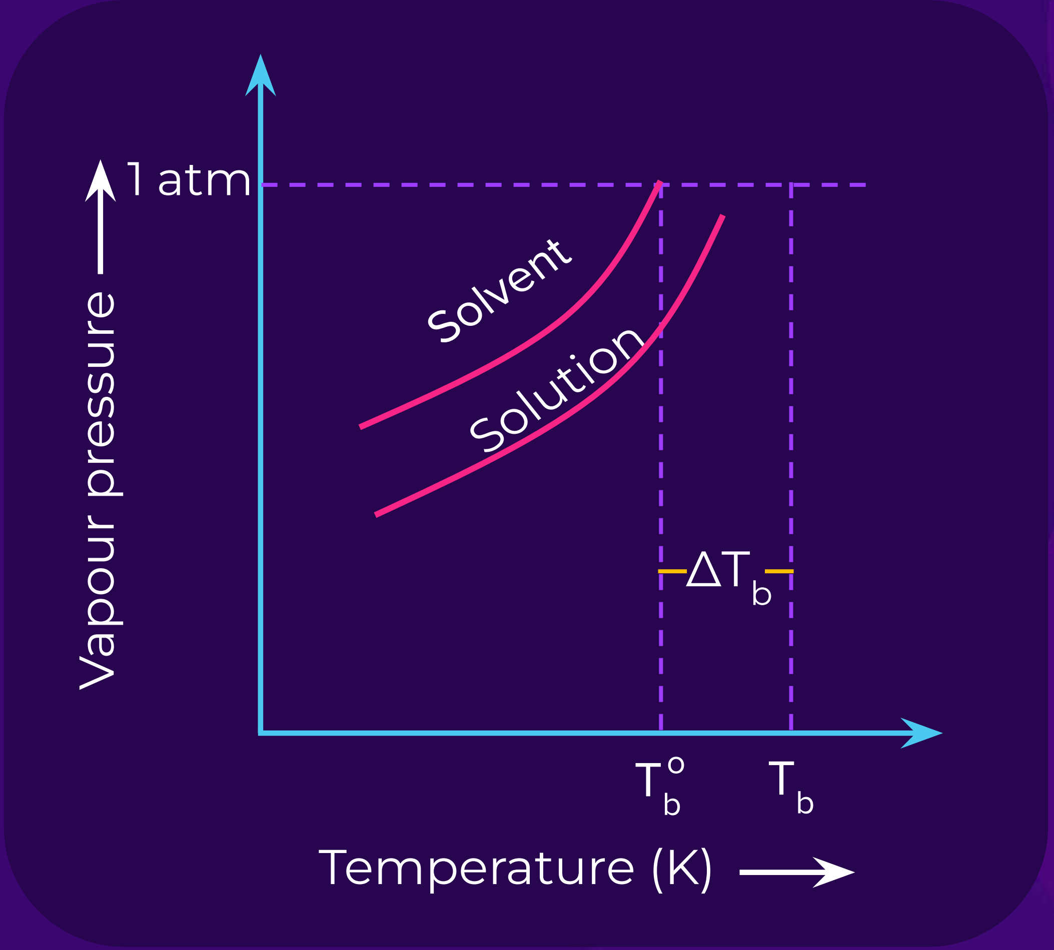
Solution (with solute)

2. Elevation in Boiling Point

T_b = B.P. of solution (K)
T_b^o= B.P. of pure solvent (K)

V.P. of solution < V.P. of pure solvent

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.



2. Elevation in Boiling Point

$$\Delta T_b = T_b - T_b^{\circ}$$

$$\Delta T_b \propto m$$

m Molality

$$\Delta T_b = K_b m$$

K_b = B.P. elevation constant or,
Molal elevation constant or,
Ebullioscopic constant

K_b

It is **equal to** elevation in boiling point of 1 molal solution.

Units K/m or °C/m or K kg mol^{-1}

$$K_b = \frac{R{T_b^o}^2 M}{1000 \times \Delta H_{vap}}$$

- T_b^o is B.P. of pure solvent (K)
- M is the molar mass of solvent in g/mol
- ΔH_{vap} is the molar enthalpy of vapourisation of the solvent (J/mol)
- R = 8.314 J/mol-K

Note

1 If solute gets associated/dissociated then **$\Delta T_b = i \times K_b \times \text{Molality}$**

2 K_b is the property of solvent

3 Elevation in B.P. is proportional to the **lowering of vapour pressure**.

$$\Delta T_b \propto \Delta P$$

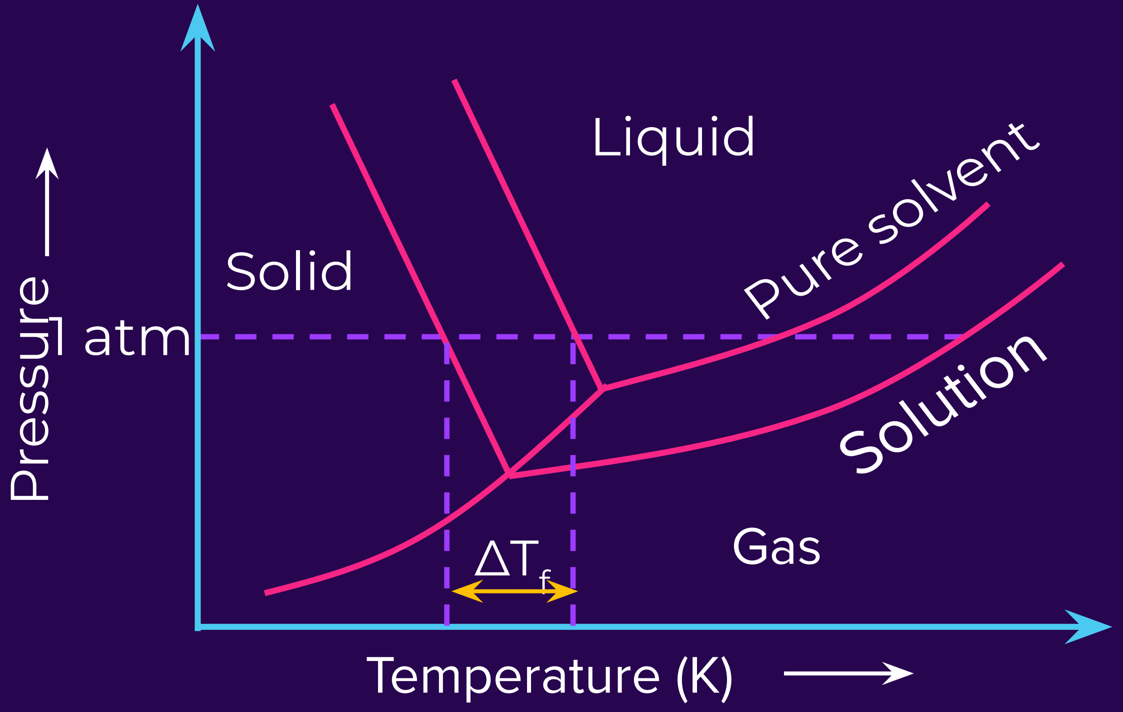
Freezing Point (F.P.)

Temperature at which, the vapour pressure of a solid becomes **equal to** the vapour pressure of liquid at 1 atm is called **normal freezing point**.

3. Depression in Freezing Point

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.**



3. Depression in Freezing Point

ΔT_f

The **difference** between F.P. of a pure solvent **T_f°** and F.P. of its solution **T_f**.

$\Delta T_f = T_f^\circ - T_f$

$\Delta T_f \propto m$

$\Delta T_f = K_f m$

m Molality

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

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

Cryoscopic Constant (K_f)

$$K_f = \frac{RT_f^{o2}M}{1000 \times \Delta H_{fus}}$$

Units

K/m or °C/m
or K kg mol^{-1}

- T_f^o 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

Note

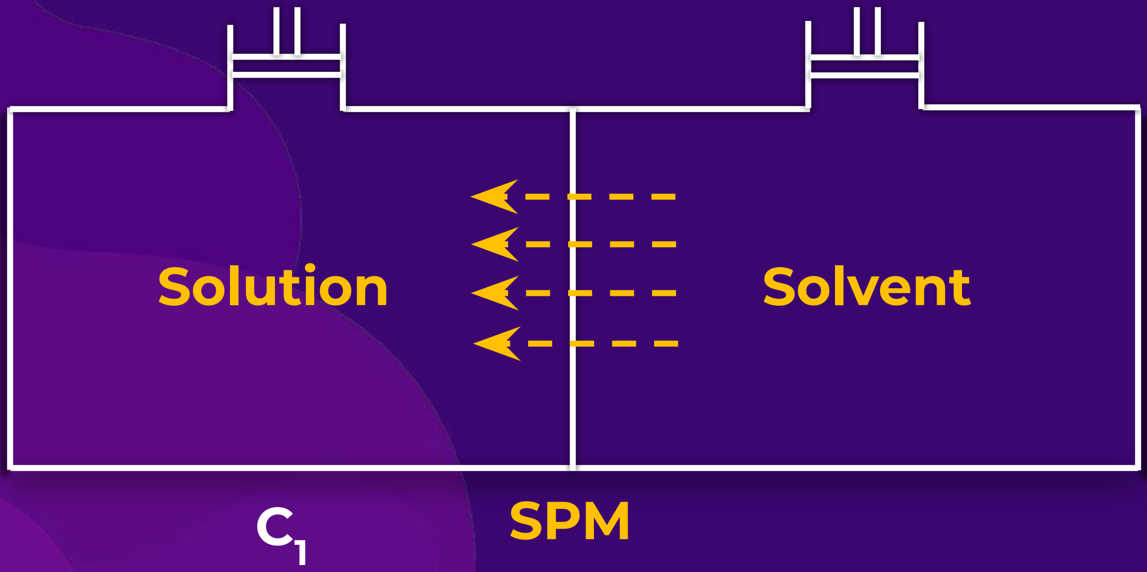
1. Depression in freezing point is proportional to the lowering of vapour pressure i.e. **$\Delta T_f \propto \Delta P$**

2. If solute gets associated/dissociated then **$\Delta T_f = i \times K_f \times \text{Molality}$**

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

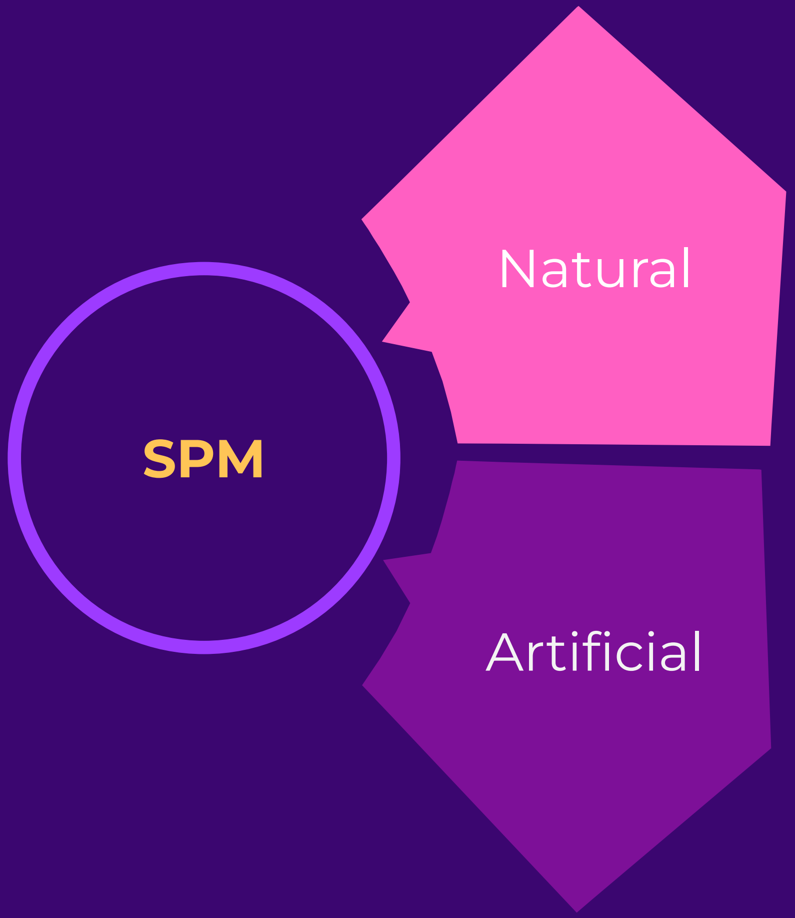
Osmosis

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)**.



Semi-permeable Membrane (SPM)

A membrane that allows **only solvent particles** to move across it.



Semi-permeable Membrane (SPM)

Natural SPM

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.

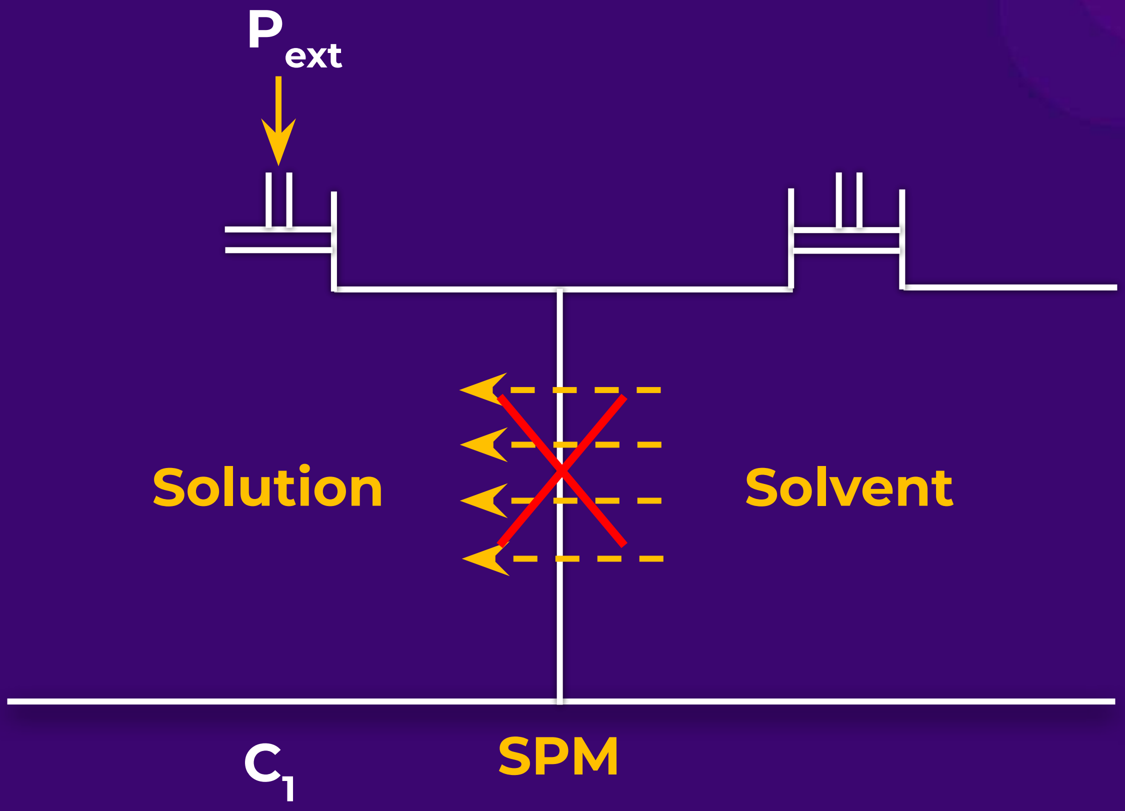
Example of Osmosis

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

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

4. Osmotic Pressure (Π)

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



$P_{ext} = Π$

4. Osmotic Pressure (Π)

$\Pi \propto$ Concentration (Molarity)

$\Pi \propto T$

$\Pi = CRT$

- Π = Osmotic pressure
- C = Concentration (mol/L)
- R= Universal gas constant
- T = Temperature (K)

4. Osmotic Pressure (Π)

$$\Pi = CRT$$

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

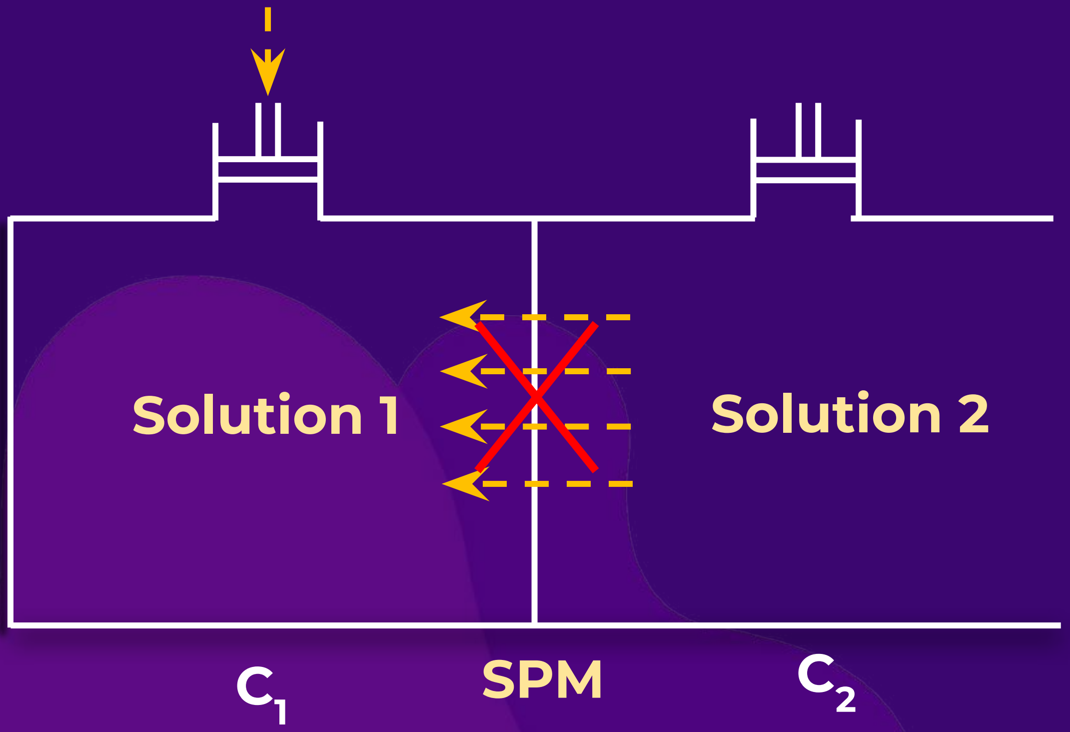
If **more than one** type of solute particles are present.

$$C_T = C_1 + C_2 + C_3 + \ldots\ldots\ldots$$

$$= \frac{n_1 + n_2 + n_3 + \ldots\ldots\ldots}{V}$$

$$\Pi = C_T RT$$

4. Osmotic Pressure (Π)



$C_1 > C_2$

$$P_{ext} = \Pi_1 - \Pi_2$$

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**.

Note

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

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

Reverse Osmosis

Used in **desalination of sea-water**

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**.

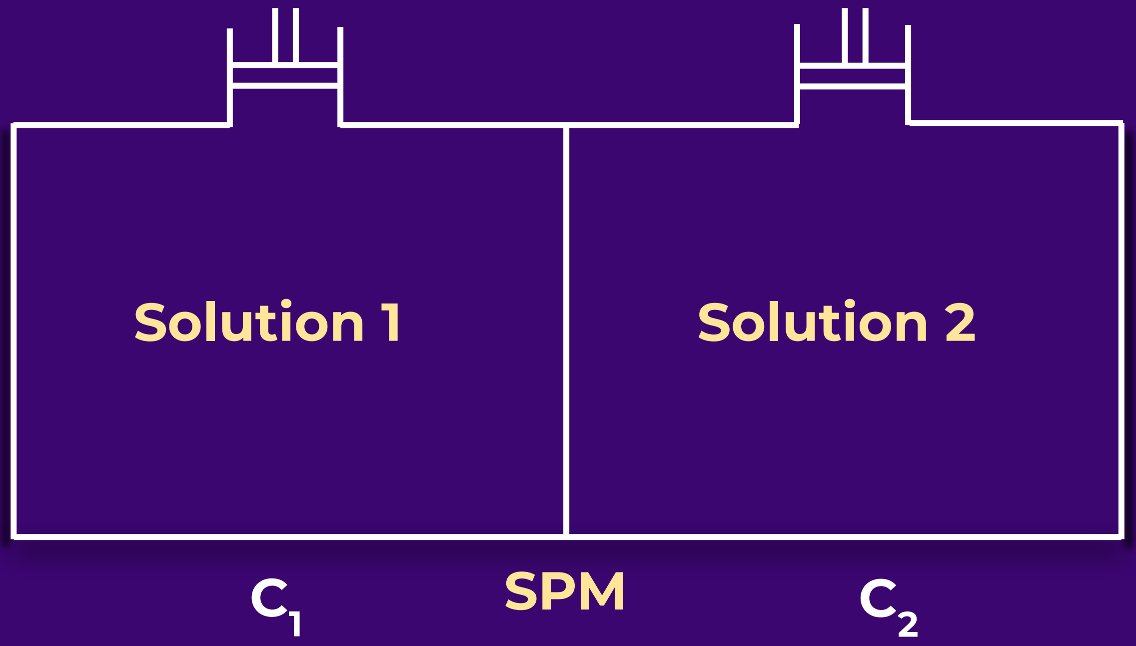
$$P_{ext} > \Pi$$

Based on the difference in osmotic pressure

1. **Isotonic** solution
2. **Hypotonic** solution
3. **Hypertonic** solution

Isotonic Solution

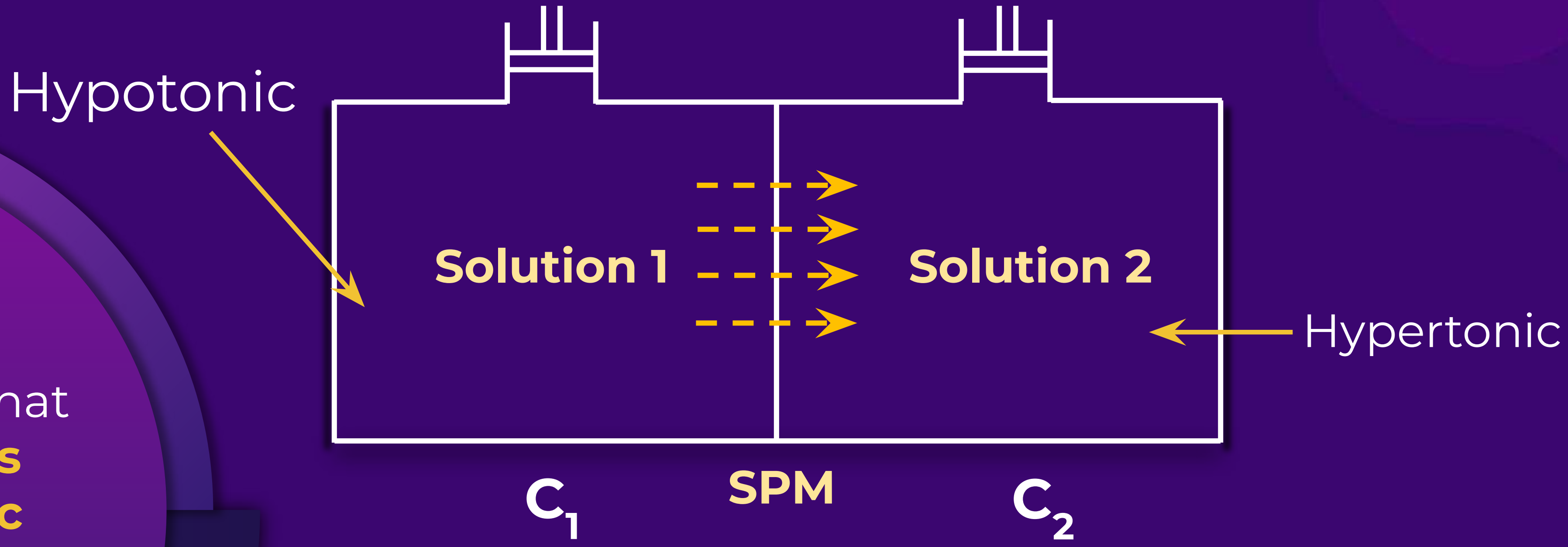
Two solutions having **same osmotic pressure** are considered as isotonic solution.



$$\Pi_1 = \Pi_2$$

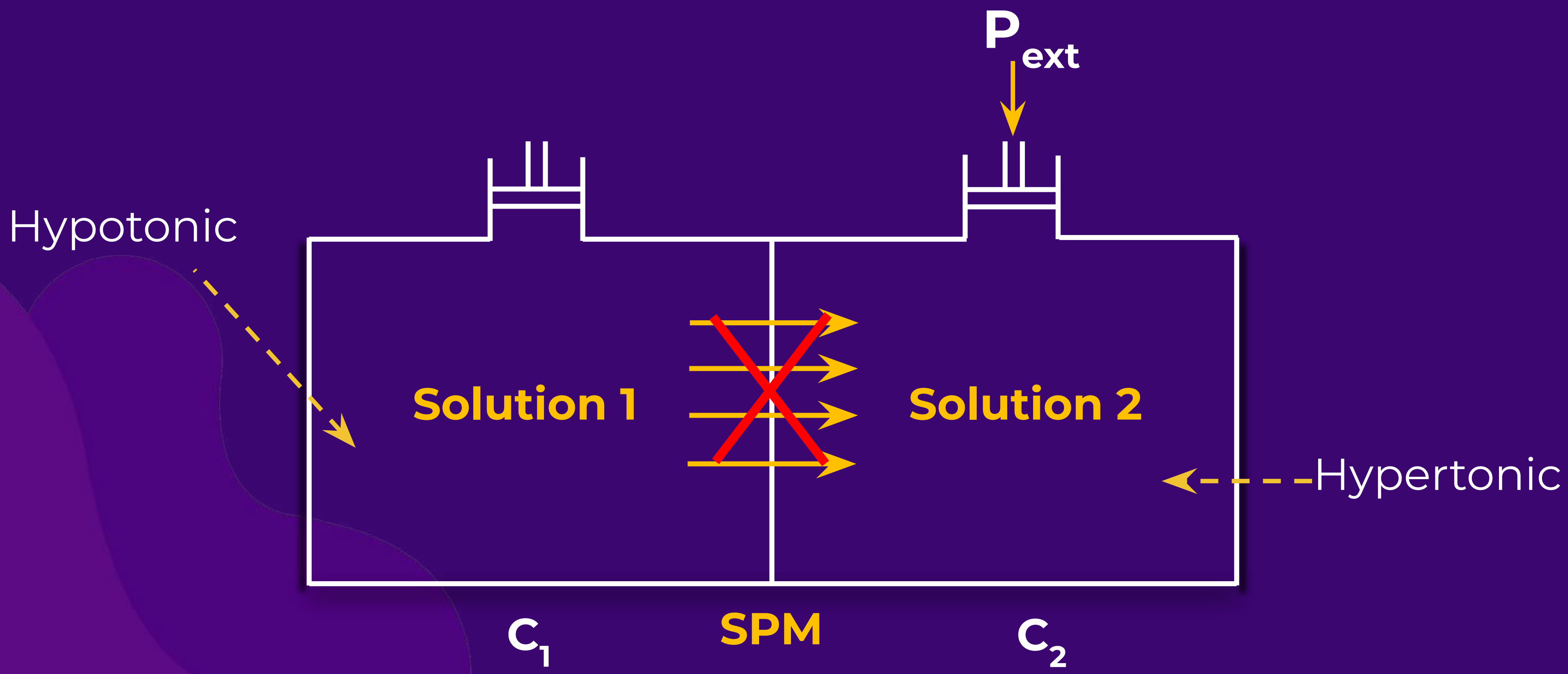
Hypotonic & Hypertonic Solutions

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.



$\Pi_1 < \Pi_2$

Hypotonic & Hypertonic Solutions



$\Pi_1 < \Pi_2$

$P_{ext} = \Pi_2 - \Pi_1$

Types of Solutions

Hypotonic Solution

Net water gain
Cell Swells

Isotonic Solution

No net
loss or gain

Hypertonic Solution

Net water loss
Cell Shrinks

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.

Application of Osmotic Pressure

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

$$M_{solute} = \frac{wRT}{\Pi V}$$

- w is mass of solute
- V is volume of the solution
- Π is osmotic pressure of the solution
- T is temperature
- R is universal gas constant

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**.

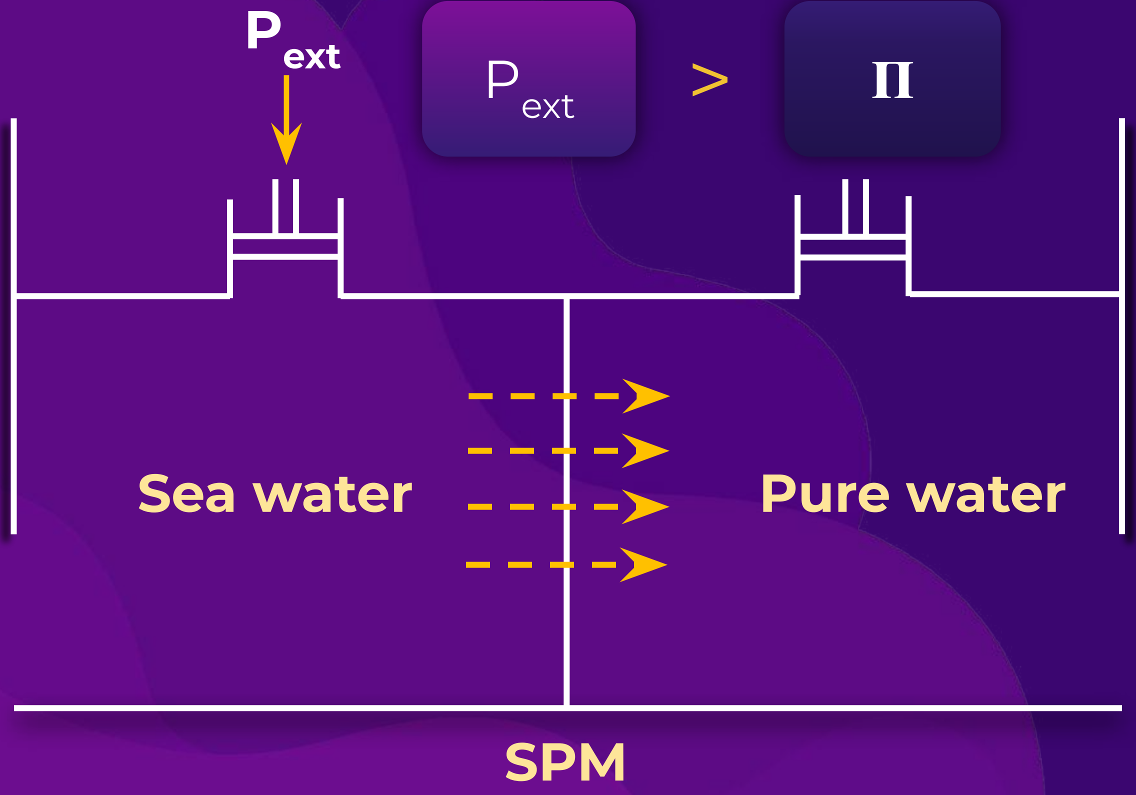
Note

If solute gets associated or dissociated then **theoretical** molar mass of **solute** will be **different** from **experimentally** calculated molar mass

$$i = \frac{\text{Theoretical molar mass of substance}}{\text{Experimental molar mass of the substance}}$$

Application of Osmotic Pressure

b. **Desalination** of water by reverse osmosis



$P_{ext} > \Pi$

c. **Dialysis**

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