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.

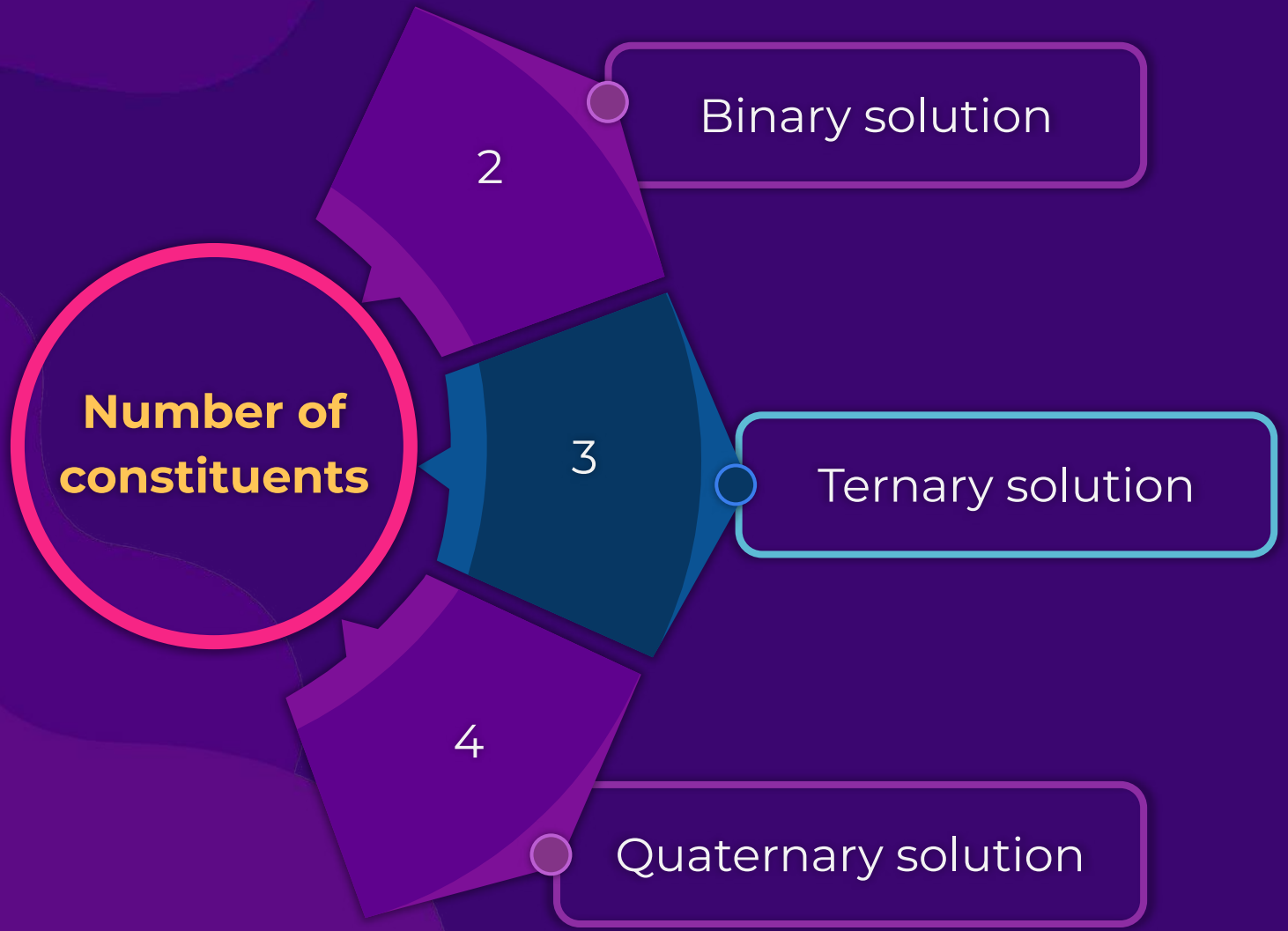
Solute - Constituents present in **relatively small** amounts.

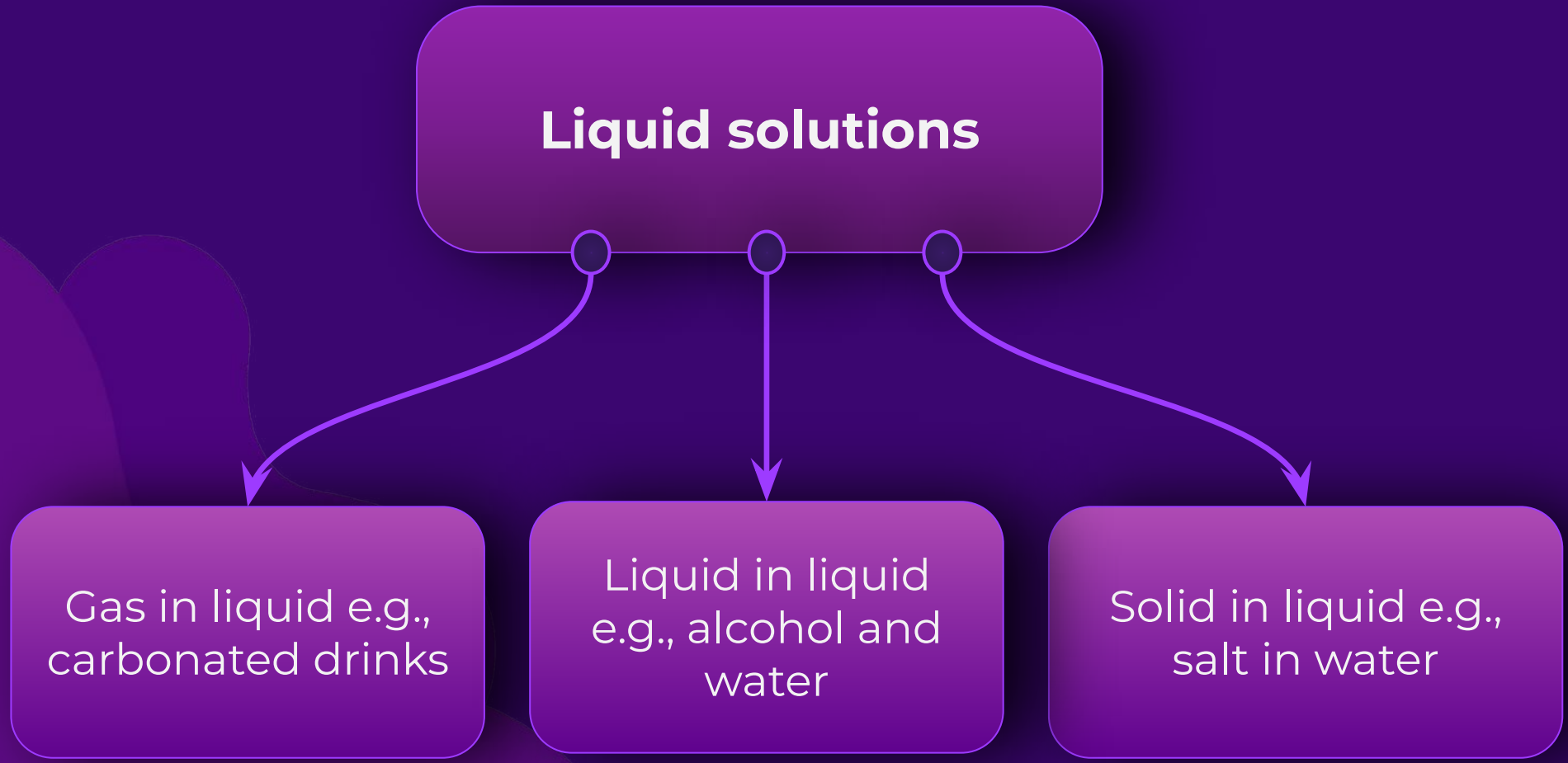
Note

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.

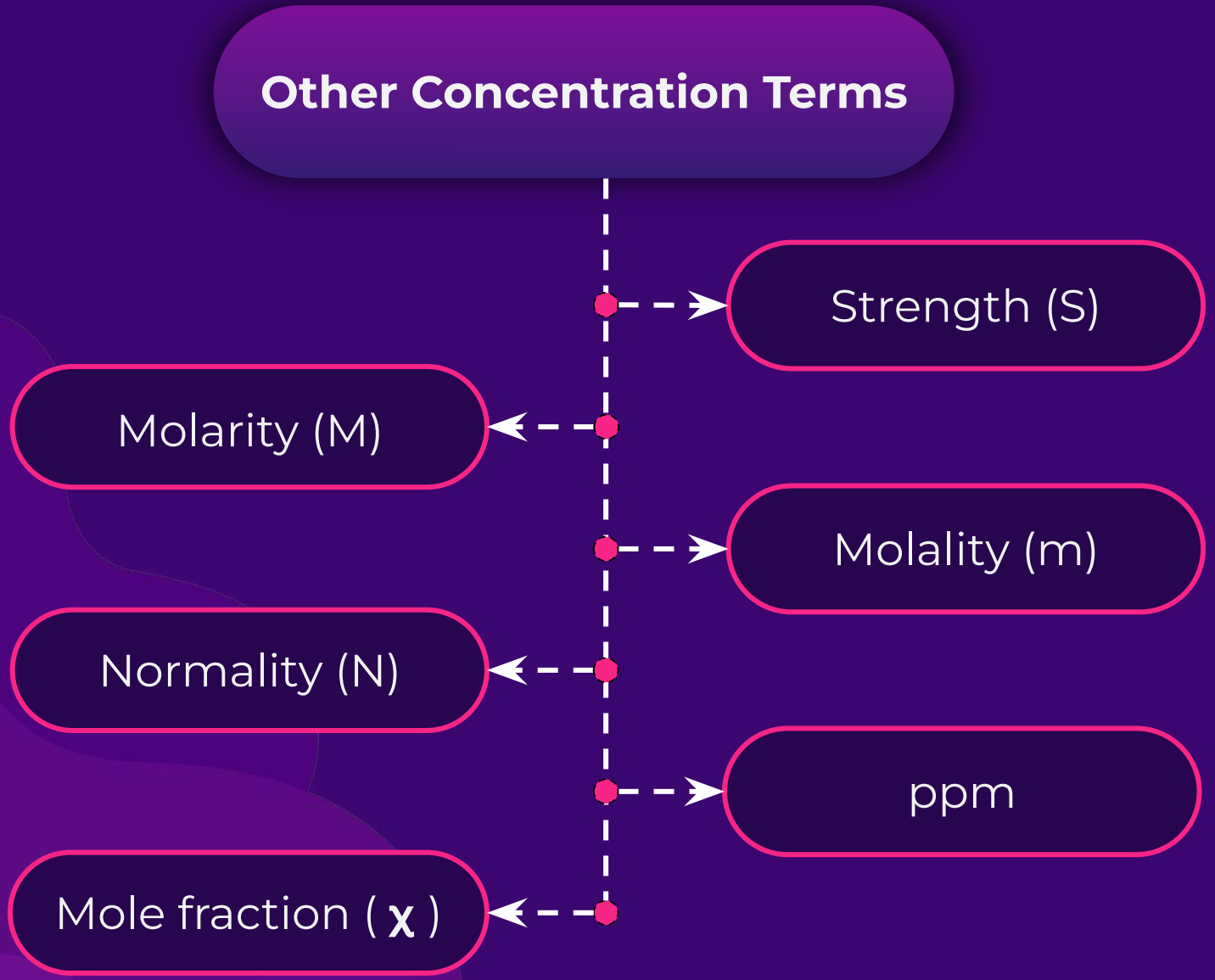
Types of solutions




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

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.
% w/w = $\frac{\text{Weight of solute (g)}}{\text{Weight of solution (g)}} \times 100$	**% w/V** = $\frac{\text{Weight of solute (g)}}{\text{Volume of solution (mL)}} \times 100$	**% 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 of Solution

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

Molarity (M)

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

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

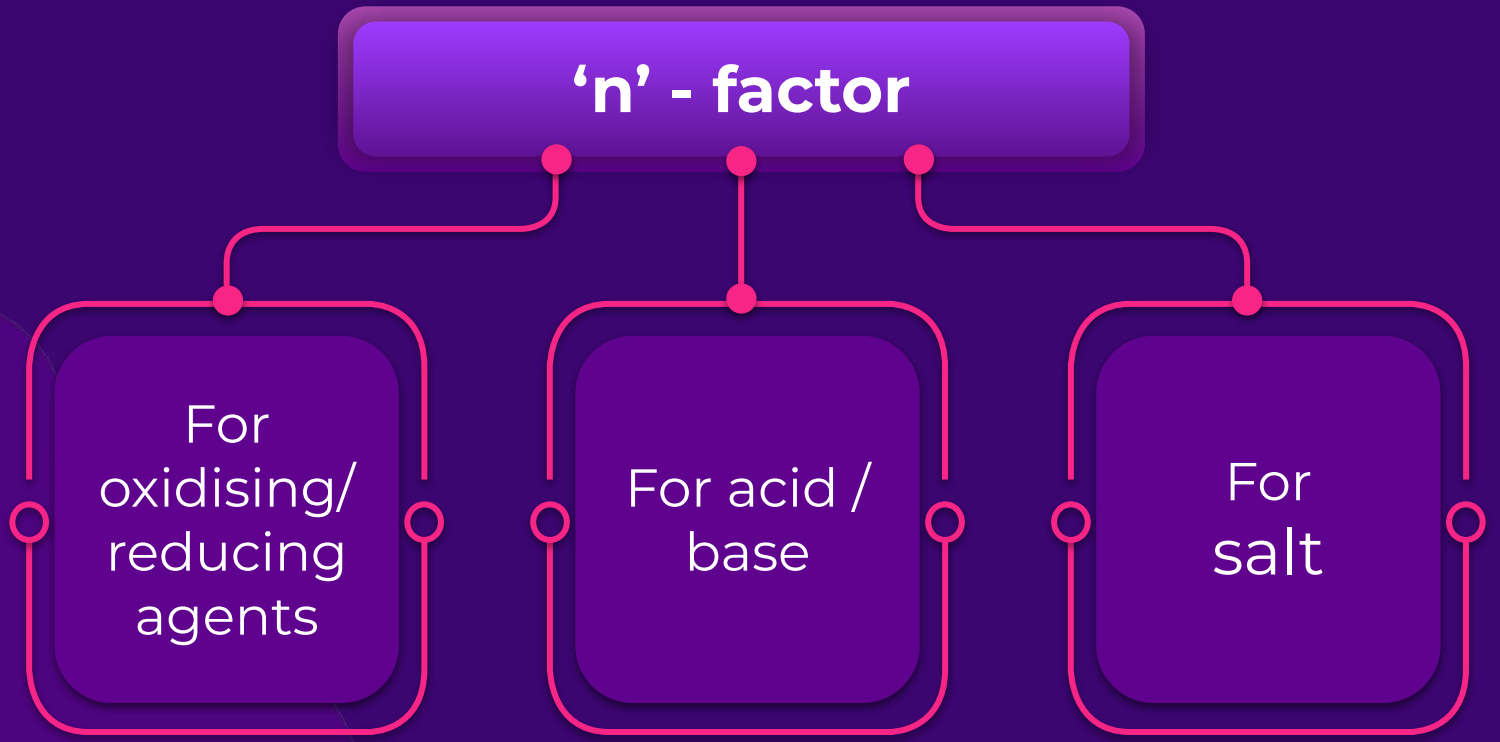
Normality (N)

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

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

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

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


‘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.

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.**

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

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

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

Mole Fraction ($\mathcal{X}$)

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

For a binary solution,

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

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

$$\mathcal{X}_{solute} + \mathcal{X}_{solvent} = 1$$

Based on the amount of the solute dissolved

- Unsaturated
- Saturated
- Supersaturated

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

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

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

Supersaturated Solution

It should be prepared in a **dust-free** vessel and at a higher temperature.

It is **metastable**. Mechanical stress, such as shaking or addition of solute, causes deposition of solute.

Solubility of a Gas in Liquid

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 solvent & gas
2. **Temperature**
3. **Pressure**

1. Nature of Solvent & Gas

Like dissolves like

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

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

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

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.

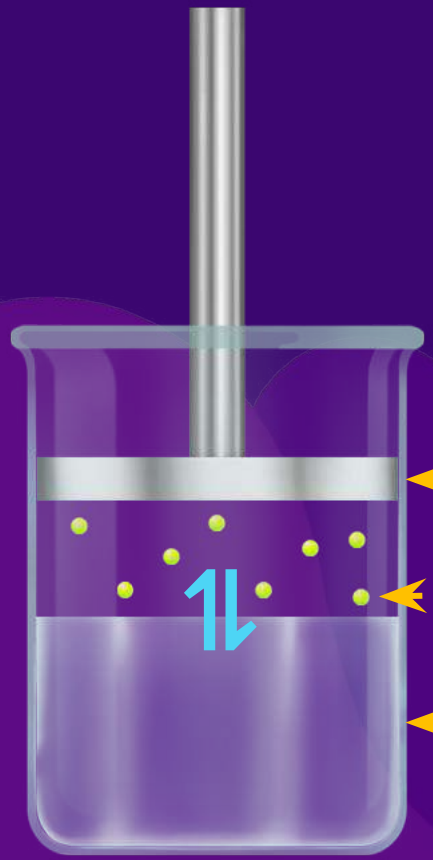
$$x \propto P$$

$$P = K_H x$$

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

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

x is the **mole fraction** of the unreacted gas in the solution.

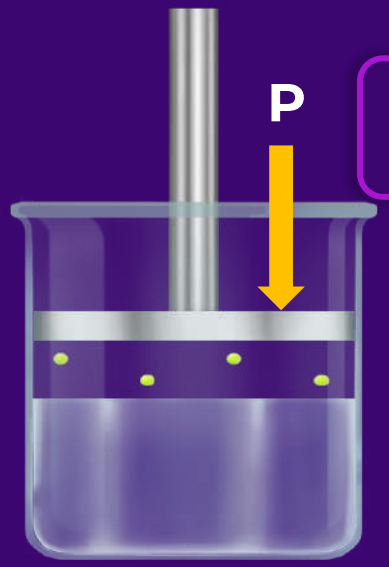


Movable frictionless piston

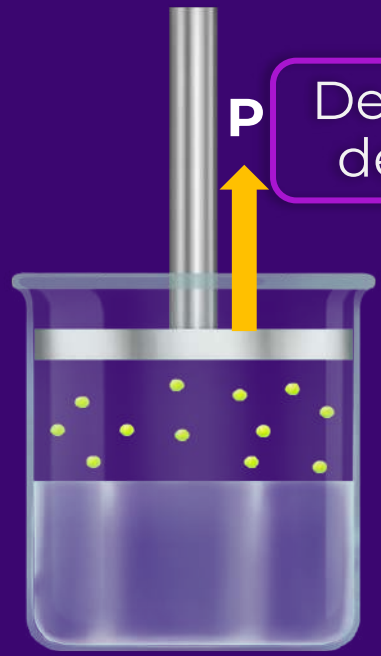
Gas

Liquid

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.**

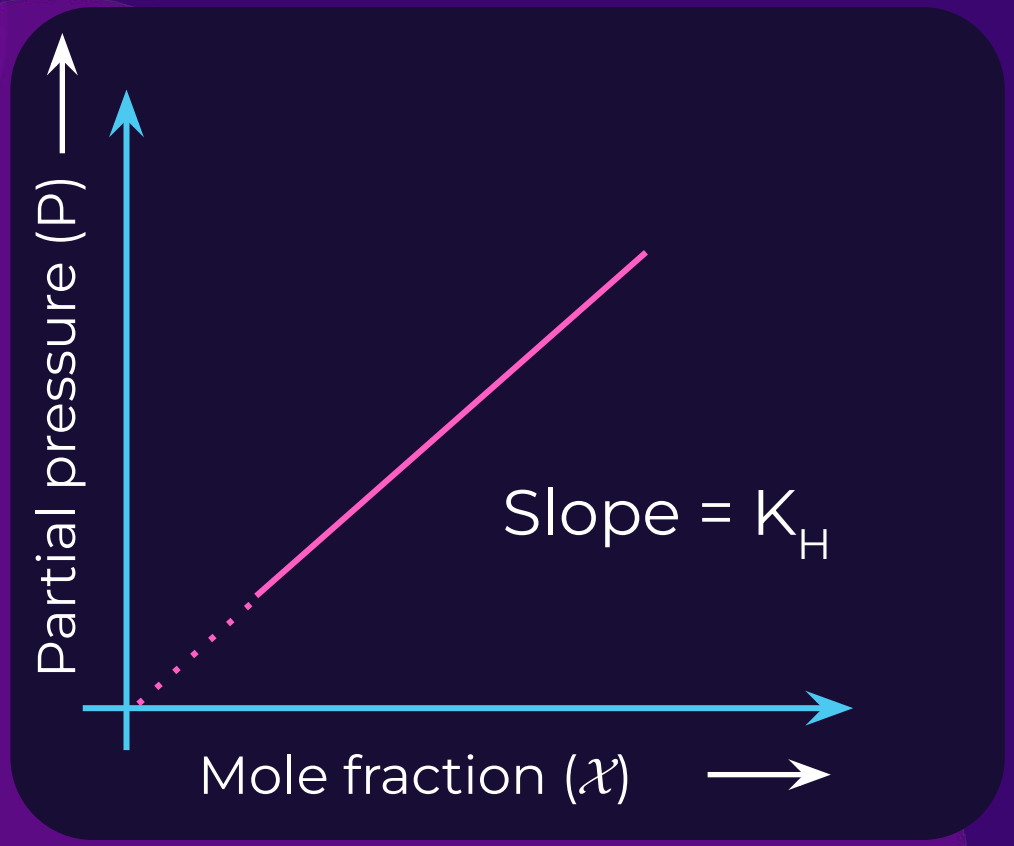
d. K_H value **increases** with increase in **temperature**.

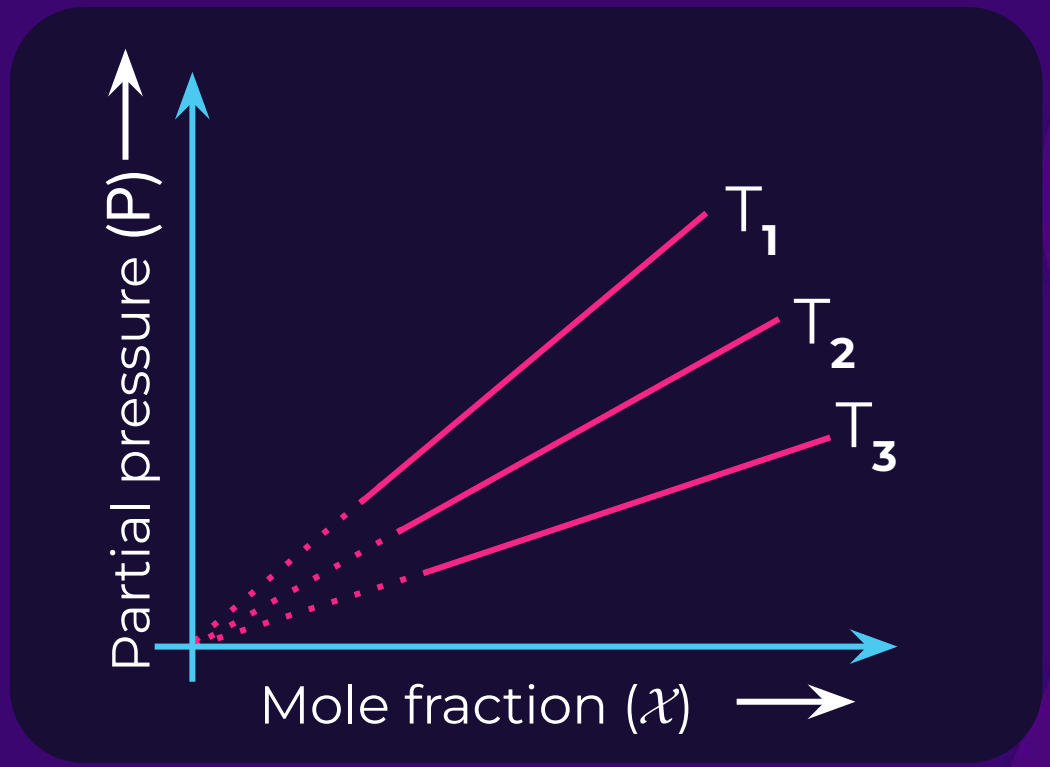
e. **Higher** the value of K_H of a gas, **lower** will be its **solubility.**

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

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.

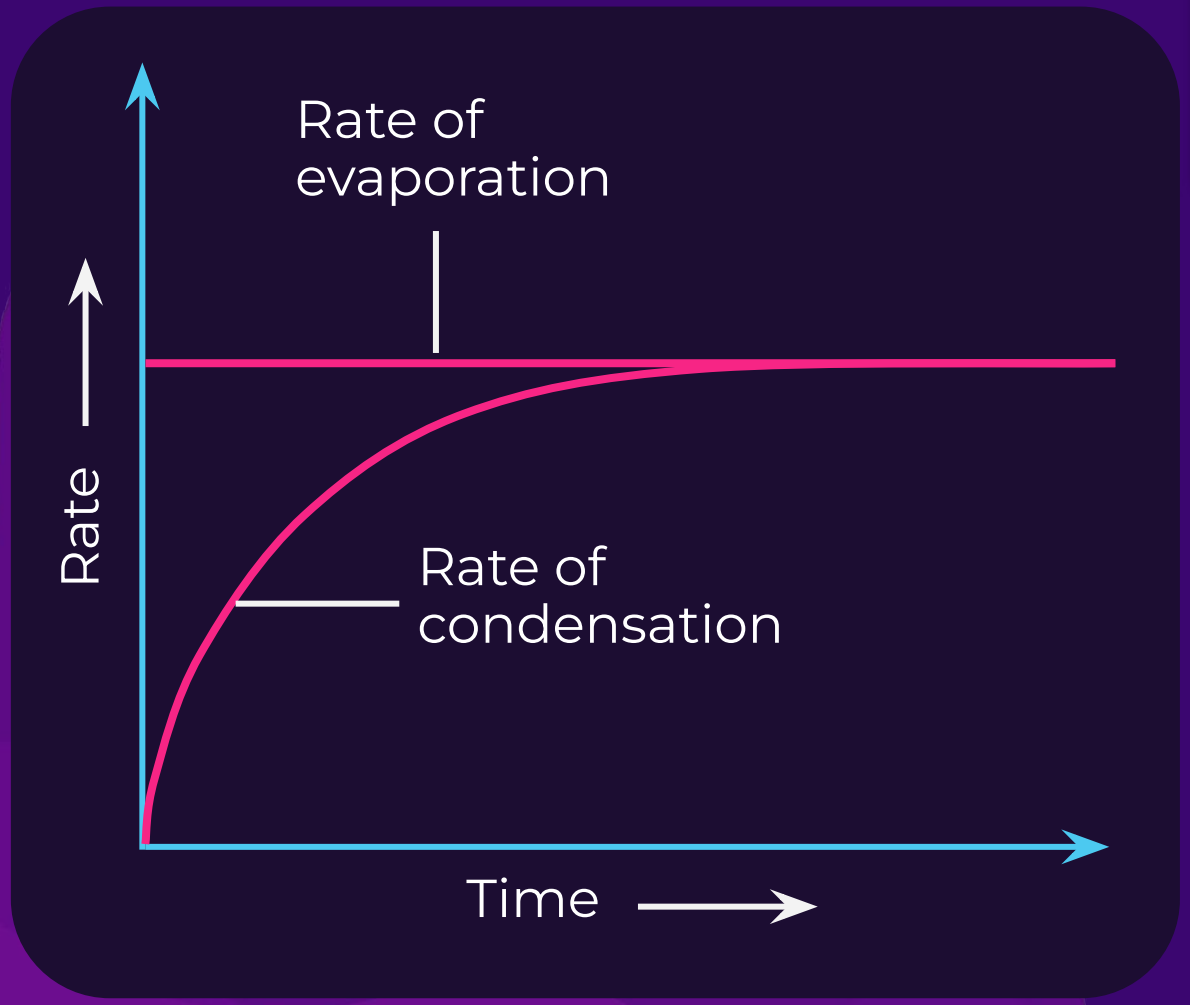
Vapour Pressure

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:

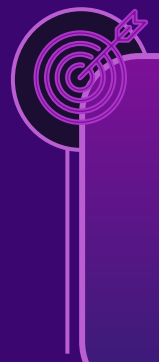
1. **Amount** of liquid taken
2. **Surface area** of the liquid
3. **Volume** or shape of the container

(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

(c) Relative Humidity (R.H.)

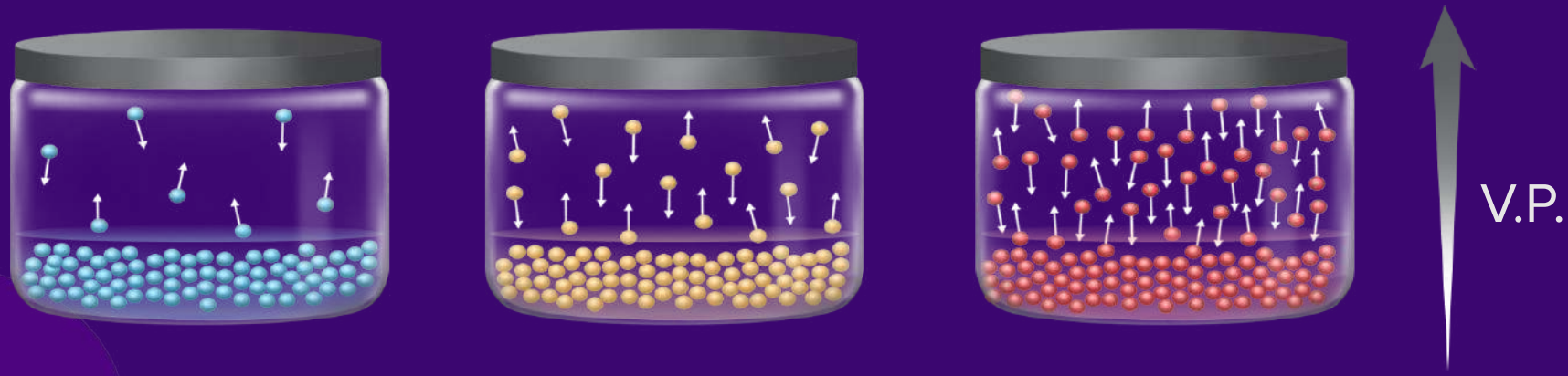
Relative humidity = $\frac{\text{Partial pressure of } H_2O \text{ vapour at given temperature}}{\text{Vapour pressure of } H_2O \text{ at same temperature}} \times 100\ \%$

A gas or gaseous mixture is said to be saturated with the vapours of a liquid if the **partial pressure** of the liquid vapours is **equal to** its (**saturated**) vapour pressure i.e. R.H. = 100%

(d) Temperature

Temperature ↑ → **Vapour pressure ↑**

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



Temperature ↑ → **K.E. of particles ↑**

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.

Dependence of vapour pressure on temperature is given by **Clausius-Clapeyron equation.**

Clausius-Clapeyron Equation

$$\ln \frac{P_1}{P_2} = -\frac{\Delta H_V}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

ΔH_V	Molar enthalpy of vapourisation of liquid
P_2	V.P. of the liquid at T_2
P_1	V.P. of the liquid at T_1

Clausius–Clapeyron equation is important for understanding the **appearance of phase diagrams**, particularly the location and shape of the liquid–vapour and solid–vapour phase boundaries.

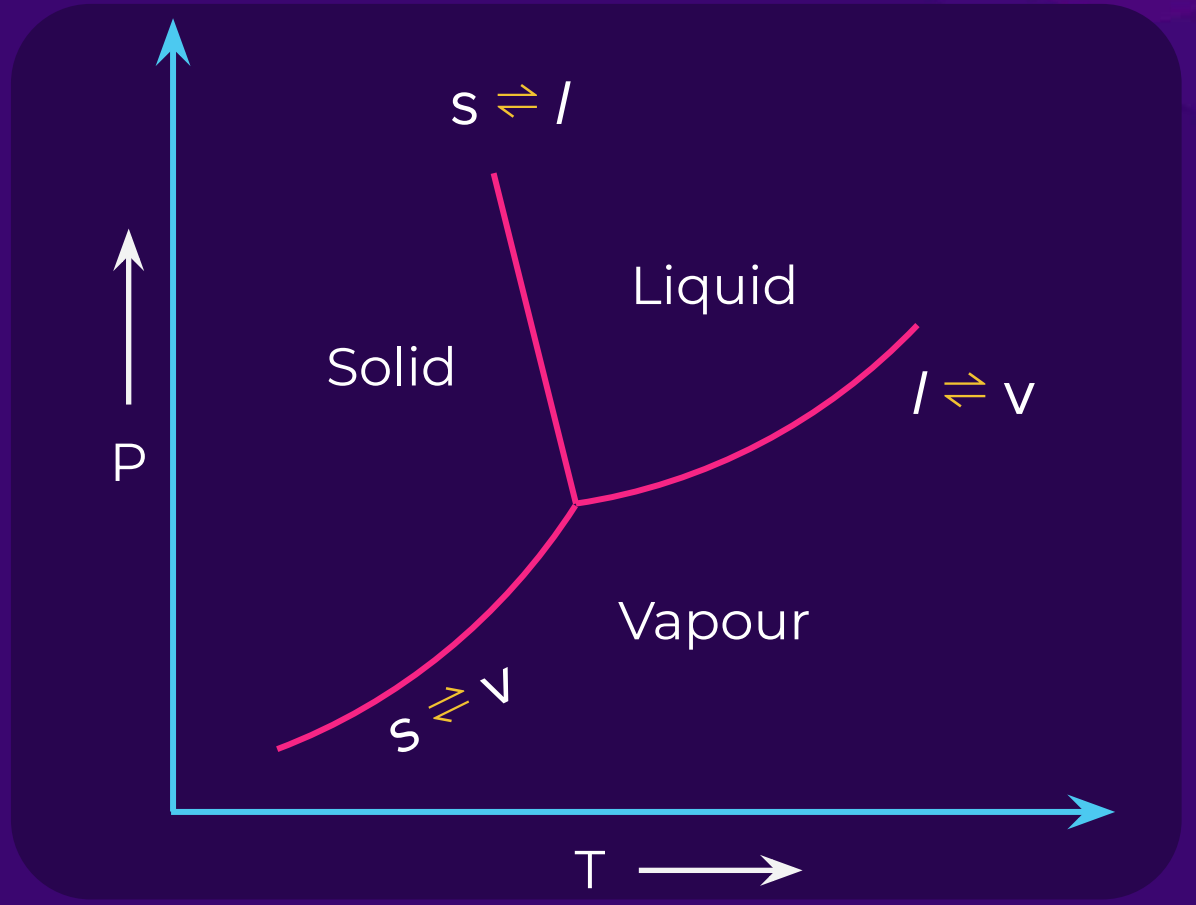
Phase of a substance is a form of matter that is **uniform throughout** in chemical composition and physical state.

Did you know?
Diamond and graphite are in different phases.

Phase Diagram

Phase diagram of a substance shows the regions of **pressure and temperature** at which its various phases are **thermodynamically stable**.

The lines **separating** the regions that are called **phase boundaries**, show the values of P and T at which two phases coexist in equilibrium.



Raoult's Law

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

$$P_A \propto \chi_A \qquad P_A = \chi_A P_A^{\circ}$$

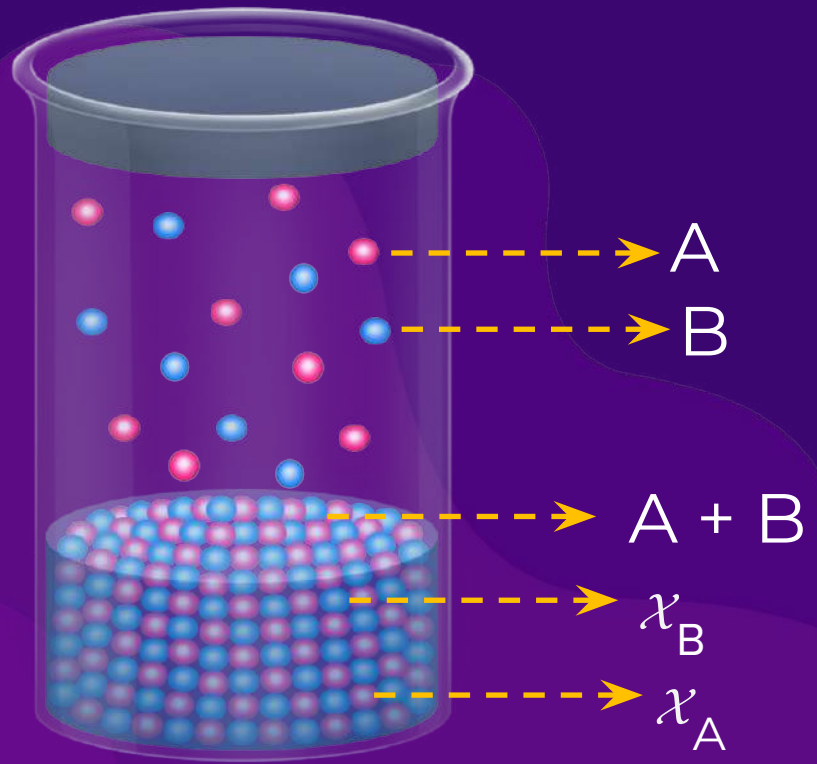
- P_A — Partial vapour pressure of component 'A'
- χ_A — Mole fraction of component 'A' in solution
- P_A° — Vapour pressure of pure component 'A' at a given temperature

For Binary Solutions of A & B

$$P_A = \chi_A P_A^o \qquad P_B = \chi_B P_B^o$$

$$P_T = P_A + P_B$$

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



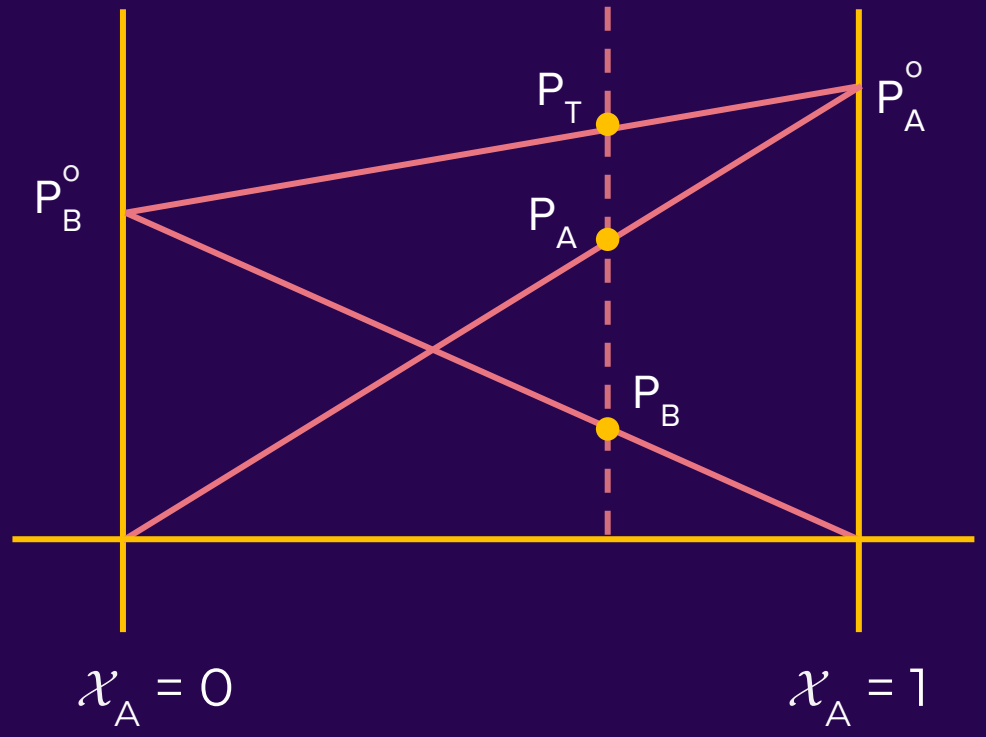
Solutions which obey **Raoult's law** over the entire range of concentration are called **ideal solutions.**

Relation between Total Pressure vs Mole Fraction

$$P_T = \chi_A P_A^{\circ} + \chi_B P_B^{\circ}$$

$$\chi_A + \chi_B = 1$$

$$P_T = (P_A^{\circ} - P_B^{\circ})\,\chi_A + P_B^{\circ}$$



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

If $P_A^{\circ} > P_B^{\circ}$ → 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

$$x_A + x_B = 1$$

$$\frac{y_A P_T}{P_A^o} + \frac{y_B P_T}{P_B^o} = 1$$

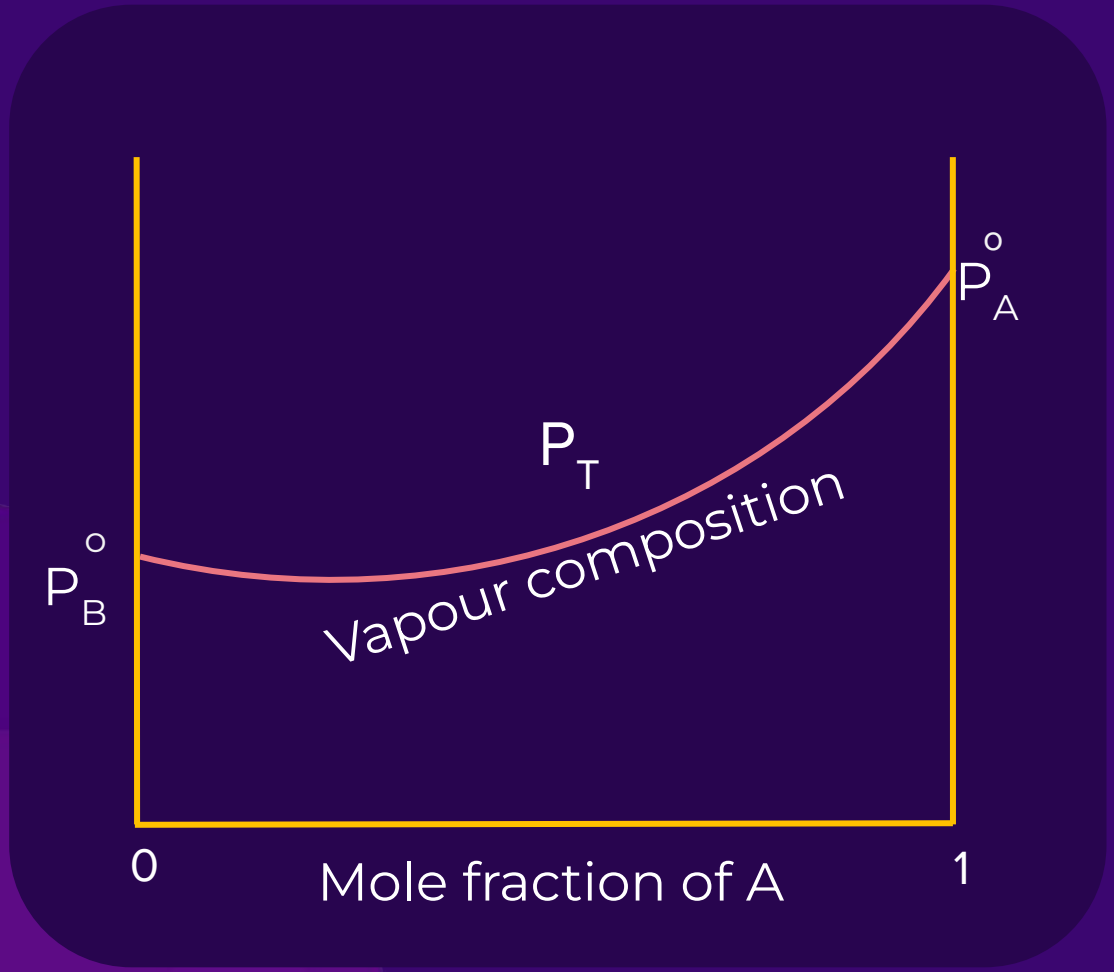
$$\Rightarrow \frac{1}{P_T} = \frac{y_A}{P_A^o} + \frac{y_B}{P_B^o}$$

$$\frac{1}{P_T} = \frac{y_A}{P_A^o} + \frac{y_B}{P_B^o}$$

$$= \frac{y_A}{P_A^o} + \frac{1 - y_A}{P_B^o}$$

$$P_T = \frac{P_A^o P_B^o}{P_A^o + (P_B^o - P_A^o)\, y_A}$$

P_T in Terms of Composition of Vapour Phase

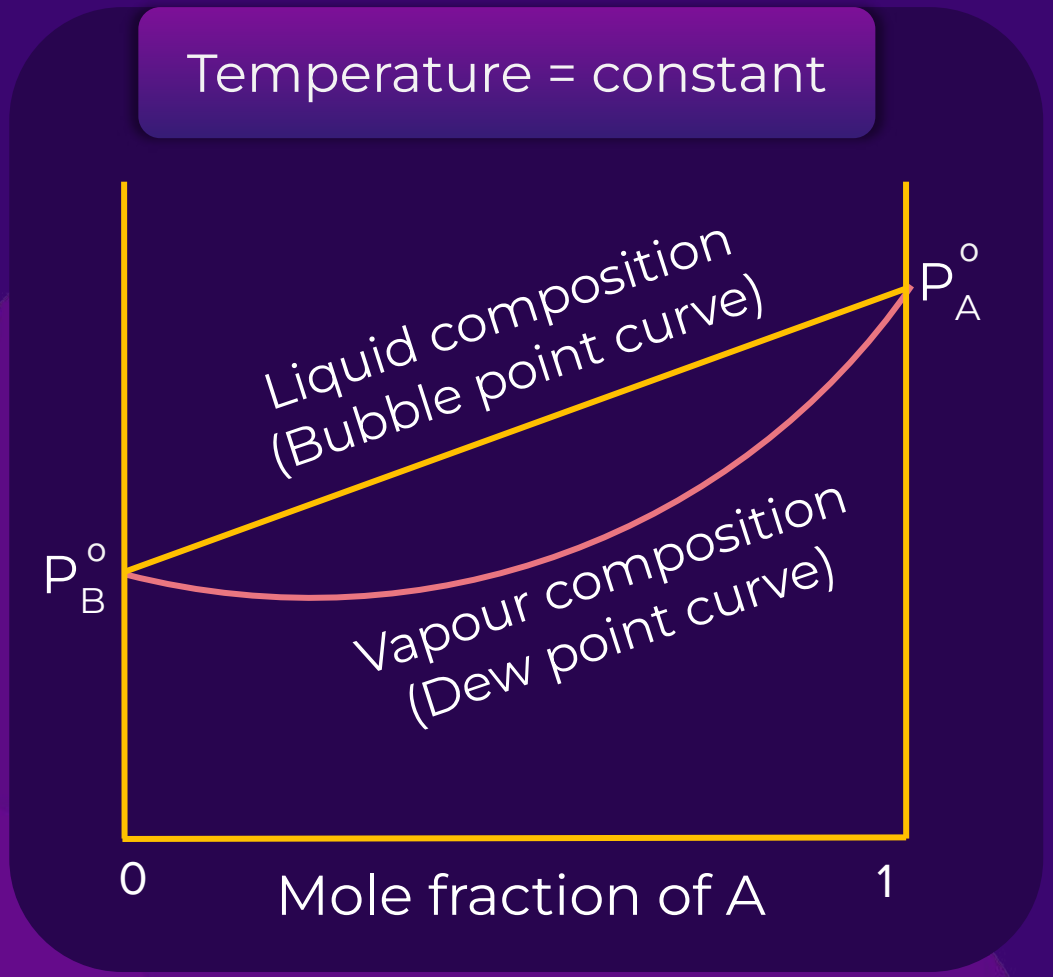


Note

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.

Pressure Versus Composition Phase Diagram

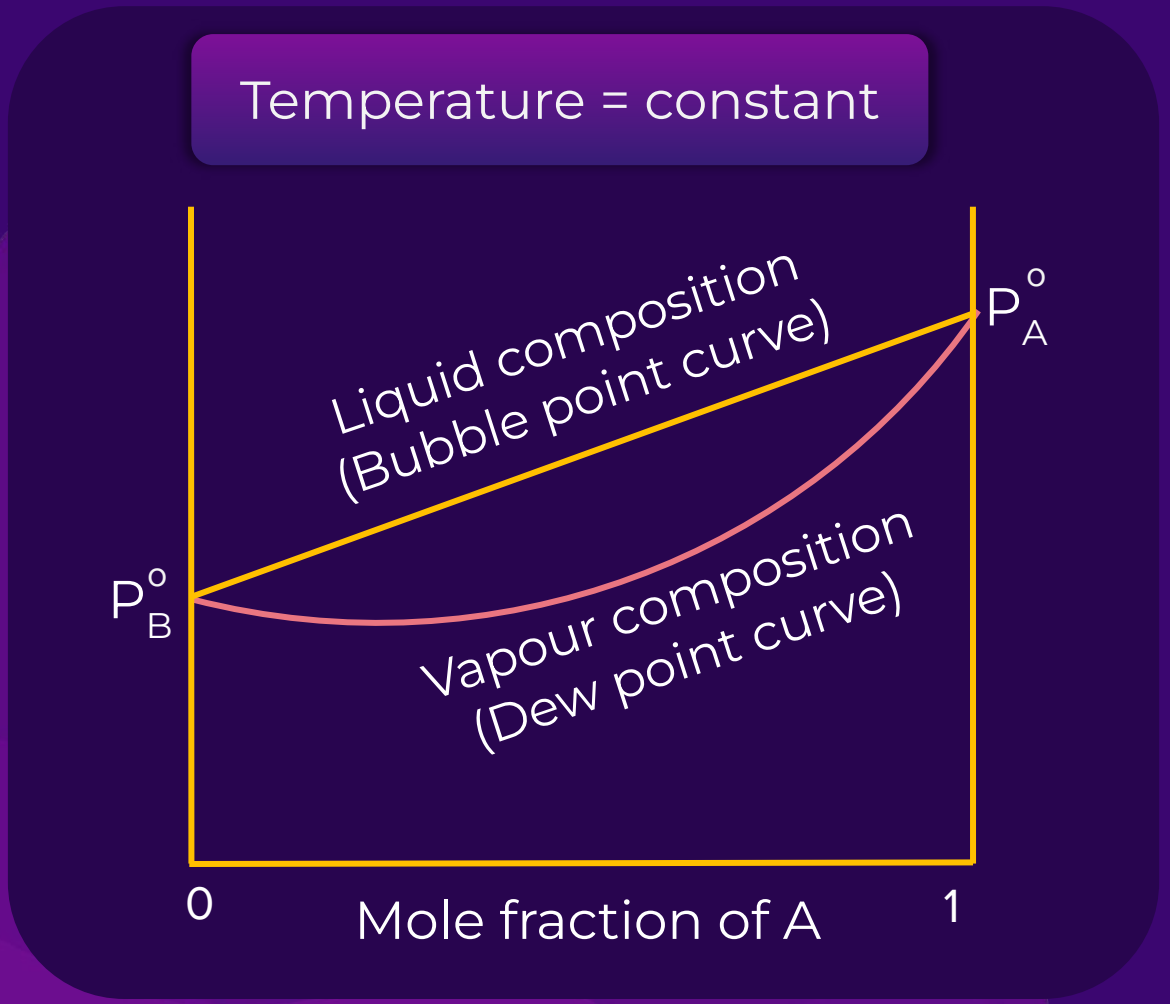


Let, initially the pressure over the solution is **very high** so that **no vapour exist** above the liquid.

On **decreasing** the pressure gradually, a point (**bubble point**) comes when we cross the bubble-point curve and **first bubble** of vapour starts forming.

The **area between** the two curves is **vapour-liquid equilibrium** region. The vapours cannot exist above the bubble point curve and liquid can't exist below the dew point curve.

Pressure Versus Composition Phase Diagram

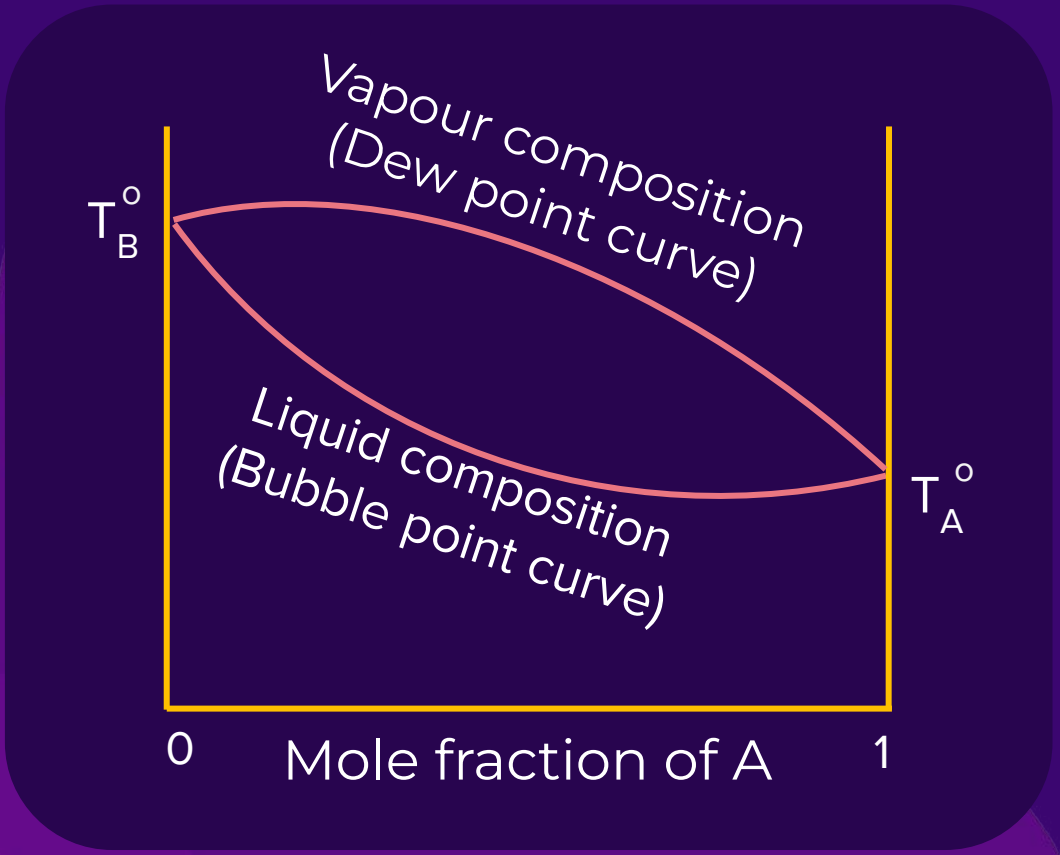


On further **decreasing** the pressure.A point (**dew point**) comes when we cross the dew-point curve.

On crossing the dew-point curve almost **all the liquid has evaporated into vapour** i.e. only the last drop of liquid (dew) remains.

Beyond this point, **no liquid** exist in the system.

Temperature vs Composition Phase Diagram

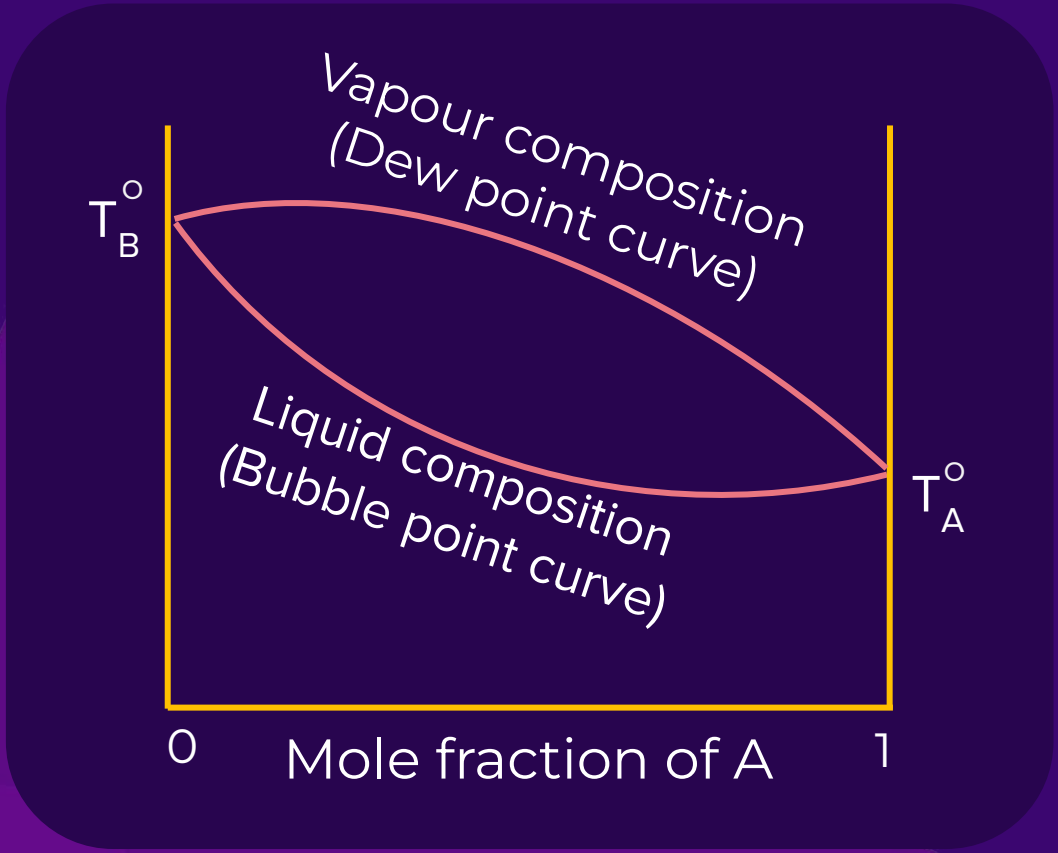


The **mole fraction** of one component is plotted on the horizontal axis and the boiling **temperature** is plotted on the vertical axis.

If a liquid has a **high vapour pressure** at a particular temperature, it means that its molecules can **escape easily** from the surface.

If liquid 'A' has **higher V.P. than 'B'** at a particular temperature, then **boiling point of 'A'** is lower than 'B'.

Temperature vs Composition Phase Diagram



Dew-point curve

Boiling temperature at the given pressure, as a function of the mole fraction in the **vapour phase**.

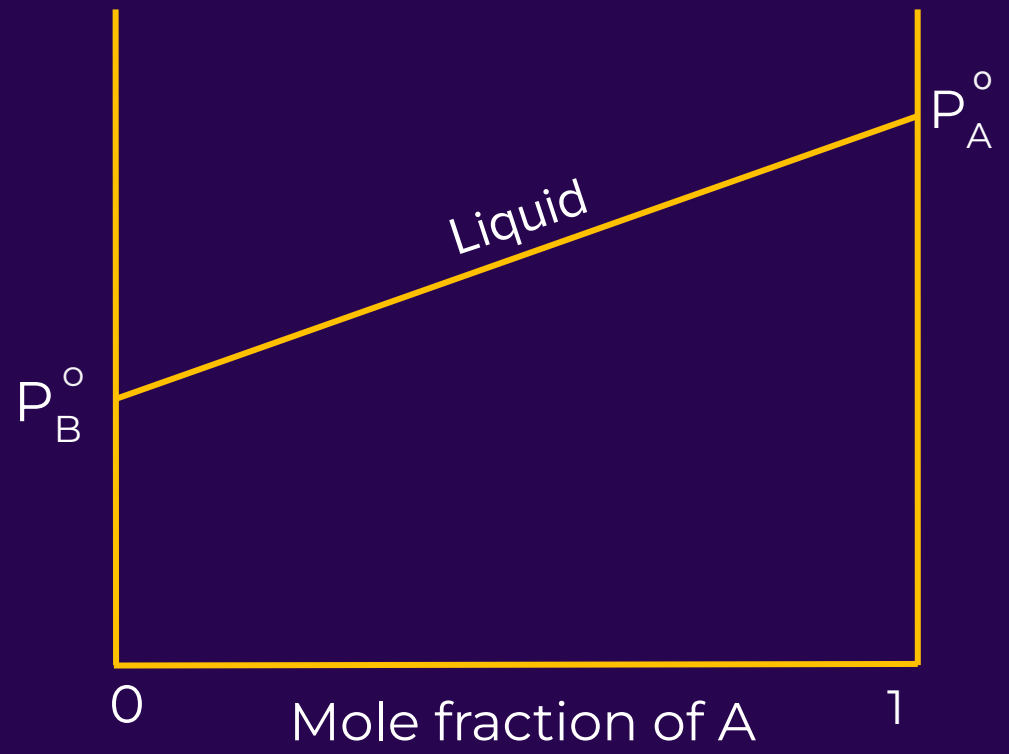
Bubble-point curve

Boiling temperature at the given pressure, as a function of the mole fraction in the **liquid phase**.

Pressure Composition Diagram

$$P_T = (P_A^o - P_B^o)\,\mathcal{X}_A + P_B^o$$

This represents equation of a **straight line** of P_T vs $\mathcal{X}_A$



P_T in Terms of Composition of Vapour Phase

$$\frac{1}{P_T} = \frac{y_A}{P_A^\circ} + \frac{y_B}{P_B^\circ}$$

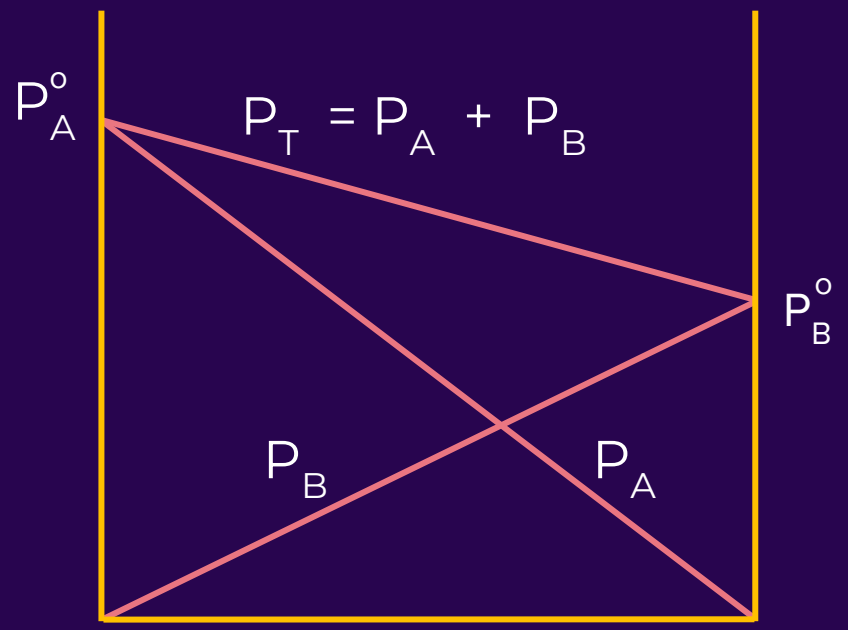
$$= \frac{y_A}{P_A^\circ} + \frac{1 - y_A}{P_B^\circ}$$

$$P_T = \frac{P_A^\circ P_B}{P_A^\circ + (P_B^\circ - P_A)\, y_A}$$

Ideal Solution

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.



Ideal Solution

Characteristics

(i) Raoult's law is **obeyed**.

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

(iii) $\Delta V_{mix} = 0$, (1L + 1L = 2L) i.e., there should not be a change in volume on mixing.

Examples

- n-Hexane and n-Heptane
- Ethyl bromide and Ethyl iodide
- Benzene and Toluene
- Chlorobenzene and Bromobenzene

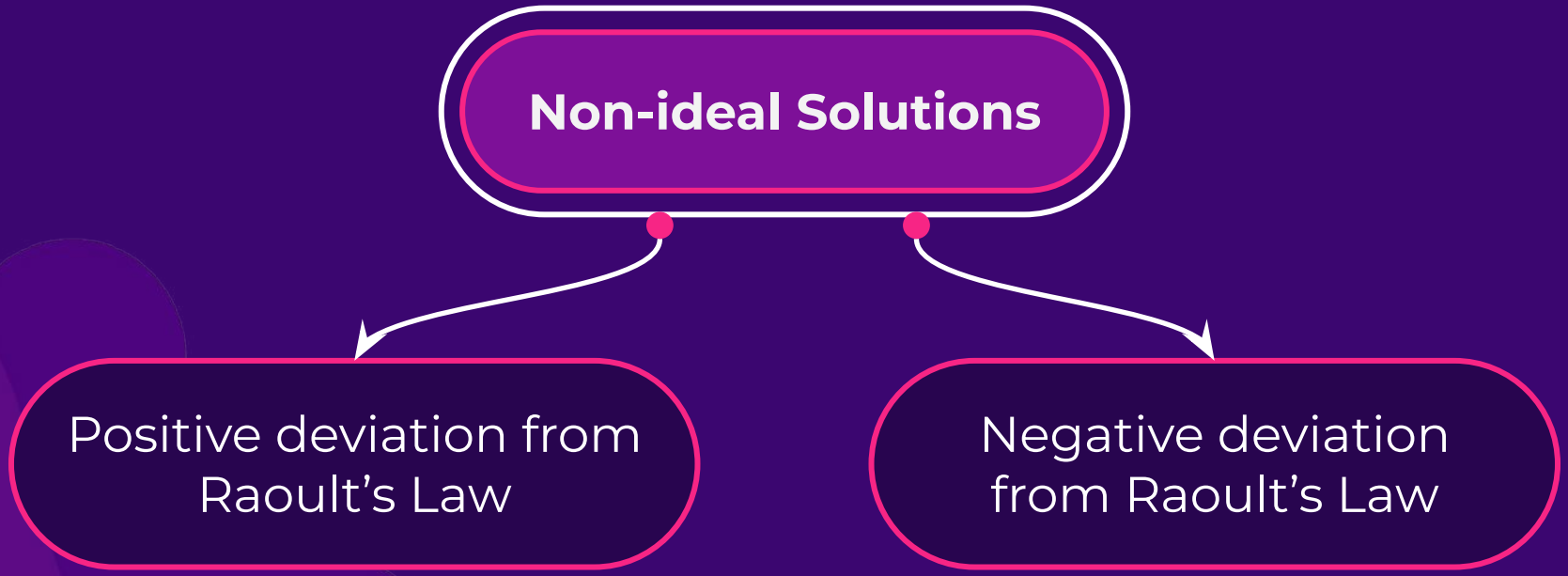
Non-Ideal Solution

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

Positive deviating 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.

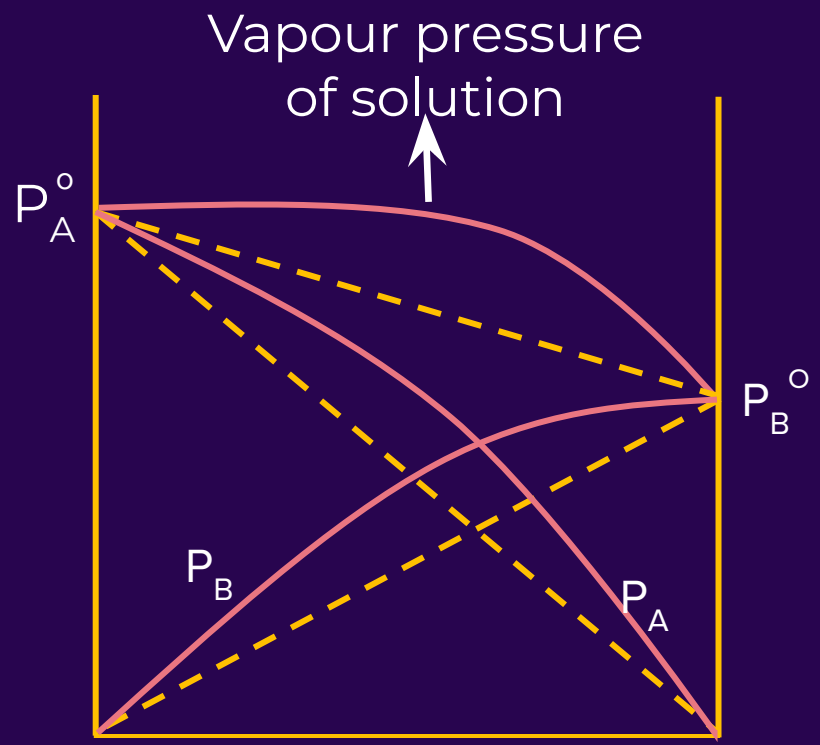
Negative deviating solution

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.

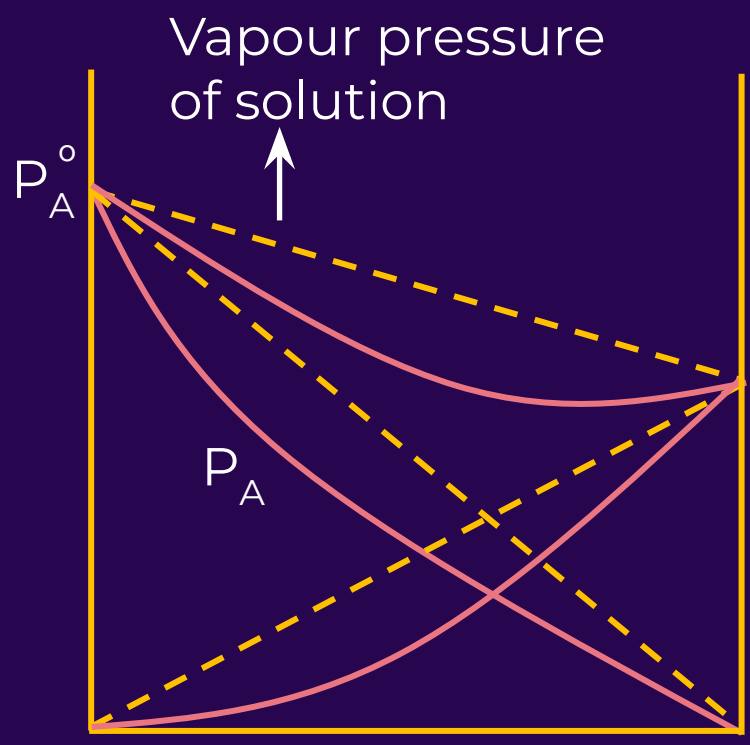
Positive deviating solution



V.P. ↑ B.P. ↓

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

Negative deviating solution



V.P. ↓ B.P. ↑

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

Positive deviating solution

Water and Ethanol

Chloroform and Water

Ethanol and CCl_4

Methanol and Chloroform

Negative deviating solution

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
$P_T = \chi_A P_A^\circ + \chi_B P_B^\circ$	$P_T > \chi_A P_A^\circ + \chi_B P_B^\circ$	$P_T < \chi_A P_A^\circ + \chi_B P_B^\circ$
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

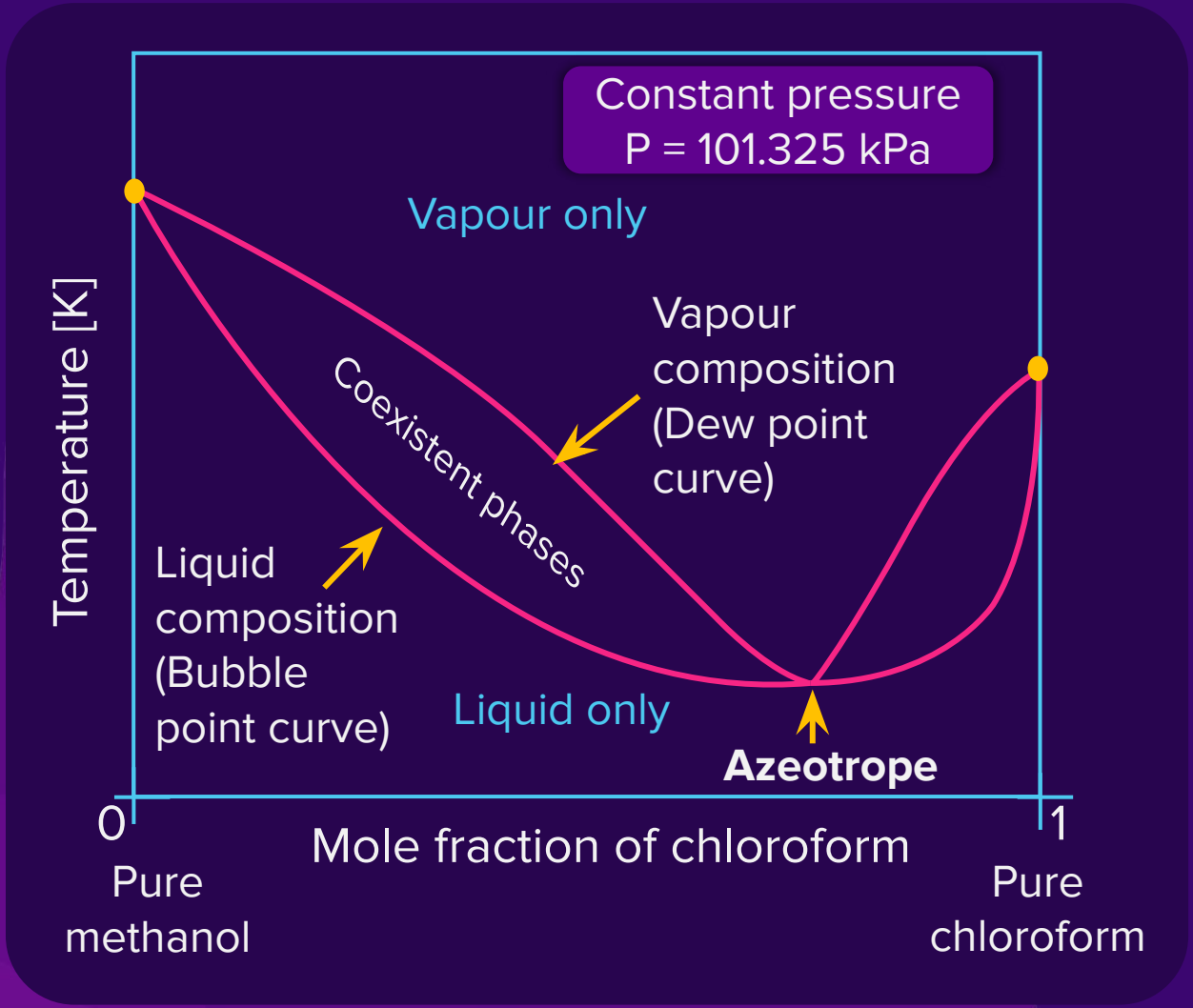
Minimum Boiling Azeotropes

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'.

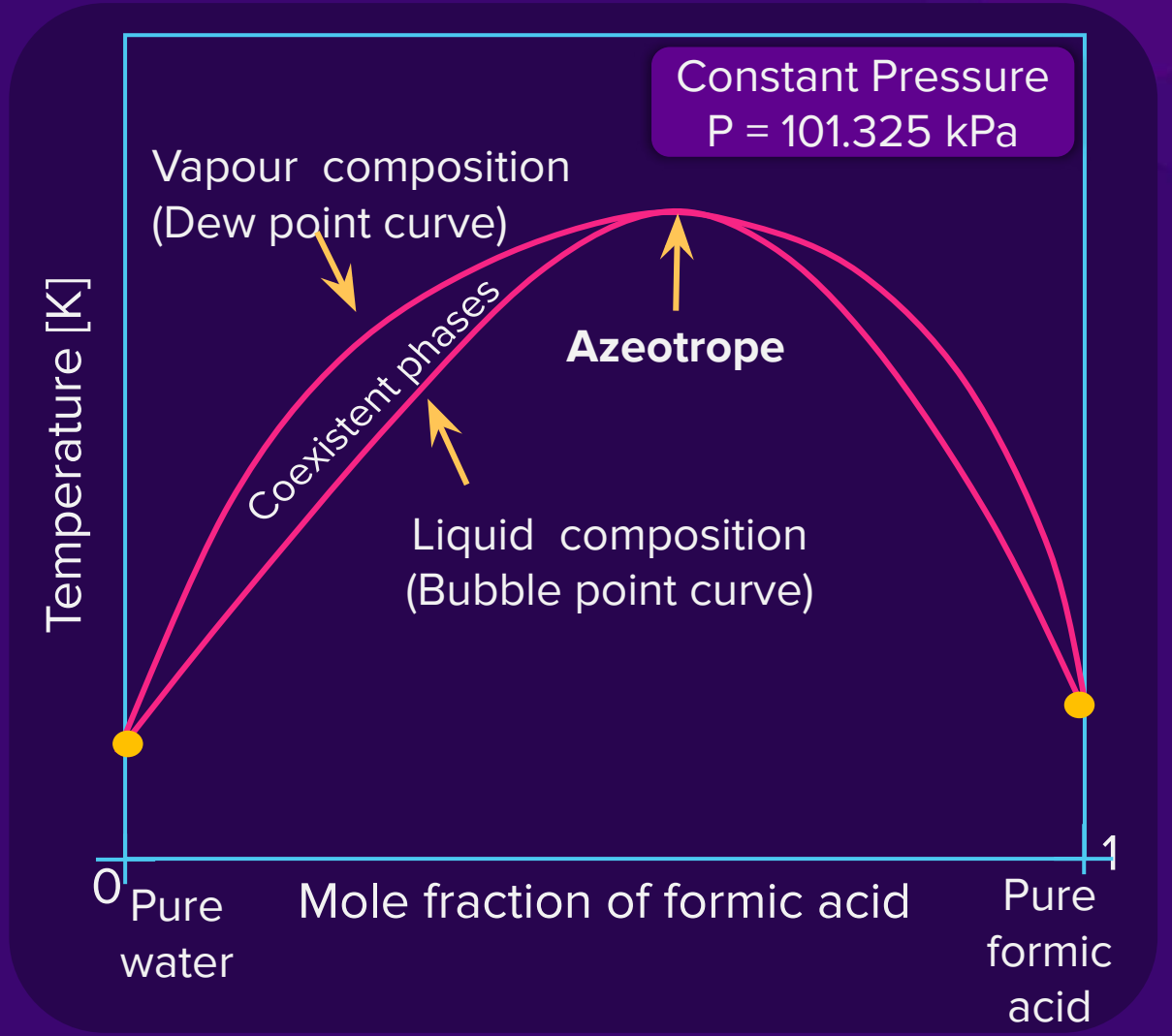
A mixture of HNO_3 and H_2O containing ≈68% HNO_3 and 32% water by mass

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

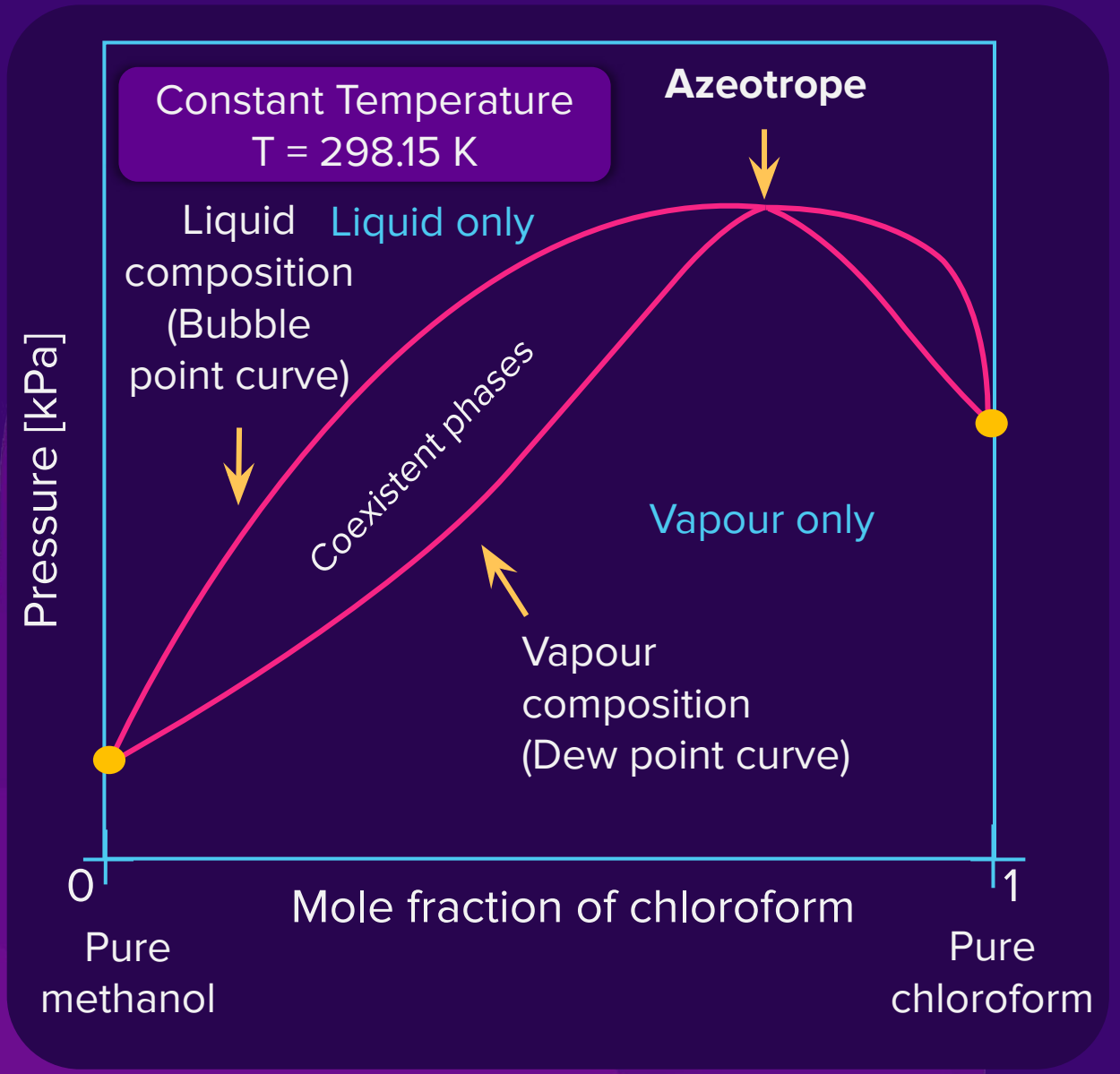
Minimum Boiling Azeotropes



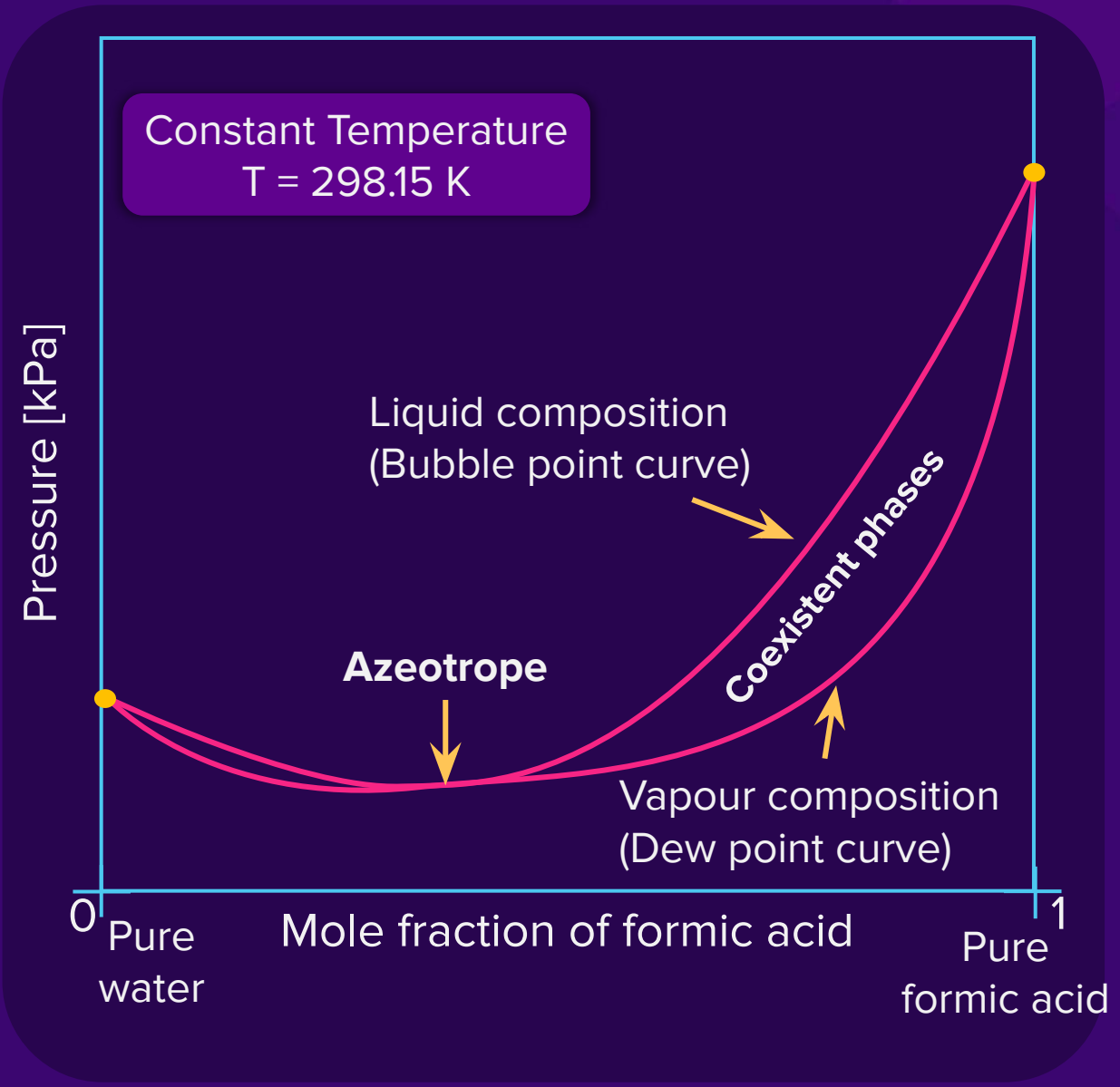
Maximum Boiling Azeotropes



Minimum Boiling Azeotropes



Maximum Boiling Azeotropes



Immiscible Liquids

A mixture of two immiscible liquids will boil when the total vapour pressure is **equal to** the external pressure.

The boiling point of the mixture is thus, **lower** than that of either constituent.

B.P. of water (pure)	=	100°C
B.P. of benzene (pure)	=	80.2°C

B.P. of a solution of two immiscible liquids is **less** than the individual B.P. of both the liquids.

This concept is used in **steam distillation**.

B.P. of water and benzene mixture	=	68.9°C

Distillation

In a simple distillation, the vapour over a boiling mixture is **withdrawn** and condensed in a separate container.

The collected liquid is called **condensate or distillate** and the remaining liquid is called **residue**.

Condensate

Higher mole fraction of the **more** volatile component than in the initial liquid mixture.

Residue

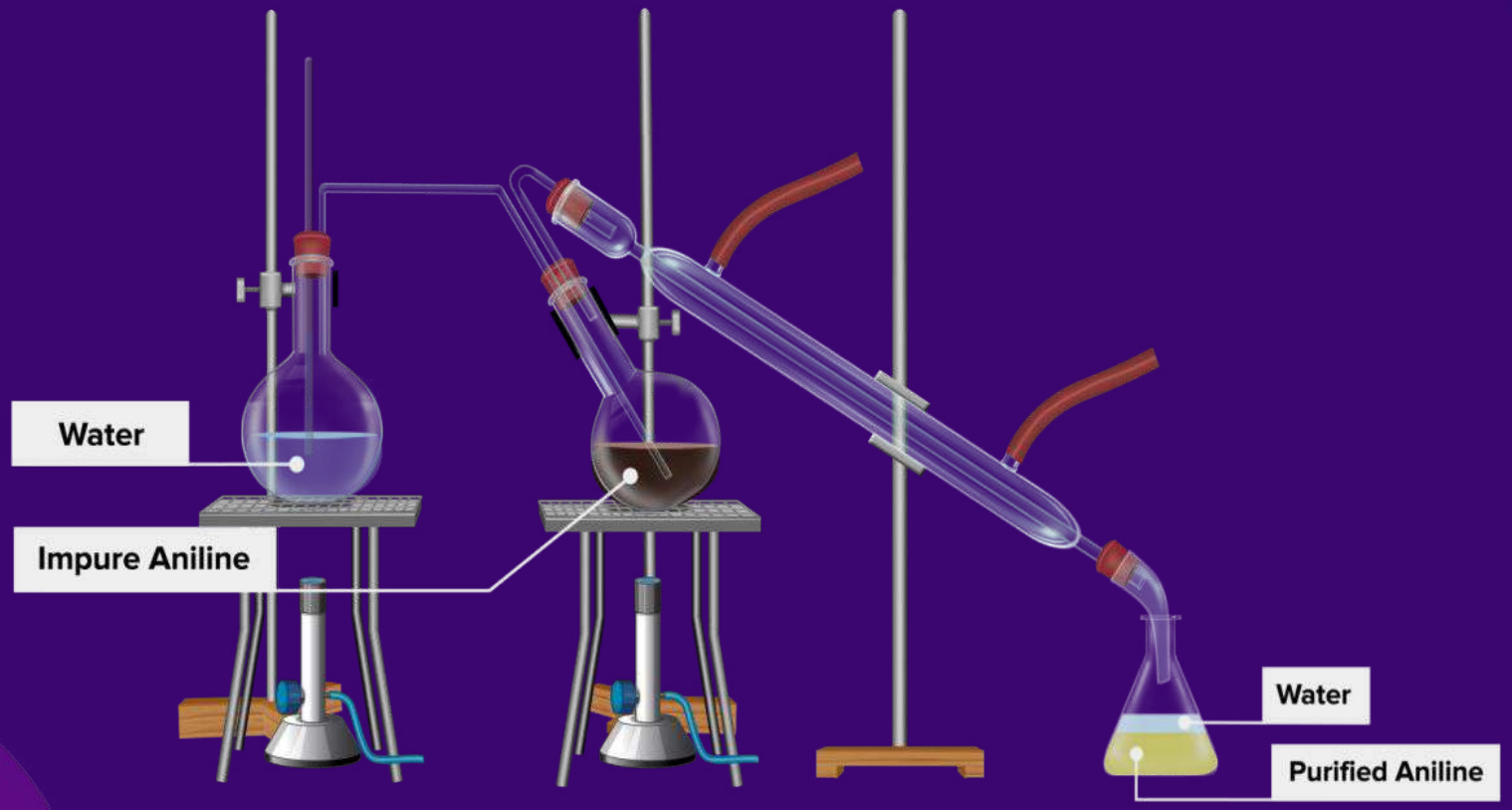
Higher mole fraction of the **less** volatile component than in the initial liquid mixture.

This is the principle of **distillation** and is used to separate a **more volatile** liquid from a **less volatile** liquid.

Steam Distillation

A liquid (generally organic) that is immiscible with water, and has a higher B.P. than water can be boiled (distilled) at a **much lower temperature** by passing steam through it.

Organic liquid can be **purified** from impurities using steam distillation.



Dissolution & Crystallisation

Dissolution

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

Crystallisation

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

Solute + Solvent $\rightleftharpoons$ Solution

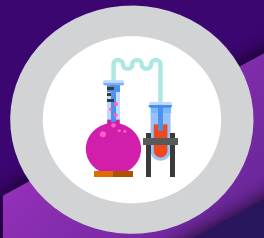
Equilibrium

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 solvent & solute



Temperature

Pressure

1. 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.

2. Effect of Temperature on Solubility

Solute + Solvent $\rightleftharpoons$ Solution

If dissolution is **exothermic** — **$\Delta H < 0$**

By Le Chatelier's principle,

T ↑ → Solubility ↓

If dissolution is **endothermic** — **$\Delta H > 0$**

By Le Chatelier's principle,

T ↑ → Solubility ↑

3. Effect of Pressure on Solubility

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.

- Relative lowering of vapour pressure
- Elevation in boiling point
- Depression in 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.

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

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.

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

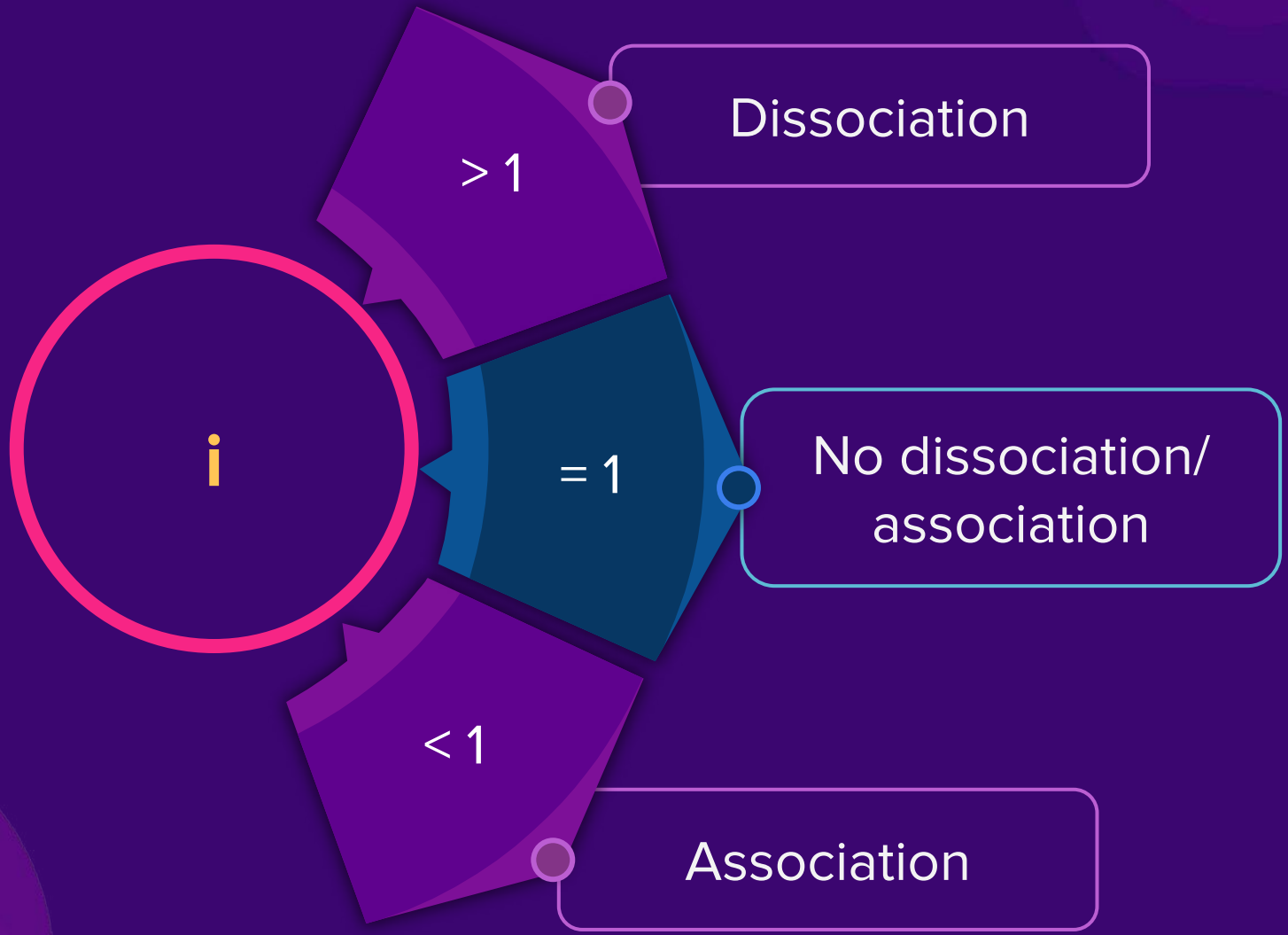
van't Hoff Factor

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

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

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

van't–Hoff Factor (i)



i for Dissociation of Electrolyte

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

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

Net concentration $= C - C\alpha + xC\alpha + yC\alpha$

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

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

i for Dissociation of Electrolyte

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

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

"α" is degree of dissociation

NaCl (100% ionised)	i =	2
$BaCl_2$ (100% ionised)	i =	3

i for Association of Electrolyte

$$nA \rightleftharpoons A_n$$

t = 0	C	0
$t = t_{eq}$	$C(1 - \beta)$	$\frac{C\beta}{n}$

If n= 2 ⟶ Dimerization
= 3 ⟶ Trimerization
= 4 ⟶ Tetramerization

At equilibrium,

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

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

Examples

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

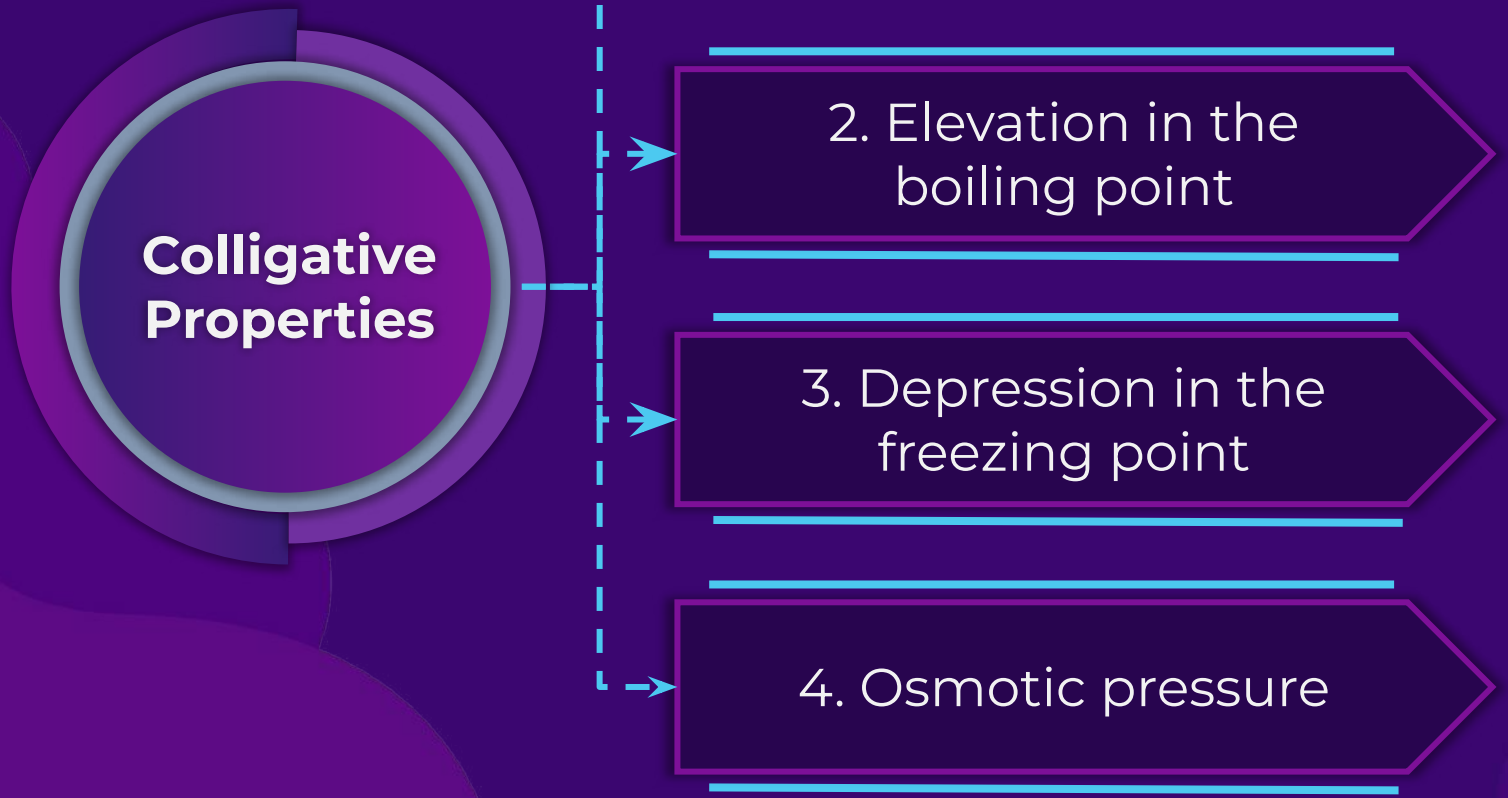
$$i = 1 + \left(\frac{1}{n} - 1\right)\beta$$

Dimerisation of CH_3COOH in benzene (100 %)

$i = 0.5$

Dimerisation of C_6H_5COOH in benzene (100 %)

$i = 0.5$

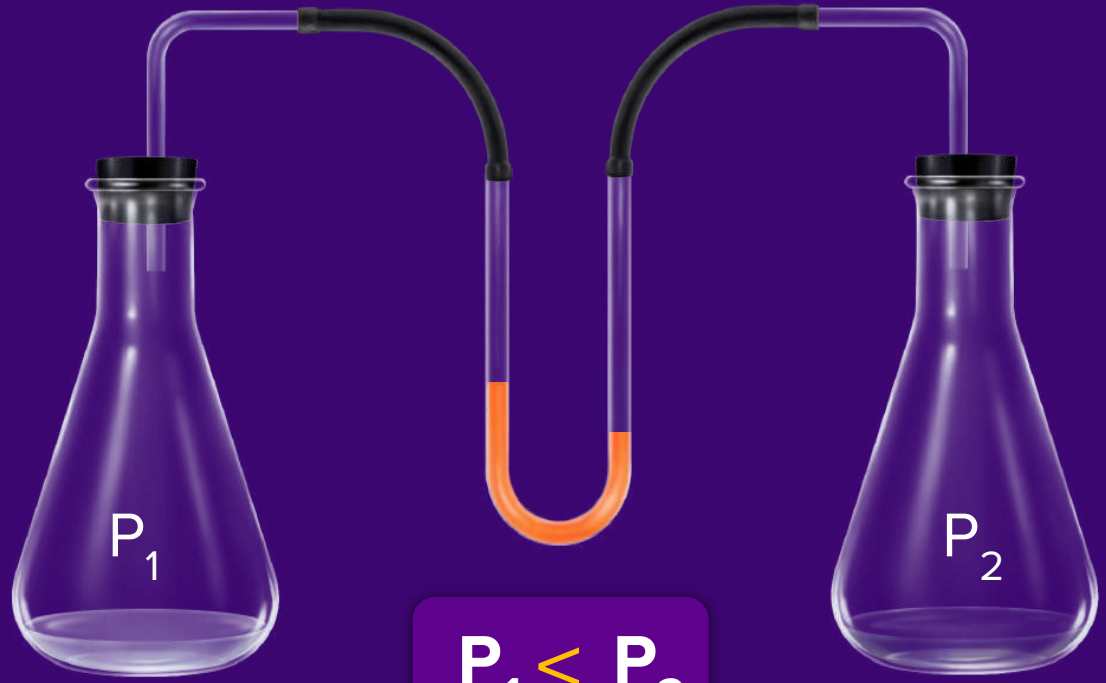

Colligative Properties
1. Relative lowering of the vapour pressure
2. Elevation in the boiling point
3. Depression in the freezing point
4. Osmotic pressure

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**.

Pure solvent A

Pure solvent A



Solution (non-volatile solute in solvent A)

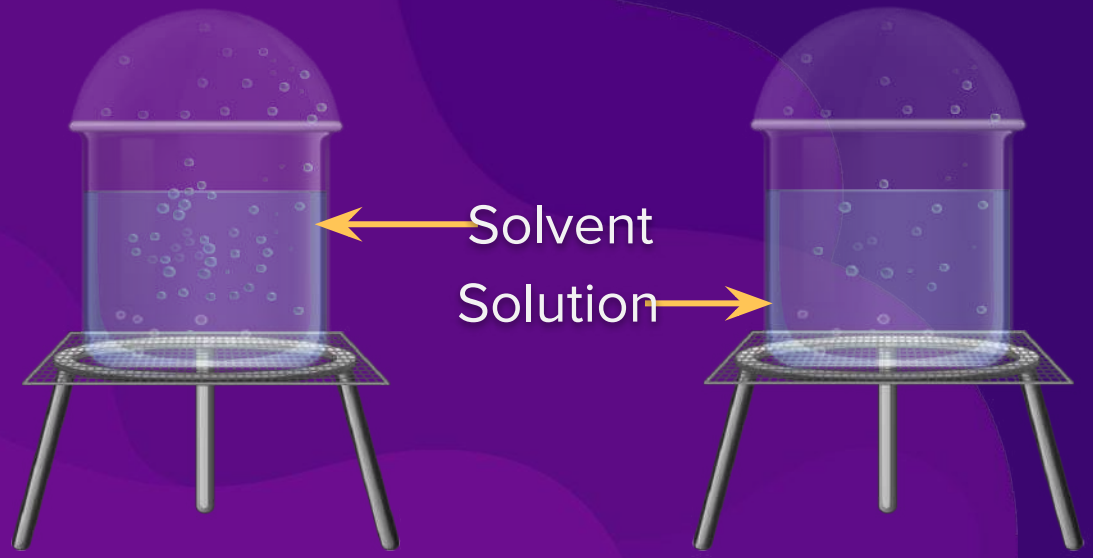
Pure solvent A

Relative Lowering of Vapour Pressure (RLVP)

Reason of Lowering of V.P.

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, $P^{\circ} > P_s$, where P° is V.P. of the pure solvent and P_s is the V.P. of the solution.

Relative Lowering of Vapour Pressure

$$\text{Lowering in V.P.} = P^{o} - P_{s} = \Delta P$$

$$\text{Relative lowering in vapour pressure (RLVP)} = \frac{\Delta P}{P^{o}} = \frac{P^{o} - P_{s}}{P^{o}} = \chi_{\text{solute}} = \frac{n}{n + N}$$

n = Number of moles of non-volatile solute

N = Number of moles of solvent in the solution

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

Relative Lowering of Vapour Pressure

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**.

$$P_S = \chi_{solvent} P^o = (1 - \chi_{solute}) P^o$$

Relative Lowering of Vapour Pressure

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

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

$$\frac{P^o - P_s}{P_s} = \frac{n}{N} = \frac{w_{solute}}{M_{solute}} \times \frac{M_{solvent}}{w_{solvent}}$$

w = Weight of species
M = Molar mass of species

Relative Lowering of Vapour Pressure

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

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

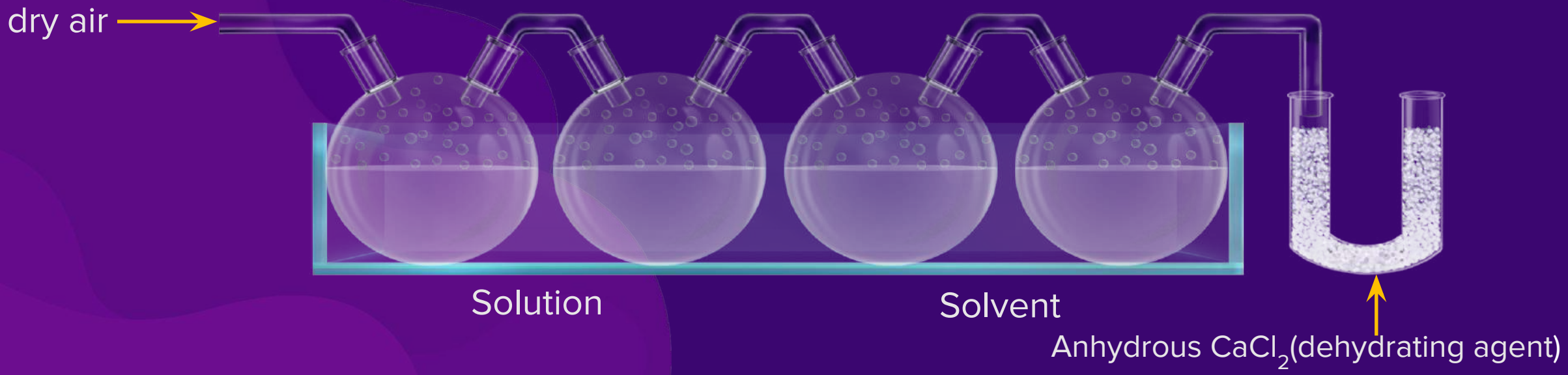
If solute gets **associated or dissociated**

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

Ostwald-Walker Method

When **dry air** is passed through a **volatile liquid**, there occurs a **loss of weight** of liquid which is **directly proportional** to its **vapour pressure**.

Greater is the **volatility** of liquid, greater will be the **loss of weight** of liquid



Ostwald-Walker Method

Step 1

1 Initially, **note down the weights** of the solution set, solvent set Containers & of dehydrating agent.

Step 2

2 Note down the same weights **after** the experiment is complete.

Loss of weight of solution containers $\propto$ P_s

Loss of weight of solvent containers $\propto$ $P^o - P_s$

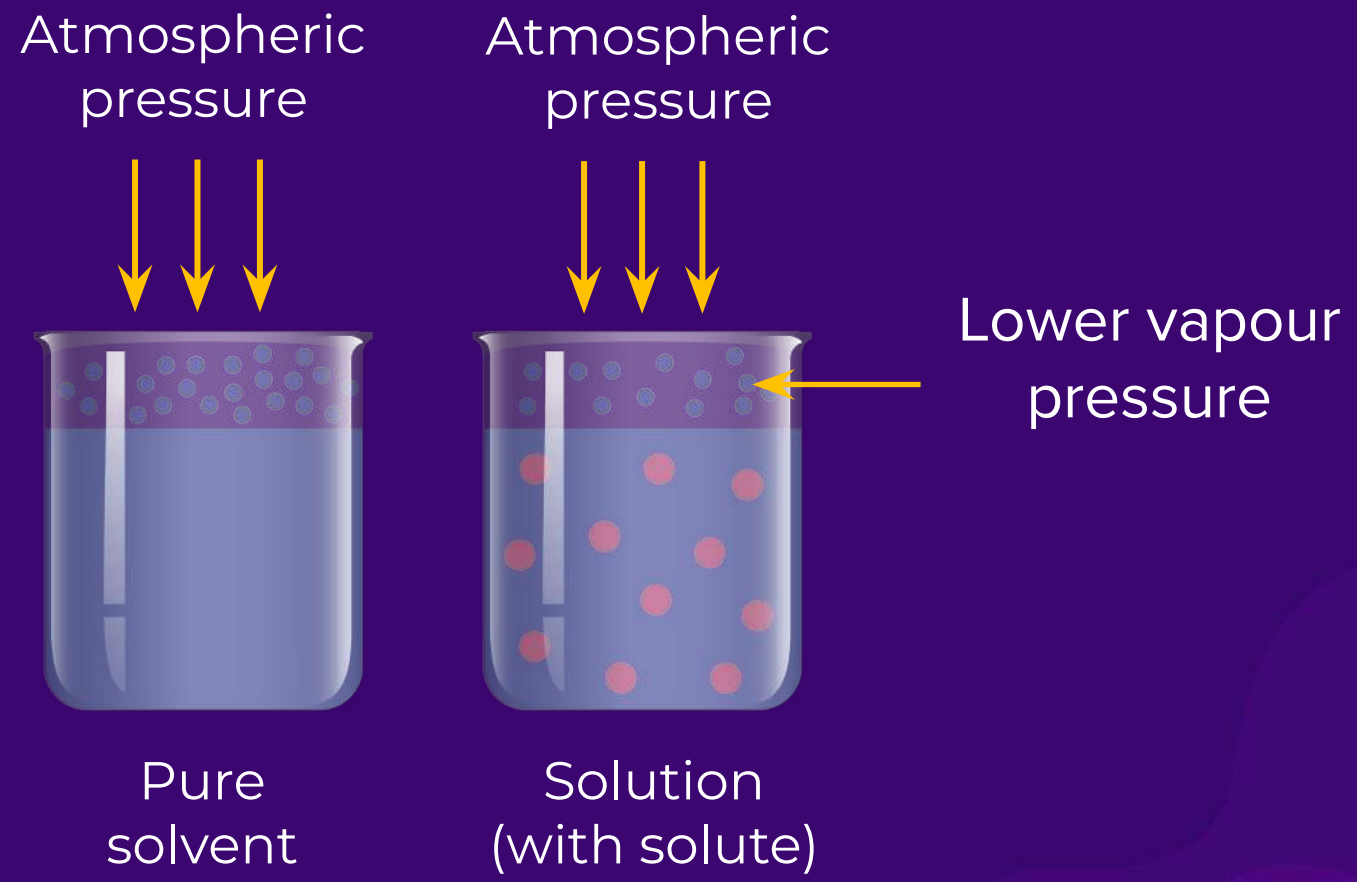
Gain in weight of dehydrating agent $\propto$ P^0

$$\frac{P^o - P_s}{P_s} = \frac{\text{Loss in weight of solvent}}{\text{Loss in weight of solution}}$$

Elevation in Boiling Point

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

Solution needs to be **heated to a higher temperature** to boil it, so that V.P. becomes equal to external pressure.



Elevation in Boiling Point

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.

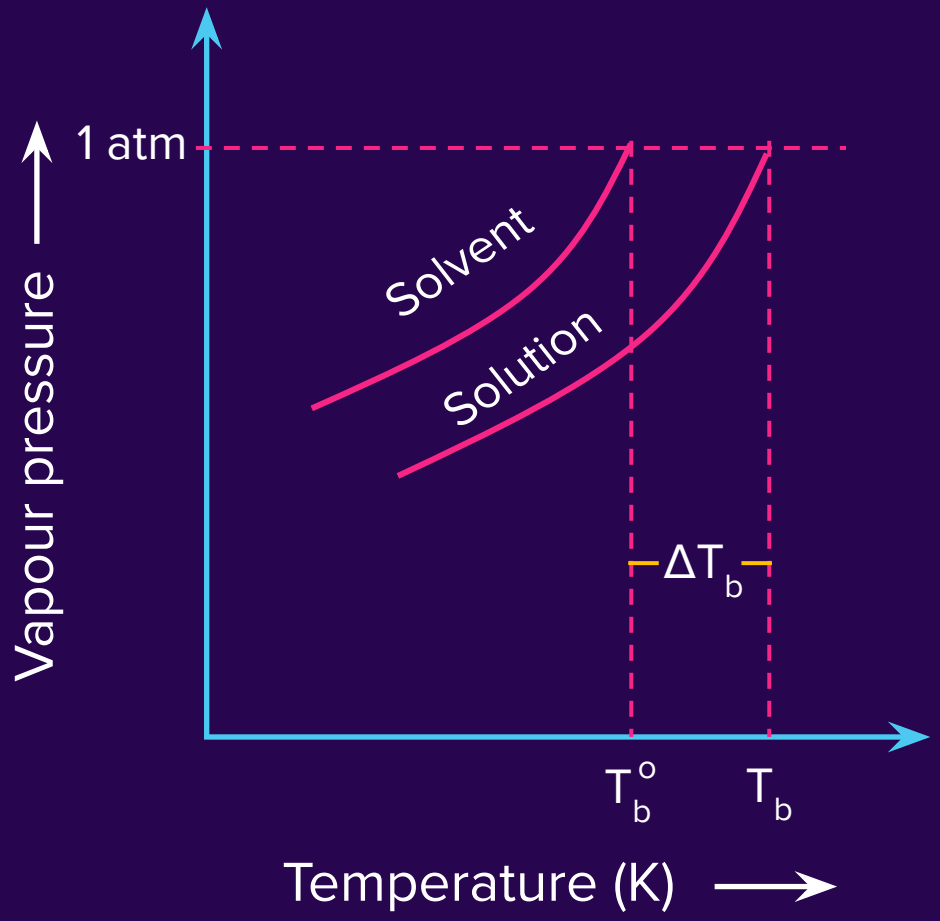
T_b = b.p. of solution (K)
T_b^o = b.p. of pure solvent (K)

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

$\Delta T_b = T_b - T_b^o$

$\Delta T_b \propto m$

m = Molality



Elevation in Boiling Point

$$\Delta T_b = K_b m$$

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}

$$K_b = \frac{RT^{\circ}_b{}^2 M}{1000 \times \Delta H_{vap}}$$

- T_b° 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

Ebullioscopic Constant (K_b)

$$L_{vap} = \frac{\Delta H_{vap}}{M}$$

For water,

- L_{vap} = 2257.2 J/g
- T_b^o = 373 K

$$K_b = \frac{RT_b^{o2}}{1000 \times L_{vap}}$$

$$K_b = \frac{8.314 \times (373)^2}{1000 \times 2257.2} \text{ K kg mol}^{-1}$$

- L_{vap} is the latent heat of vaporisation (J/g)

$$= 0.52 \text{ K kg mol}^{-1}$$

Note

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

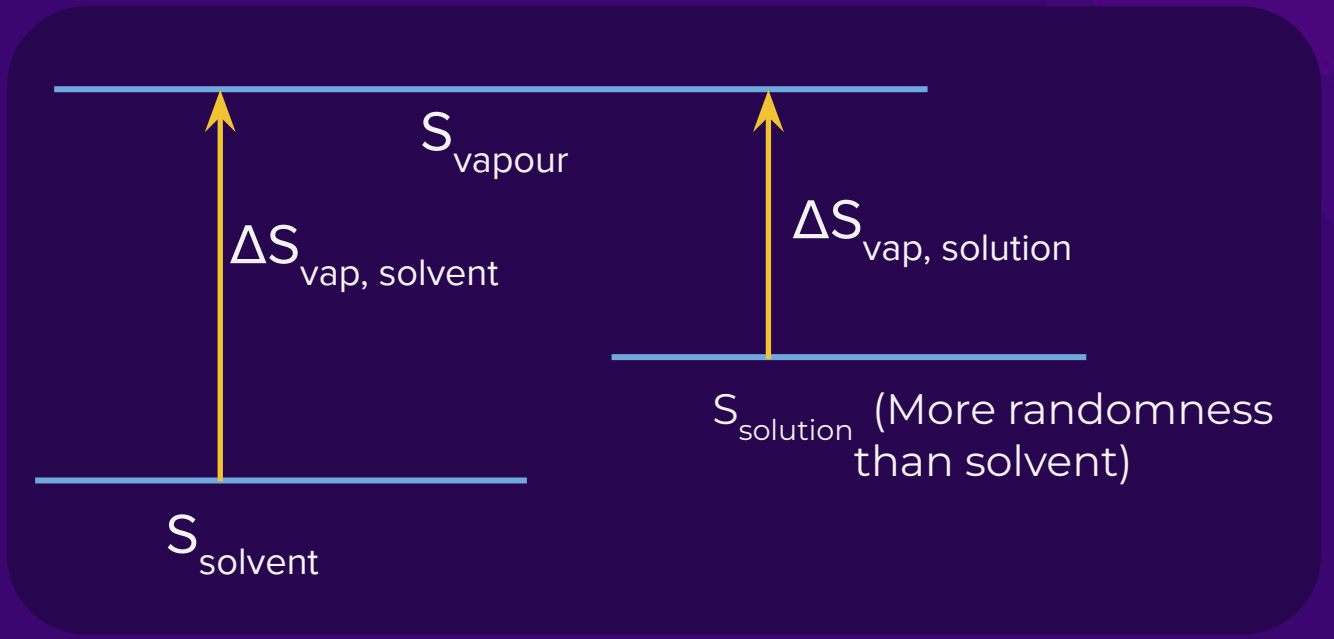
2. K_b is the property of solvent

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

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

Understanding Elevation of B.P. Using ΔS

$$\Delta S_{vap,\ solvent} > \Delta S_{vap,\ solution}$$



Since, $\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b}$

$$\frac{\Delta H_{vap,\ solvent}}{T_{b,\ solvent}} > \frac{\Delta H_{vap,\ solution}}{T_{b,\ solution}}$$

As only solvent particles are going into vapours,

$$\Delta H_{vap,\ solvent} = \Delta H_{vap,\ solution} \Rightarrow T_{b,\ solvent} < T_{b,\ solution}$$

Freezing Point (F.P.)

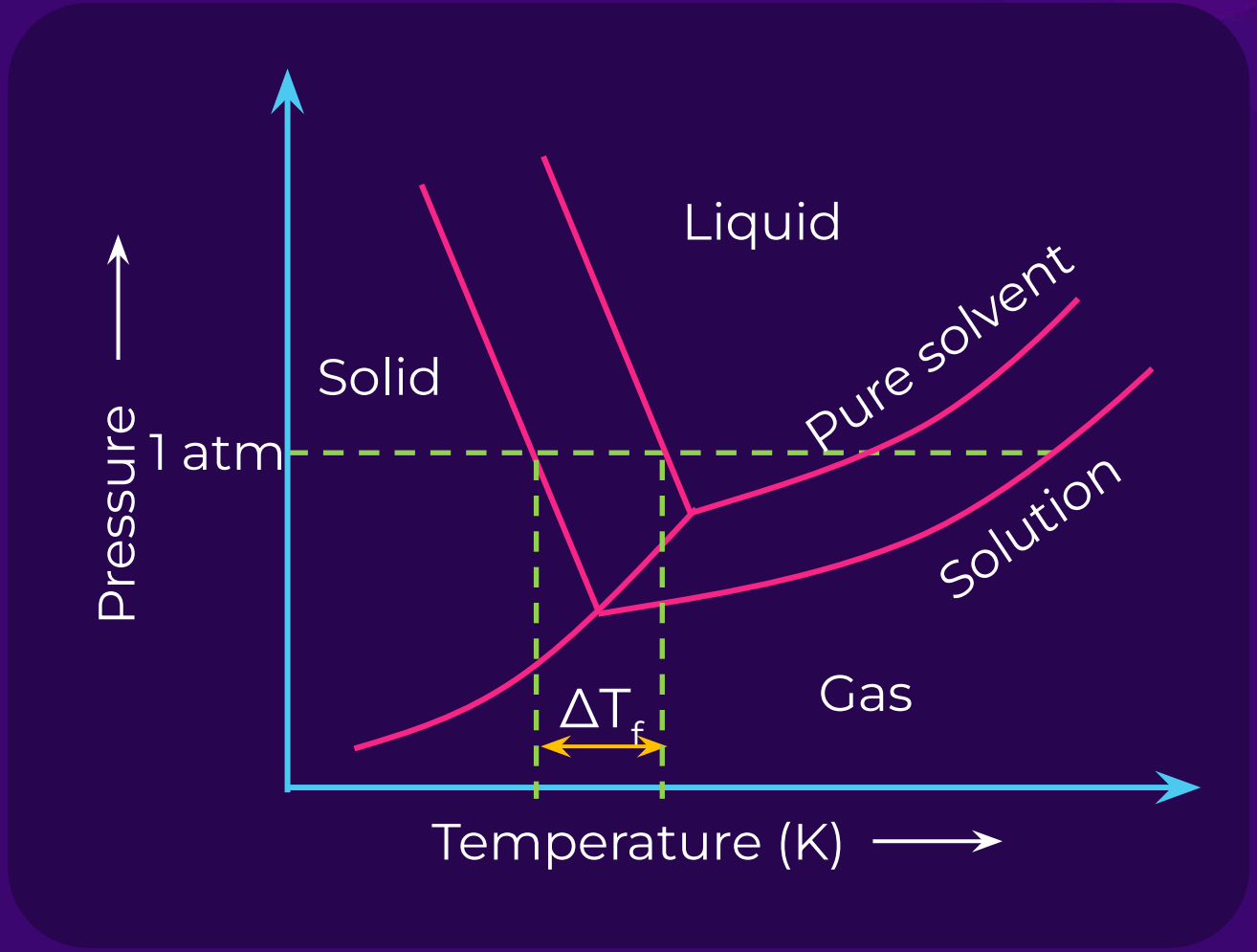
Temperature at which, the vapour pressure of a solid becomes **equal to** the vapour pressure of liquid at 1 atm is called **normal freezing point**.

V.P. of solid = V.P. of liquid

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.**



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)

$$K_f = \frac{RT_f^{o\,2}M}{1000 \times \Delta H_{fus}}$$

$$L_{fus} = \frac{\Delta H_{fus}}{M}$$

Units K/m or °C/m or K kg mol^{-1}

$$K_f = \frac{RT_f^{o\,2}}{1000 \times L_{fus}}$$

- 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

- L_{fus} is latent heat of fusion (J/g or cal/g)

K_f of Water

For water

- L_{fus} = 334.72 J/g
- T_f^o = 273 K

$$K_f = \frac{8.314 \times (273)^2}{1000 \times 334.72} \text{ K kg mol}^{-1}$$

$$= 1.86 \text{ K kg mol}^{-1}$$

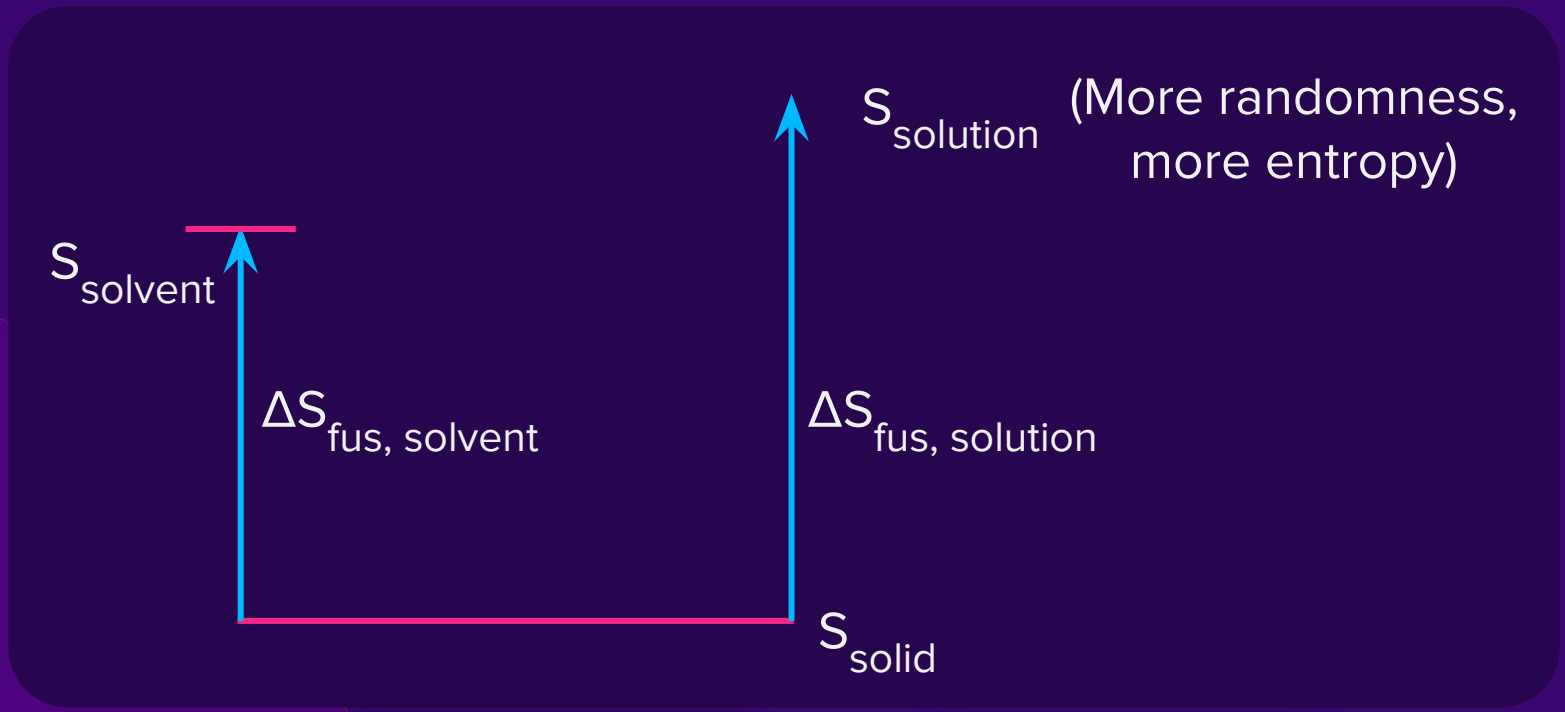
Note

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.

Understanding Depression in F.P. Using ΔS



$$\Delta S_{fus,\ solution} > \Delta S_{fus,\ solvent}$$

$$\Delta S_{fus} = \frac{\Delta H_{fus}}{T_f}$$

Understanding Depression in F.P. Using ΔS

$$\frac{\Delta H_{fus,\ solvent}}{T_{f,\ solvent}} < \frac{\Delta H_{fus,\ solution}}{T_{f,\ solution}}$$

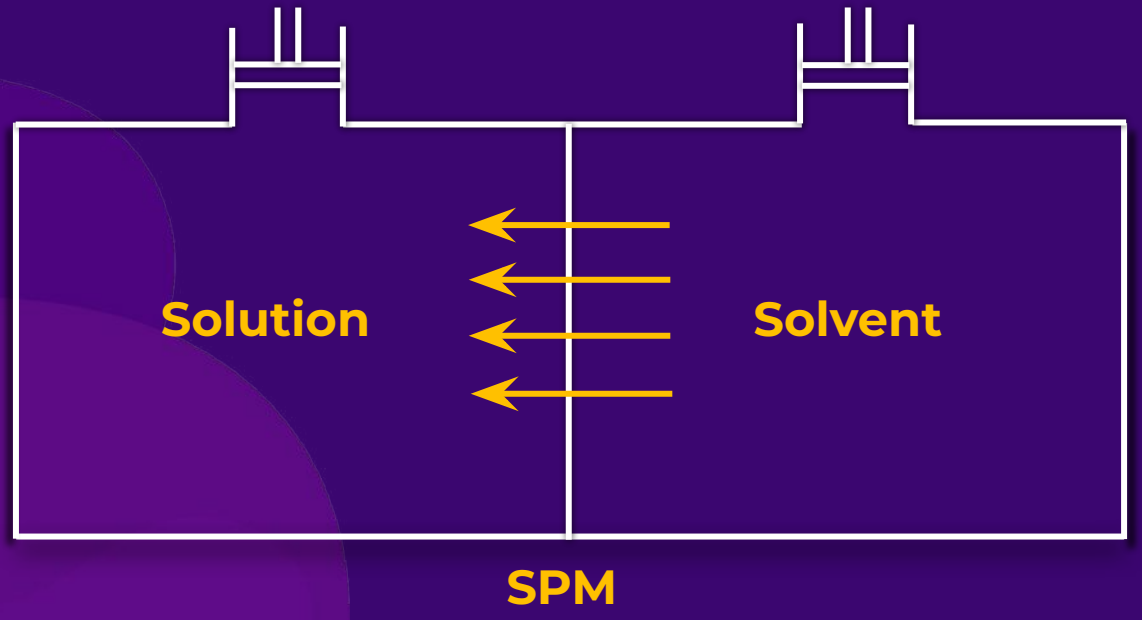
As only solvent particles freeze,

$$\Delta H_{fus,\ solvent} = \Delta H_{fus,\ solution}$$

$$\Rightarrow T_{f,\ solvent} > T_{f,\ solution}$$

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.

SPM

- Natural
- Artificial

Animal/plant cell membrane formed just below the outer skins.

$Cu_2[Fe(CN)_6]$ & Silicate of Ni, Fe, Co can act as SPM.

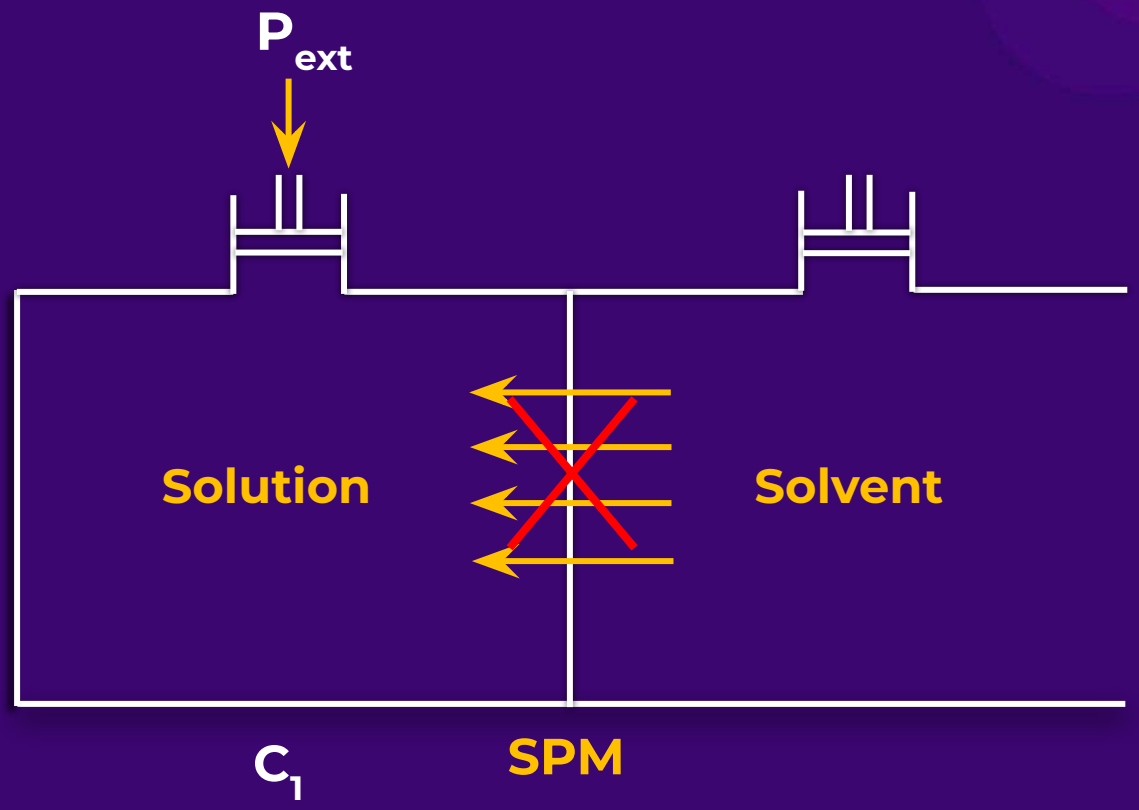
Example of Osmosis

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**.

Osmotic Pressure (Π)

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



$P_{ext} = \Pi$

van't – Hoff Formula

$\Pi \propto$ Concentration (Molarity)

$\Pi \propto T$

$\Pi = CST$

- Π = Osmotic pressure
- C = Concentration (mol/L)
- S = Ideal solution constant
- T = Temperature (K)

van't – Hoff Formula

s — Ideal solution constant

$S = 8.314\ J\ mol^{-1}\ K^{-1}$

S = R (Ideal gas constant)

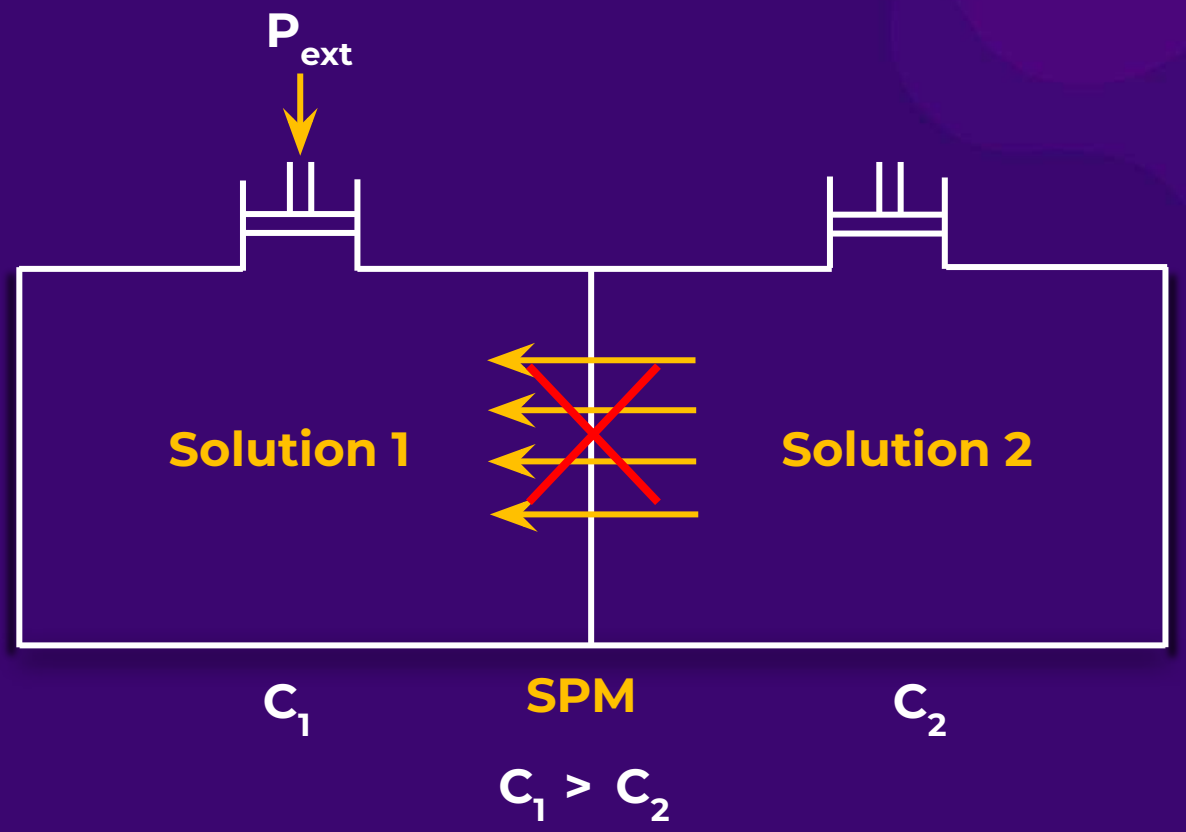
$\Pi = CRT$

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

Osmotic Pressure (Π)

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

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



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

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.**

Reverse Osmosis

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**.

$$P_{ext} > \Pi$$

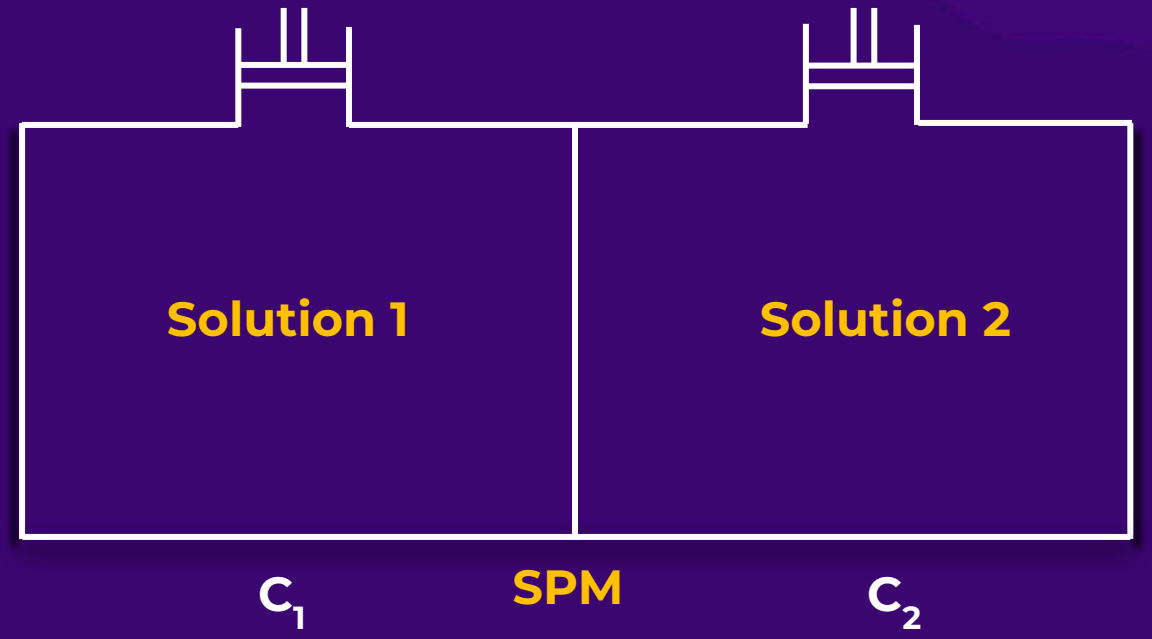
Used in **desalination of sea-water**

Based on the difference in osmotic pressure, the solutions can be classified as:

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

Isotonic Solution

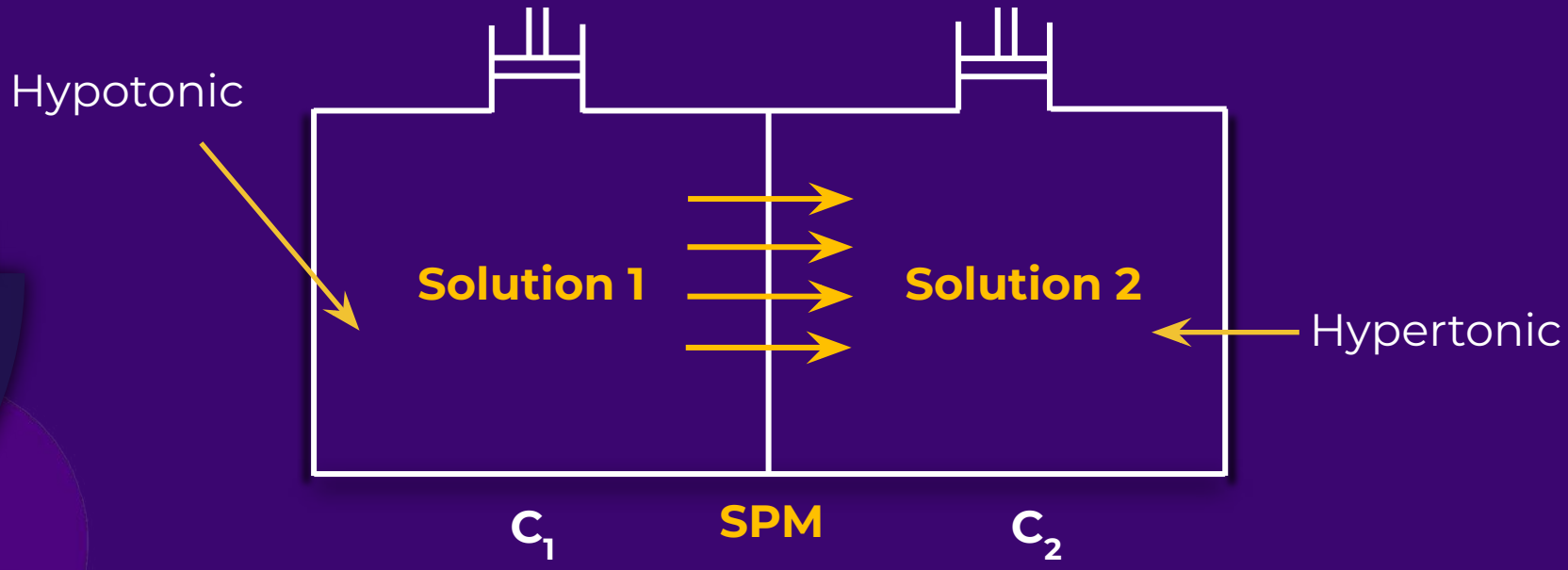
Two solutions having **same osmotic pressure** are considered as isotonic solution.



$$\Pi_1 = \Pi_2$$

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.



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

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.

Applications 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

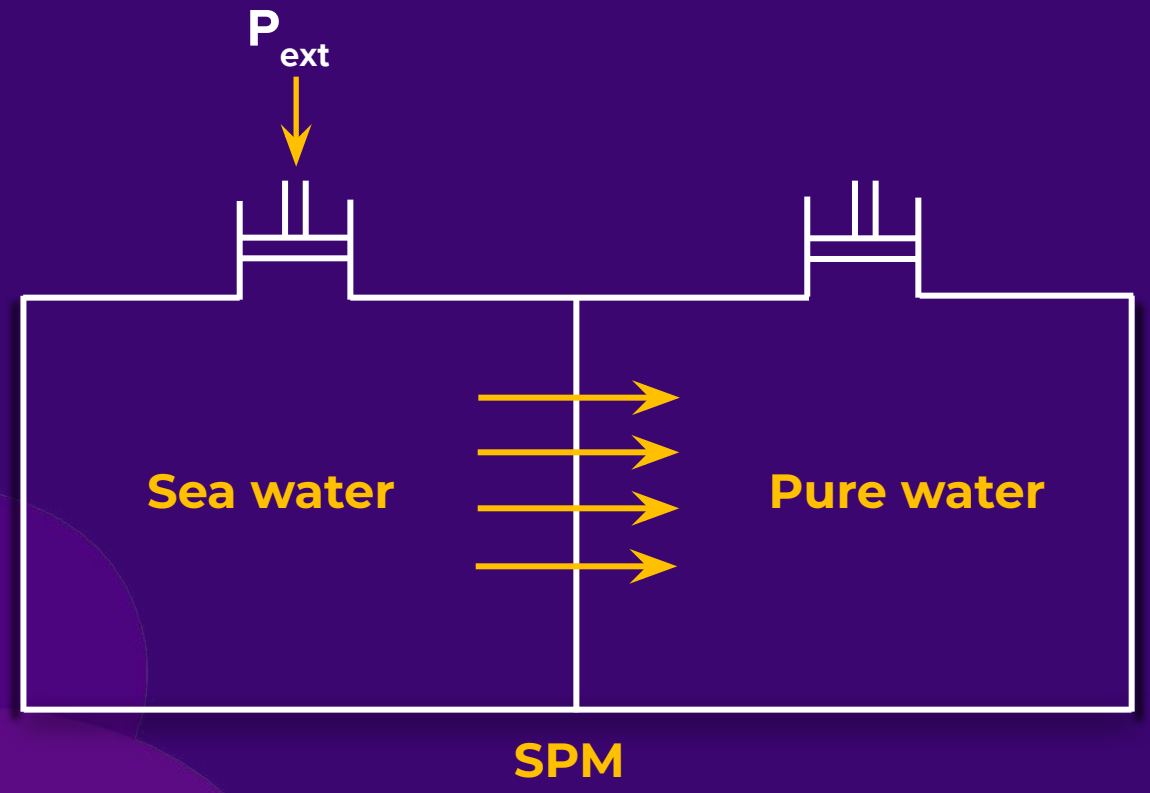
This method has the advantage over other methods as pressure measurement is around the **room temperature**.

Note

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

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

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



$P_{ext} > \Pi$

c. Dialysis

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