



Collegedunia NCERT Notes

The Ultimate NCERT Revision Guide for Class 12 Chemistry (2026-27 / New NCERT)

Chapter 1: Solutions

Concentration units • Henry's law • Raoult's law • Colligative properties • van't Hoff factor

Class 12th • CBSE • JEE / NEET ready

What this chapter is about

A **solution** is a homogeneous mixture of two or more substances. This chapter teaches how to **quantify** composition (mass percent, mole fraction, molarity, molality), how solubility responds to temperature and pressure (**Henry's law**), how vapour pressure of solutions behaves (**Raoult's law**), what makes a solution ideal or non-ideal, and how four properties — vapour pressure lowering, boiling point elevation, freezing point depression, and osmotic pressure — depend only on the *number* of solute particles (**colligative properties**). Electrolytes need a correction factor: **van't Hoff i** .

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1 Types of Solutions

A solution contains a **solvent** (the component present in larger amount, which fixes the physical state of the solution) and one or more **solutes**. In a binary solution there is one solvent and one solute. The state of the solution follows the state of the solvent.

1.1 Nine combinations by state

Depending on the physical states of solvent and solute, nine binary combinations are possible. The table below summarises them.

Type	Solute	Solvent	Example
Gaseous	Gas	Gas	Air ($O_2 + N_2$)
Gaseous	Liquid	Gas	Water vapour in air (humidity)
Gaseous	Solid	Gas	Camphor in N_2
Liquid	Gas	Liquid	O_2 in water, soda water
Liquid	Liquid	Liquid	Ethanol in water
Liquid	Solid	Liquid	Glucose / salt in water
Solid	Gas	Solid	H_2 adsorbed in palladium
Solid	Liquid	Solid	Dental amalgam (Hg in Ag)
Solid	Solid	Solid	Brass (Cu + Zn), bronze

Key idea

The phase of the *solvent* decides the phase of the solution. Most of this chapter focuses on **liquid solutions** — solid or gas dissolved in a liquid — because they are the most common in chemistry and biology.

Real-World Application

Brass, bronze, and stainless steel are solid–solid solutions (alloys); **soda water** is a gas–liquid solution; the **air we breathe** is a gas–gas solution. Solutions are not laboratory curiosities — they are everywhere.

2 Expressing the Concentration of Solutions

Composition is described *qualitatively* (dilute / concentrated) or *quantitatively*. Only quantitative descriptions are useful in calculation. We will meet seven units; each has a setting where it shines.

2.1 Mass percentage (w/w)

Mass % of a component

$$\text{Mass \% of A} = \frac{\text{Mass of A in the solution}}{\text{Total mass of the solution}} \times 100$$

A **10% glucose solution by mass** means 10 g of glucose plus 90 g of water in every 100 g of solution. Used commonly in industry — e.g. commercial bleach is described as 3.62% sodium hypochlorite by mass.

2.2 Volume percentage (V/V)

Volume % of a component

$$\text{Volume \% of A} = \frac{\text{Volume of A}}{\text{Total volume of solution}} \times 100$$

35% (V/V) ethylene glycol in water is the standard car antifreeze — it lowers the freezing point of the coolant to about -17.6°C .

2.3 Mass by volume percentage (w/V)

The mass of solute (in grams) dissolved in 100 mL of solution. Common in medicine and pharmacy — a saline drip is labelled "0.9% w/V NaCl", meaning 0.9 g of NaCl in every 100 mL.

2.4 Parts per million (ppm)

For trace quantities, percentages become inconveniently tiny. Use ppm.

Parts per million

$$\text{ppm} = \frac{\text{Number of parts of A}}{\text{Total number of parts of all components}} \times 10^6$$

A litre of sea water (≈ 1030 g) contains about 6×10^{-3} g of dissolved oxygen, i.e. ≈ 5.8 ppm of O_2 . Pollutant levels in air and water are routinely reported in ppm or $\mu\text{g mL}^{-1}$.

2.5 Mole fraction (x)

Mole fraction

For a component A in a mixture of components A, B, ..., i:

$$x_A = \frac{n_A}{n_A + n_B + \dots + n_i} = \frac{n_A}{\sum n_j}$$

And $x_1 + x_2 + \dots + x_i = 1$.

Mole fraction is dimensionless. It is the natural unit for relating vapour pressure to composition (Raoult's law) and for handling gas mixtures.

Worked example — mole fraction

Find the mole fraction of ethylene glycol ($C_2H_6O_2$) in a 20% by mass aqueous solution.

Take 100 g of solution: 20 g glycol + 80 g water.

Molar mass of $C_2H_6O_2 = 12 \times 2 + 1 \times 6 + 16 \times 2 = 62 \text{ g mol}^{-1}$.

$$n_{\text{glycol}} = \frac{20}{62} = 0.322 \text{ mol}, \quad n_{\text{water}} = \frac{80}{18} = 4.444 \text{ mol}$$

$$x_{\text{glycol}} = \frac{0.322}{0.322 + 4.444} = 0.068, \quad x_{\text{water}} = 1 - 0.068 = 0.932$$

2.6 Molarity (M)

Molarity

$$M = \frac{\text{Moles of solute}}{\text{Volume of solution in litres}} \quad (\text{unit: mol L}^{-1} \text{ or M})$$

A 0.25 M NaOH solution contains 0.25 mol of NaOH per litre of solution. Molarity is the workhorse of titrations and volumetric chemistry — volumes are easy to measure with pipettes and burettes.

Worked example — molarity

5 g of NaOH in 450 mL of solution.

$$n_{\text{NaOH}} = \frac{5}{40} = 0.125 \text{ mol}, \quad V = 450 \text{ mL} = 0.450 \text{ L}$$

$$M = \frac{0.125}{0.450} = 0.278 \text{ mol L}^{-1}$$

2.7 Molality (m)

Molality

$$m = \frac{\text{Moles of solute}}{\text{Mass of solvent in kg}} \quad (\text{unit: mol kg}^{-1} \text{ or m})$$

A 1.00 m KCl solution = 1 mol (74.5 g) of KCl dissolved in 1 kg of water (not 1 kg of solution).

Molarity vs molality — when to use which

Molarity depends on volume, which changes with temperature, so it is *temperature-dependent*. **Molality, mass %, mole fraction, and ppm** all use mass and are therefore *temperature-independent*. For colligative-property calculations (boiling-point elevation, freezing-point depression) always use **molality**.

Common Mistake

Students mix up the denominators: molarity is per **litre of solution**, molality is per **kg of solvent**. Saying "0.5 mol in 1 L of water" is neither — you must specify *solution* (M) or *solvent* (m).

Memory Aid

M for Molarity — M for Mixture (whole solution); m for molality — m for Mother liquid (solvent only). The capital letter "owns" the whole solution; the small letter is just the solvent.

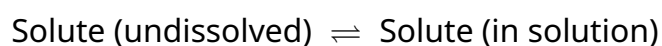
3 Solubility and Henry's Law

Solubility is the maximum amount of a substance that can dissolve in a specified amount of solvent at a specified temperature. It depends on (i) nature of solute and solvent, (ii) temperature, and (iii) pressure (mainly for gases).

3.1 Solubility of a solid in a liquid — *like dissolves like*

A polar solute dissolves in a polar solvent (NaCl, sugar in water); a non-polar solute dissolves in a non-polar solvent (naphthalene in benzene). The rule of thumb is **like dissolves like** — intermolecular forces between solute and solvent must be comparable to those broken on each side.

When the rates of dissolution and crystallisation match, **dynamic equilibrium** is reached:



The concentration of solute at this stage is the **solubility**, and the solution is called **saturated**. A solution holding less than this is **unsaturated**; one holding more (made by careful cooling) is **supersaturated**.

Le Chatelier \Rightarrow effect of temperature

- If dissolution is **endothermic** ($\Delta_{\text{sol}}H > 0$): solubility *increases* with temperature. Example: KCl, KNO_3 in water.
- If dissolution is **exothermic** ($\Delta_{\text{sol}}H < 0$): solubility *decreases* with temperature. Example: $\text{Ce}_2(\text{SO}_4)_3$, Li_2CO_3 .

Pressure has negligible effect on solubility of a solid in a liquid (both are essentially incompressible).

3.2 Solubility of a gas in a liquid

Gases dissolve to widely different extents: O_2 barely dissolves in water (≈ 8 mg per litre at 25°C), HCl is extremely soluble. Solubility is highly sensitive to pressure — this is governed by **Henry's law**.

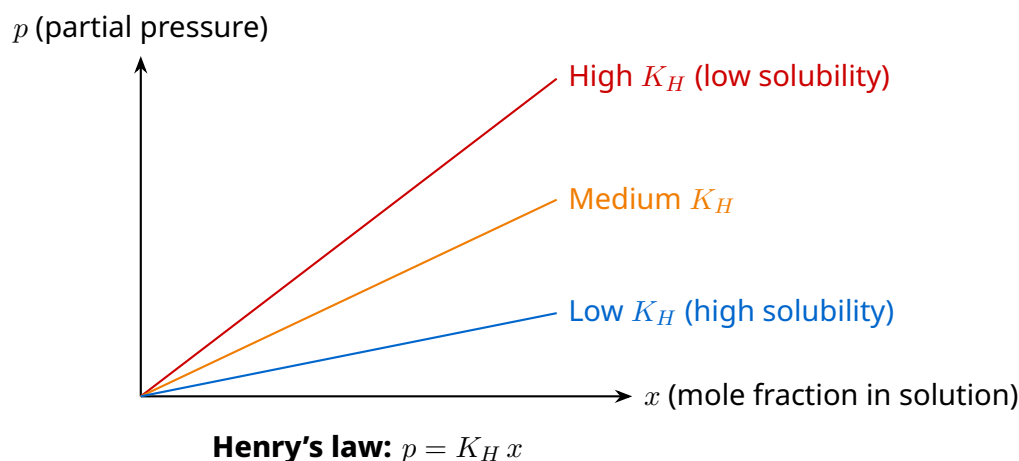
Henry's Law

At constant temperature, the partial pressure of a gas in the vapour phase (p) is directly proportional to its mole fraction in the solution (x):

$$p = K_H x$$

K_H = Henry's law constant; depends on **gas + solvent + temperature**; SI unit: same as pressure (kbar or bar).

- Plot p versus x : a straight line through the origin, slope K_H .
- **Higher K_H at a given temperature \Rightarrow lower solubility.** A gas with $K_H = 144$ kbar (e.g. N_2 in water at 293 K) needs huge pressure to drive small amounts into solution.
- For most gases, K_H **increases with temperature** — gas solubility **decreases as T rises** (dissolution of a gas is generally exothermic).



Real-World — Henry's law in action

- **Soda water and soft drinks** are bottled under high CO_2 pressure to keep CO_2 dissolved; the fizz on opening is Henry's law in reverse.
- **Scuba divers' bends.** At depth, air is breathed at high pressure — N_2 dissolves into blood. On rapid ascent, dissolved N_2 bubbles out, blocking capillaries (decompression sickness). Divers' tanks therefore use helium-oxygen (heliox) mixes; helium is far less soluble in blood.
- **High-altitude anoxia.** Low partial pressure of O_2 at high altitudes means less dissolved O_2 in blood — climbers feel weak and dizzy.

Quick Tip

If a question gives partial pressure and asks for solubility (mole fraction), just write $x = p/K_H$. If K_H is in kbar and p in bar, convert: x is dimensionless.

4 Vapour Pressure — Raoult's Law

In a closed container at constant temperature, a pure liquid is in equilibrium with its own vapour. The **vapour pressure** is the pressure exerted by this vapour at equilibrium — a measure of how readily the liquid escapes into the vapour phase. Adding a solute changes this pressure. **Raoult's law** quantifies the change for liquid-liquid solutions of two volatile components.

4.1 Raoult's law for a binary solution of two volatile liquids

Let the two components be 1 and 2 with pure vapour pressures p_1^* and p_2^* at the temperature considered, and let x_1, x_2 be their mole fractions in solution.

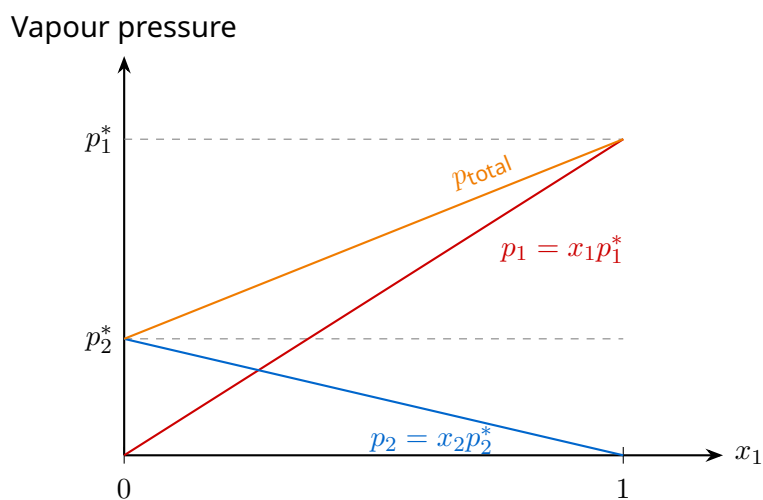
Raoult's Law (volatile + volatile)

$$p_1 = x_1 p_1^*, \quad p_2 = x_2 p_2^*$$

Total vapour pressure of the solution (Dalton):

$$p_{\text{total}} = p_1 + p_2 = x_1 p_1^* + x_2 p_2^* = p_2^* + (p_1^* - p_2^*)x_1$$

So a plot of p_{total} versus x_1 is a straight line going from p_2^* (at $x_1 = 0$) to p_1^* (at $x_1 = 1$). Each partial pressure plot is also a straight line.



Vapour pressures vs. composition (ideal solution)

Composition of the vapour phase

The vapour is richer in the *more volatile* component. If y_1, y_2 are vapour-phase mole fractions, by Dalton:

$$y_1 = \frac{p_1}{p_{\text{total}}}, \quad y_2 = \frac{p_2}{p_{\text{total}}}$$

This is the principle of **fractional distillation** — repeatedly vapourise and condense to enrich in the more volatile component.

4.2 Raoult's law as a special case of Henry's law

For a gaseous solute dissolved in a liquid, Henry's law writes $p = K_H x$. If the gas is the *liquid component itself* (vapour above its own liquid), then $K_H = p^*$ and Henry's law reduces exactly to Raoult's law. The two laws are limiting forms of the same physics:

- Solvent (component in large amount) obeys **Raoult's law**.
- Solute (small amount, especially a gas) obeys **Henry's law**.

4.3 Raoult's law when the solute is non-volatile

If the solute is a non-volatile solid (e.g. glucose, urea, NaCl) dissolved in a volatile solvent (e.g. water), only the solvent contributes to vapour pressure:

Raoult's law — non-volatile solute

$$p_{\text{solution}} = x_{\text{solvent}} p_{\text{solvent}}^*$$

And the **relative lowering** of vapour pressure equals the mole fraction of solute:

$$\frac{p^* - p_{\text{soln}}}{p^*} = x_{\text{solute}}$$

Adding non-volatile solute molecules to the solvent reduces the fraction of solvent molecules at the surface — fewer of them can escape into the vapour — so the vapour pressure drops. This is the foundation of all four colligative properties (Section 6).

Memory Aid

Solvent obeys Raoult; gas-solute obeys Henry. Raoult — Roomy (lots of it); Henry — Handful (tiny amount).

5 Ideal and Non-Ideal Solutions

5.1 Ideal solutions

An **ideal solution** obeys Raoult's law over the entire composition range. Two conditions characterise it:

- $\Delta_{\text{mix}}H = 0$ (no heat absorbed or released on mixing)
- $\Delta_{\text{mix}}V = 0$ (volume of solution = sum of volumes of components)

This happens when the A–B intermolecular forces in solution are essentially equal to the A–A and B–B forces in the pure liquids. Classic examples: **benzene + toluene**, **n-hexane + n-heptane**, **bromoethane + chloroethane**. No solution is perfectly ideal — they are approximations.

5.2 Non-ideal solutions — positive deviation

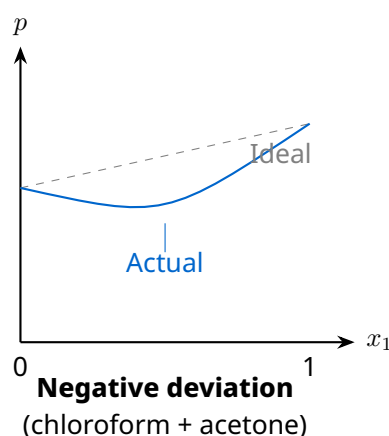
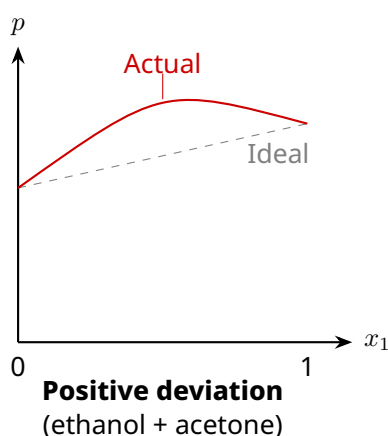
If A–B interactions are *weaker* than A–A and B–B, the molecules escape more readily, and the actual vapour pressure is **higher** than predicted by Raoult's law.

- p_{total} curve lies *above* the ideal straight line.
- $\Delta_{\text{mix}}H > 0$ (endothermic), $\Delta_{\text{mix}}V > 0$ (slight expansion).
- Examples: **ethanol + acetone**, **carbon disulphide + acetone**.

5.3 Non-ideal solutions — negative deviation

If A–B interactions are *stronger* than A–A and B–B (e.g. H-bonds form between A and B), molecules are held back, and the actual vapour pressure is **lower** than ideal.

- p_{total} curve lies *below* the ideal straight line.
- $\Delta_{\text{mix}}H < 0$ (exothermic), $\Delta_{\text{mix}}V < 0$ (slight contraction).
- Examples: **chloroform + acetone** (H-bond between CHCl_3 H and acetone O), **phenol + aniline**, HNO_3 + **water**.



5.4 Azeotropes

An **azeotrope** is a mixture that boils at a constant temperature without change in composition — meaning the vapour above it has exactly the same composition as the liquid. Azeotropes **cannot** be separated by ordinary fractional distillation.

- **Minimum-boiling azeotrope:** arises from large positive deviation.
Example: ethanol–water (95.6% ethanol, b.p. 351.15 K).
- **Maximum-boiling azeotrope:** arises from large negative deviation.
Example: HNO_3 –water (68% HNO_3 , b.p. 393.5 K).

Test yourself

You add solute A to solvent B and the test-tube feels hot. Predict the deviation.

Answer: Exothermic mixing \Rightarrow A–B forces are stronger than A–A and B–B \Rightarrow vapour pressure lower than ideal \Rightarrow **negative deviation**.

Property	Positive deviation	Negative deviation
A–B interaction	Weaker than A–A, B–B	Stronger than A–A, B–B
$\Delta_{\text{mix}}H$	> 0 (endothermic)	< 0 (exothermic)
$\Delta_{\text{mix}}V$	> 0 (slight expansion)	< 0 (slight contraction)
p_{total} vs. ideal	Higher	Lower
Azeotrope type	Minimum-boiling	Maximum-boiling
Example	Ethanol + acetone	Chloroform + acetone

Common Mistake

“Positive deviation = higher boiling point” is wrong. Higher vapour pressure means the liquid escapes more readily, so it actually boils at a *lower* temperature. Positive deviation \Rightarrow minimum-boiling azeotrope. Track vapour pressure and boiling point as inverses.

6 Colligative Properties

A **colligative property** depends only on the *number* of solute particles, not on their chemical nature. The four colligative properties of solutions are:

1. Relative lowering of vapour pressure (Δp)
2. Elevation of boiling point (ΔT_b)
3. Depression of freezing point (ΔT_f)
4. Osmotic pressure (π)

All four originate from the same phenomenon: **adding a non-volatile solute lowers the vapour pressure of the solvent.**

6.1 Relative lowering of vapour pressure

From Raoult’s law for a non-volatile solute:

$$\frac{p^* - p_{\text{soln}}}{p^*} = x_{\text{solute}} = \frac{n_2}{n_1 + n_2}$$

For dilute solutions $n_1 \gg n_2$, so $n_1 + n_2 \approx n_1$:

Dilute-solution form

$$\frac{p^* - p_{\text{soln}}}{p^*} \approx \frac{n_2}{n_1} = \frac{w_2/M_2}{w_1/M_1}$$

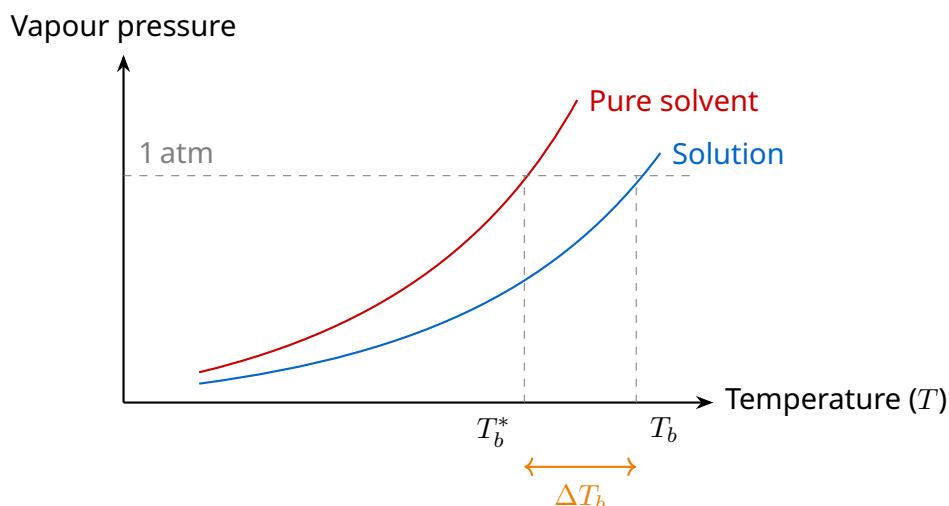
where w_1, w_2 = masses and M_1, M_2 = molar masses of solvent and solute. This rearranges to give the molar mass of the solute:

$$M_2 = \frac{w_2 M_1 p^*}{w_1 (p^* - p_{\text{soln}})}$$

So a measurement of vapour-pressure lowering gives the molar mass of an unknown non-volatile solute.

6.2 Elevation of boiling point (ΔT_b)

A liquid boils when its vapour pressure equals atmospheric pressure. A non-volatile solute lowers the vapour pressure, so a higher temperature is needed to reach atmospheric pressure — the boiling point rises.



Boiling-point elevation

$$\Delta T_b = K_b \cdot m$$

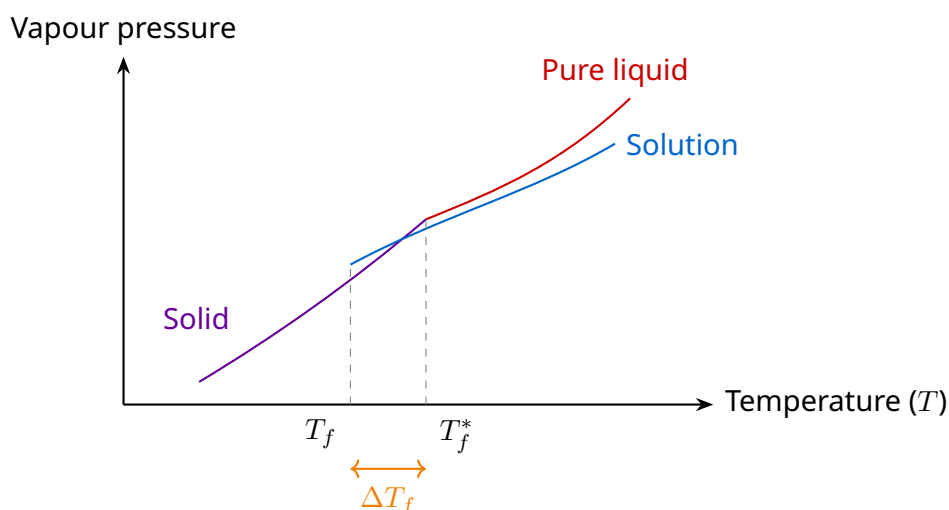
m = molality of solute; K_b = **ebullioscopic** (molal boiling-point elevation) constant of the solvent — units K kg mol^{-1} . For water $K_b = 0.52 \text{ K kg mol}^{-1}$.
If we substitute $m = (w_2/M_2)/(w_1/1000)$ where masses are in g:

$$M_2 = \frac{1000 K_b w_2}{\Delta T_b w_1}$$

- K_b depends only on the *solvent*, not the solute.
- It is the elevation in boiling point produced by a 1 molal solution of any (non-electrolyte) solute.

6.3 Depression of freezing point (ΔT_f)

A liquid freezes when the vapour pressures of liquid and solid phases become equal. Adding a non-volatile solute lowers the liquid's vapour pressure, so equilibrium with the solid is reached at a *lower* temperature — the freezing point drops.



Freezing-point depression

$$\Delta T_f = K_f \cdot m$$

K_f = **cryoscopic** (molal freezing-point depression) constant of the solvent — units K kg mol^{-1} . For water $K_f = 1.86 \text{ K kg mol}^{-1}$.

Molar mass of the solute:

$$M_2 = \frac{1000 K_f w_2}{\Delta T_f w_1}$$

Real-World Application

- **Ethylene glycol antifreeze** in car radiators uses freezing-point depression — water that would otherwise freeze and burst the engine block stays liquid down to -17.6°C in 35% (V/V) glycol.
- **Salting icy roads.** NaCl is sprinkled to lower the freezing point of any thin water layer below the air temperature — the layer can't refreeze.
- **Sea water doesn't freeze at 0°C :** dissolved salts depress the freezing point to roughly -2°C .

K_b and K_f derivations — JEE extension

The molal constants are themselves derivable from thermodynamics:

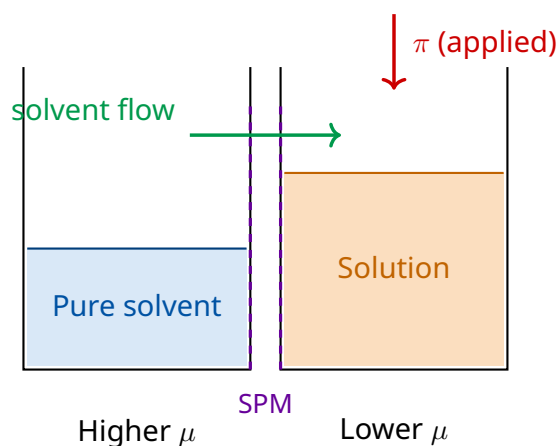
$$K_b = \frac{R M_1 T_b^2}{1000 \Delta_{\text{vap}}H}, \quad K_f = \frac{R M_1 T_f^2}{1000 \Delta_{\text{fus}}H}$$

where M_1 is the molar mass of the solvent and the enthalpies are per mole. Useful for predicting K values for non-tabulated solvents.

6.4 Osmosis and osmotic pressure (π)

Osmosis is the spontaneous flow of solvent (not solute) from a region of higher chemical potential (pure solvent or dilute solution) to a region of lower chemical potential (concentrated solution) through a **semipermeable membrane**.

Osmotic pressure (π) is the external pressure that must be applied to the solution side to *just stop* the inflow of solvent.



Why does solvent flow?

Adding solute lowers the chemical potential (and the vapour pressure) of the solvent in the solution. Solvent molecules naturally migrate from pure solvent (higher μ) into the solution (lower μ) through a semipermeable membrane. The pressure that exactly balances and stops this migration is the osmotic pressure π .

For dilute solutions, π obeys the van't Hoff equation, which is strikingly similar in form to the ideal-gas law:

Osmotic pressure — van't Hoff equation

$$\pi = CRT$$

$$\pi V = nRT \quad \Longleftrightarrow \quad \pi = \frac{n}{V}RT = CRT$$

where C = molar concentration (mol L^{-1}), $R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$, T in K. To find molar mass of a non-volatile non-electrolyte:

$$M_2 = \frac{w_2 RT}{\pi V}$$

- Osmotic pressure measurements are done at room temperature — avoiding the heat that would denature large biomolecules. So π is the **preferred method for determining molar masses of proteins, polymers and macromolecules**.

- π values are easily measurable even for dilute ($< 1\%$) solutions — another advantage over ΔT_b or ΔT_f , which require larger concentrations to give measurable temperature changes.

Isotonic, hypertonic, hypotonic

Two solutions with the *same* osmotic pressure at the same temperature are **isotonic**.

- A solution with *higher* osmotic pressure than another is **hypertonic** relative to it.
- A solution with *lower* osmotic pressure is **hypotonic** relative to it.

0.9% (w/V) NaCl ("normal saline") is isotonic with human blood plasma; this is why it is used in IV drips. If the IV fluid were hypotonic (e.g. pure water), red blood cells would swell and burst by osmosis (**haemolysis**). If hypertonic (high-salt), they would shrivel (**crenation**).

6.5 Reverse osmosis

If a pressure *greater* than π is applied on the solution side, solvent flows in the *reverse* direction — from solution back to pure solvent. This is **reverse osmosis (RO)**.

Real-World Application

Desalination plants use reverse osmosis to push fresh water out of sea water through cellulose acetate or polyamide membranes. Domestic RO water purifiers work on the same principle. Pressures required exceed about 30 atm for typical sea water.

Memory Aid

"Same number of particles, same effect" — four colligative properties: V.P. lowering, Boiling-point elevation, Freezing-point depression, Osmotic pressure \Rightarrow **"VBFO"** = "Very Big Family of Osmosis". Each one depends on *how many* particles, not *which*.

Common Mistake

A **1 M sucrose** solution and a **1 M NaCl** solution do *not* produce equal ΔT_f or π . NaCl dissociates into $\text{Na}^+ + \text{Cl}^-$ — twice the particle count — so NaCl shows roughly double the colligative effect. Use the van't Hoff factor (next section).

7 Abnormal Molar Masses and the van't Hoff Factor

For solutes that **dissociate** (electrolytes like NaCl, K₂SO₄) or **associate** (e.g. benzoic acid dimerises in benzene), the experimentally measured molar mass differs from the calculated formula molar mass. The Dutch chemist **van't Hoff** introduced a correction factor i to handle this.

7.1 Definition of the van't Hoff factor

van't Hoff factor i

$$\begin{aligned}
 i &= \frac{\text{Observed colligative property}}{\text{Calculated property (no dissociation/association)}} \\
 &= \frac{\text{Normal (theoretical) molar mass}}{\text{Abnormal (observed) molar mass}} \\
 &= \frac{\text{Actual no. of particles after dissociation/association}}{\text{No. of particles initially taken}}
 \end{aligned}$$

- **Dissociation** (e.g. $\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-$): $i > 1$.
- **Association** (e.g. $2 \text{C}_6\text{H}_5\text{COOH} \rightarrow (\text{C}_6\text{H}_5\text{COOH})_2$ in benzene): $i < 1$.
- **Non-electrolyte** (urea, glucose): $i = 1$.

7.2 Modified colligative formulas

All four colligative property expressions are multiplied by i :

Colligative properties with i

$$\begin{aligned}
 \frac{p^* - p_{\text{soln}}}{p^*} &= i x_2 \\
 \Delta T_b &= i K_b m \\
 \Delta T_f &= i K_f m \\
 \pi &= i CRT
 \end{aligned}$$

7.3 Predicting i for common solutes

Solute	Dissociation/Asso	Theoretical i
Urea, glucose, sucrose (non-electrolyte)	None	1
NaCl, KCl	→ 2 ions	2
K ₂ SO ₄ , CaCl ₂ , Ba(NO ₃) ₂	→ 3 ions	3
Al ₂ (SO ₄) ₃	→ 5 ions	5
K ₄ [Fe(CN) ₆]	→ 5 ions	5
Acetic acid in benzene (dimer)	2 → 1	0.5
Benzoic acid in benzene (dimer)	2 → 1	0.5

Caveat: the *actual* i for strong electrolytes is slightly less than the theoretical maximum because of ion pairing in solution. KCl in water gives $i \approx 1.9$, not exactly 2.

7.4 Degree of dissociation (α) and association from i

For a solute that dissociates into n particles with degree α :

Dissociation

$$i = 1 + (n - 1)\alpha \iff \alpha = \frac{i - 1}{n - 1}$$

For a solute that associates — n molecules combine into 1 aggregate, degree of association α :

Association

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

For a dimer ($n = 2$): $i = 1 - \alpha/2$.

Worked example — i from ΔT_f

2.0 g of benzoic acid (C₆H₅COOH, $M = 122$) in 25 g of benzene gives $\Delta T_f = 1.62$ K. K_f of benzene = 4.9 K kg mol⁻¹. Find i and α .

$$\text{Molality } m = \frac{2.0/122}{25/1000} = \frac{0.01639}{0.025} = 0.6557 \text{ mol kg}^{-1}.$$

$$\text{Calculated } \Delta T_f \text{ (no association)} = K_f \cdot m = 4.9 \times 0.6557 = 3.213 \text{ K.}$$

$$i = \frac{\Delta T_f(\text{obs.})}{\Delta T_f(\text{calc.})} = \frac{1.62}{3.213} \approx 0.504$$

So $i \approx 1/2$, indicating dimer formation. For dimer: $i = 1 - \alpha/2 \Rightarrow \alpha = 2(1 - i) = 2(1 - 0.504) \approx 0.99$ (essentially complete dimerisation).

Real-World Application

Why doctors check serum sodium and serum osmolality. The osmotic pressure of blood plasma is tightly regulated by ion concentrations. A serum Na^+ drop (hyponatremia) corresponds to a drop in plasma osmolality — water then enters cells (including brain cells) by osmosis. The van't Hoff factor of dissolved ions is what makes electrolyte balance a life-or-death physiological variable.

Spotting which colligative formula to use

- Asked about vapour pressure → Raoult: $\Delta p/p^* = i x_2$.
- Solute is a salt and asked about freezing or boiling → $\Delta T = iK_m$.
- Asked to find molar mass of a polymer or protein → osmotic pressure $\pi V = inRT$.
- Solute "dimerises" or "associates" or "in benzene" → $i < 1$.

8 Quick Reference Summary

8.1 Master formula list

Concentration units

$$\text{Mass \%} = \frac{w_{\text{solute}}}{w_{\text{soln}}} \times 100 \quad \text{Volume \%} = \frac{V_{\text{solute}}}{V_{\text{soln}}} \times 100$$

$$\text{ppm} = \frac{\text{parts of solute}}{\text{total parts}} \times 10^6 \quad x_A = \frac{n_A}{\sum n}$$

$$M = \frac{n_{\text{solute}}}{V_{\text{soln}} (\text{L})}, \quad m = \frac{n_{\text{solute}}}{w_{\text{solvent}} (\text{kg})}$$

Solubility

Henry's law: $p = K_H x$. Larger $K_H \Rightarrow$ smaller solubility. K_H increases with T for most gases (gas solubility decreases as T rises).

Raoult's law

Two volatile: $p_{\text{total}} = x_1 p_1^* + x_2 p_2^*$. Vapour composition $y_i = p_i / p_{\text{total}}$.

Non-volatile solute: $\frac{p^* - p}{p^*} = x_2$.

Four colligative properties (with van't Hoff i)

$$\frac{p^* - p}{p^*} = i x_2 \quad \Delta T_b = i K_b m$$

$$\Delta T_f = i K_f m \quad \pi = i C R T$$

Molar mass from each property

$$M_2 = \frac{w_2 M_1 p^*}{w_1 (p^* - p)} \quad M_2 = \frac{1000 K_b w_2}{\Delta T_b w_1}$$

$$M_2 = \frac{1000 K_f w_2}{\Delta T_f w_1} \quad M_2 = \frac{w_2 R T}{\pi V}$$

 i from degree of dissociation / association

Dissociation (n particles, degree α): $i = 1 + (n - 1)\alpha$.

Association ($n \rightarrow 1$, degree α): $i = 1 - \alpha(1 - 1/n)$.

8.2 Key constants

Constant	Value	Notes
R (gas constant)	0.0821 L atm K ⁻¹ mol ⁻¹	Used in $\pi = CRT$
R (SI)	8.314 J K ⁻¹ mol ⁻¹	For K_b, K_f derivations
K_b (water)	0.52 K kg mol ⁻¹	Molal b.p. elevation
K_f (water)	1.86 K kg mol ⁻¹	Molal f.p. depression
K_f (benzene)	4.9 K kg mol ⁻¹	Common in problems
K_b (benzene)	2.53 K kg mol ⁻¹	Common in problems
K_f (camphor)	39.7 K kg mol ⁻¹	Very large \Rightarrow Rast method
K_H (N ₂ in water, 293 K)	76.48 kbar	Higher $K_H \Rightarrow$ less soluble
K_H (CO ₂ in water, 298 K)	1.67 kbar	Quite soluble

8.3 Comparison: the four colligative properties

Property	Formula	Best used for
Δp (rel. lowering)	$\Delta p/p^* = i x_2$	Volatile solvent + non-volatile solute
ΔT_b (elevation)	$\Delta T_b = i K_b m$	Solutes that don't decompose on heating
ΔT_f (depression)	$\Delta T_f = i K_f m$	Most common in lab (large K_f)
π (osmotic)	$\pi = i CRT$	Polymers, proteins (room-T measurement)

Last-minute checklist before the exam

- Concentrations: know which units are temperature-independent (mass %, ppm, mole fraction, molality) versus temperature-dependent (molarity).
- Henry's law applies to gases above a solution; remember " K_H up, solubility down".
- Raoult and Henry are limiting forms — Raoult for the solvent, Henry for the solute (especially gas).
- Ideal vs. non-ideal — four criteria: p_{total} direction, ΔH sign, ΔV sign, and azeotrope type.
- Always multiply colligative formulas by i if the solute is an electrolyte.
- Predict i from the formula — count the ions.
- Osmotic pressure is the most precise for molar-mass determination of large molecules.