JEE MAIN · PAPER 1 · CHEMISTRY

05 Solutions

Formula & concept sheet

How concentration is expressed, how a dissolved solute changes the vapour pressure of a solvent (Raoult's law), and the four colligative properties that follow, with the van't Hoff factor for electrolytes and association, and Henry's law for gases. Each idea is explained first, then the formulas, shortcuts and traps.

INSIDE THIS SHEET

1 Ways of expressing concentration 2

2 Vapour pressure and Raoult's law 2

3 Colligative properties: vapour pressure, boiling and freezing points 4

4 Osmosis and osmotic pressure 5

5 van't Hoff factor: dissociation and association 6

6 Henry's law: solubility of gases 7

7 Worked examples 7

8 Last-minute checklist 8

READ ALONGSIDE NCERT XII · Solutions

HOW TO USE THIS SHEET

1 **Skim**
Read the Key ideas, then the formula cards.

2 **Memorise**
Learn the formulas and check every Trap box.

3 **Test**
Do the worked examples, then this chapter's PYQs.

4 **Revise**
Use the last-minute checklist before the exam.

Formula memorise · **Key idea** why it works · **Trap** marks lost here · **PYQ** how it is asked

Practise this chapter with real past-paper questions on Prep Vault. Written for revision, not as a first read.

CHAPTER 05

Solutions

NCERT XII · Solutions

Covers: concentration terms · vapour pressure and Raoult's law · ideal and non-ideal solutions, azeotropes · relative lowering of vapour pressure · elevation of boiling point · depression of freezing point · osmotic pressure · molar mass from colligative properties · van't Hoff factor, dissociation and association · Henry's law.

1 Ways of expressing concentration

- A **solution** is a homogeneous mixture; the component present in the larger amount is the **solvent**, the other the **solute**. For a binary solution of solute 2 in solvent 1 we write n_2, w_2, M_2 and n_1, w_1, M_1.
- Terms that use **volume** (molarity, % w/v) change with temperature because the volume expands; terms that use only **mass** or **moles** (molality, mole fraction, % w/w) do not. That is why molality appears in ΔT_b and ΔT_f formulas, and molarity in π.

CONCENTRATION TERMS

TERM	DEFINITION	FORMULA	UNIT
mole fraction x	moles of one component per total moles	$x_2 = \dfrac{n_2}{n_1 + n_2},\ x_1 + x_2 = 1$	none
molality m	moles of solute per kg of solvent	$m = \dfrac{1000\, w_2}{M_2\, w_1}$	mol kg^{-1}
molarity M	moles of solute per litre of solution	$M = \dfrac{n_2}{V(\text{L})}$	mol L^{-1}
mass percent	g of solute per 100 g of solution	$\dfrac{w_2}{w_1 + w_2} \times 100$	%
volume percent	mL of solute per 100 mL of solution	$\dfrac{V_2}{V} \times 100$	%
ppm	parts of solute per 10^6 parts of solution	$\dfrac{\text{mass of solute}}{\text{mass of solution}} \times 10^6$	ppm

MOLARITY FROM MASS PERCENT

$$M = \frac{10\, d\, x\%}{M_2}$$

d in g mL^{-1}, $x\%$ = mass percent; 10 converts per 100 g to per 1000 mL

MOLALITY FROM MOLARITY

$$m = \frac{1000\, M}{1000\, d - M\, M_2}$$

d in g mL^{-1}, so $1000d$ is grams of solution per litre; molality and molarity are nearly equal only for dilute aqueous solutions

TRAP

The solvent mass in molality is the **solvent only**, not the solution. 1 m means 1 mol in 1 kg of solvent, which is more than 1 L of solution. Use $x_2 = \dfrac{m\, M_1}{1000 + m\, M_1}$ to go from molality to mole fraction ($M_1 = 18$ for water).

QUICK CHECK

Conc. HNO_3 is 68% w/w, $d = 1.41$ g mL^{-1}. Molarity and molality?

Answer: $M = \dfrac{10 \times 1.41 \times 68}{63} = 15.2$ M; $m = \dfrac{68/63}{0.032} = 33.7$ m (68 g solute with 32 g solvent).

2 Vapour pressure and Raoult's law

- At a given temperature a liquid is in equilibrium with its vapour at a fixed **vapour pressure** p°, which rises with temperature; the liquid boils when it equals the external pressure. A solution of volatile liquids has a vapour pressure that depends on its composition.
- In a liquid mixture the molecules of each component are partly replaced at the surface by the other, so each component's partial pressure falls in proportion to its mole fraction. This is Raoult's law, and it holds exactly for an **ideal** solution.

RAOULT'S LAW The partial vapour pressure of each volatile component is its mole fraction in the liquid times the vapour pressure of the pure component: $p_A = x_A p_A^\circ$. For a mixture the total is $p_{total} = p_A + p_B = p_B^\circ + (p_A^\circ - p_B^\circ)x_A$, a straight line in x_A.

TOTAL PRESSURE

$$p = x_A p_A^\circ + x_B p_B^\circ$$

the liquid line on a p-x graph

VAPOUR COMPOSITION

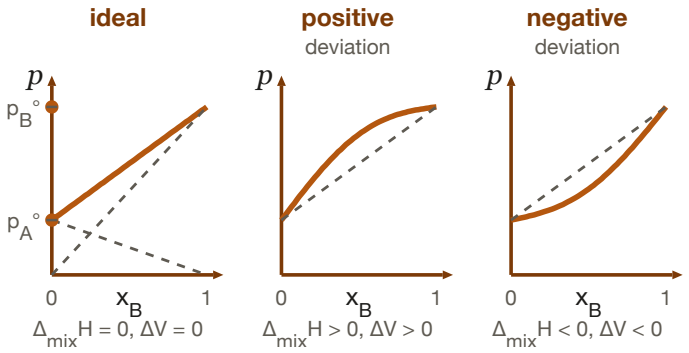
$$y_A = \frac{p_A}{p_{total}}$$

Dalton; the vapour is richer in the more volatile component (p° larger)

NON-VOLATILE SOLUTE

$$p = x_1 p_1^\circ, \quad \frac{p^\circ - p}{p^\circ} = x_2$$

relative lowering of vapour pressure equals the mole fraction of the solute



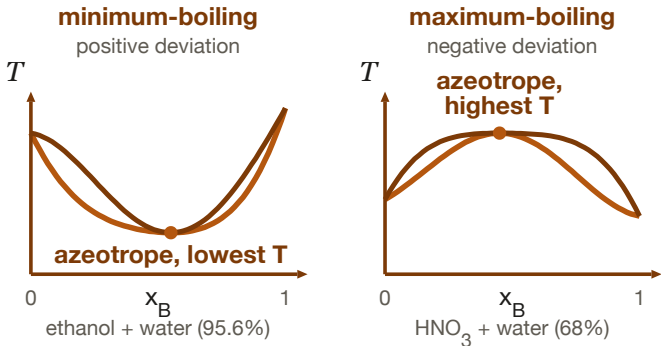
Raoult: $p_A = x_A p_A^\circ$; deviations show up as curves above or below the straight ideal line

READING THE THREE PLOTS

- Each plot is p against x_B: the dashed lines are the partial pressures, the full line the total.
- Ideal: the total is a straight line from p_A° to p_B°.
- Positive deviation: the curve bulges above the line (weaker A—B attraction, $\Delta_{mix}H > 0$).
- Negative deviation: the curve sags below it (stronger A—B attraction, $\Delta_{mix}H < 0$).

IDEAL AND NON-IDEAL SOLUTIONS

	IDEAL	POSITIVE DEVIATION	NEGATIVE DEVIATION
A—B forces	same as A—A and B—B	weaker than A—A, B—B	stronger
$\Delta_{mix}H$, $\Delta_{mix}V$	$0, 0$	$> 0, > 0$	$< 0, < 0$
vapour pressure	on the Raoult line	above the line	below the line
azeotrope	none	minimum boiling	maximum boiling
examples	benzene + toluene; n-hexane + n-heptane; bromoethane + chloroethane	ethanol + water; ethanol + acetone; acetone + CS_2	chloroform + acetone (H bond); HNO_3 + water; HCl + water; phenol + aniline



an azeotrope boils at constant composition and cannot be separated by distillation

AZEOTROPE A liquid mixture that boils at a constant temperature and has the same composition in liquid and vapour, so it cannot be separated by fractional distillation. Positive deviation gives a **minimum**-boiling azeotrope (ethanol + water, about 95% ethanol); negative deviation gives a **maximum**-boiling one (HNO_3 + water, about 68% HNO_3). The percentages are approximate.

WHY IT WORKS

Weaker A—B attraction lets molecules escape more easily, so the pressure is higher than Raoult predicts and mixing absorbs heat and expands the volume. Stronger A—B attraction (hydrogen bonds between chloroform and acetone) holds molecules in, so the pressure is lower and mixing releases heat.

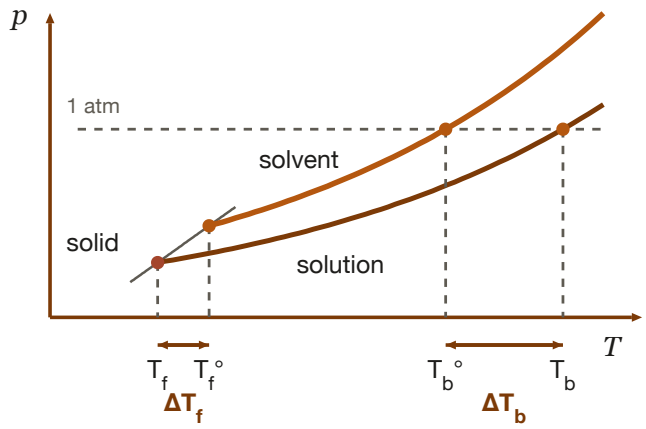
QUICK CHECK

Benzene (75 torr) and toluene (22 torr) are mixed in equal moles. Total pressure and mole fraction of benzene in the vapour?

Answer: $p = 0.5(75) + 0.5(22) = 48.5$ torr; $y_{benzene} = \dfrac{37.5}{48.5} = 0.77.$

3 Colligative properties: vapour pressure, boiling and freezing points

COLLIGATIVE PROPERTIES Properties of a dilute solution that depend only on the **number** of dissolved particles, not on what they are: relative lowering of vapour pressure, elevation of boiling point, depression of freezing point and osmotic pressure. They apply to a **non-volatile** solute in a dilute solution.



solute lowers vapour pressure: boiling point rises by ΔT_b, freezing point falls by ΔT_f

WHAT THE P-T GRAPH SHOWS

- The solute lowers the vapour pressure, so the solution curve lies below the solvent curve.
- The solution must be heated further to reach 1 atm: the boiling point rises by ΔT_b.
- The solution's vapour-pressure curve meets the solid's curve at a lower temperature: the freezing point falls by ΔT_f.
- The depression is larger than the elevation for the same solution because $K_f > K_b$ for water.

RELATIVE LOWERING

$$\frac{p^\circ - p}{p^\circ} = i\,x_2 \approx i\frac{w_2 M_1}{M_2 w_1}$$

dilute: $n_2 \ll n_1$; exact form $(p^\circ - p)/p = i\,n_2/n_1$

ELEVATION OF BOILING POINT

$$\Delta T_b = i\,K_b\,m$$

K_b in K kg mol^{-1}, molality m; new $T_b = T_b^\circ + \Delta T_b$

DEPRESSION OF FREEZING POINT

$$\Delta T_f = i\,K_f\,m$$

new $T_f = T_f^\circ - \Delta T_f$ (the freezing point is **lowered**)

MOLAR MASS FROM ΔT

$$M_2 = \frac{1000\,K\,w_2}{\Delta T\,w_1}$$

w_2 solute and w_1 solvent in g; for a non-electrolyte ($i = 1$)

CONSTANTS FROM SOLVENT DATA

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

T in K, ΔH in J mol^{-1}, M_1 in g mol^{-1}; water gives 0.512 and 1.86 K kg mol^{-1}

CRYOSCOPIC AND EBULLIOSCOPIC CONSTANTS (K KG MOL^{-1})

SOLVENT	K_b	K_f	SOLVENT	K_b	K_f
water	0.52	1.86	benzene	2.53	5.12
ethanol	1.20	1.99	acetic acid	3.07	3.90
CCl_4	5.03	31.8	cyclohexane	2.79	20.0

TRAP

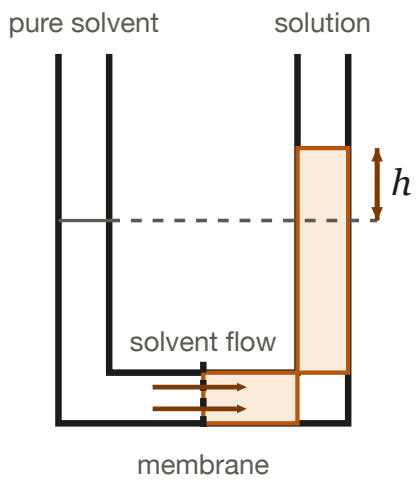
K_b and K_f belong to the **solvent**, are per molal (not molar), and are independent of the solute. A positive ΔT_f means the freezing point went **down**. Use the constants the question gives: textbooks print 0.52 and 0.512 for water.

QUICK CHECK

Which freezes first on cooling: 0.1 m glucose or 0.1 m NaCl (assume $i = 2$)?

Answer: Glucose: $\Delta T_f = 0.186$ K; NaCl: 0.372 K. The glucose solution has the smaller depression, so it starts to freeze at the higher temperature.

4 Osmosis and osmotic pressure



osmotic pressure $\pi = h\rho g$ balances the flow; $\pi = CRT$

OSMOSIS The net flow of solvent through a **semipermeable membrane** from the dilute side to the concentrated side (it lets solvent through, not solute). The flow stops when the extra pressure on the concentrated side, the **osmotic pressure** π, balances it.

OSMOTIC PRESSURE

$$\pi = i\,C\,R\,T = i\frac{n_2}{V}RT$$

C molarity; $R = 0.0821$ L atm K^{-1} mol^{-1} (atm) or 0.083 L bar K^{-1} mol^{-1} (bar); T in K

MOLAR MASS FROM π

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

best for macromolecules (proteins, polymers): a measurable π at room temperature, no heating needed

ACROSS A MEMBRANE

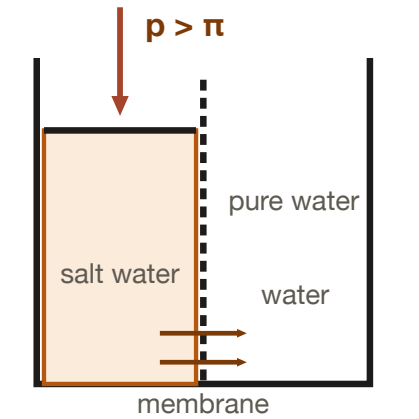
$$\Delta\pi = \left(\sum iC_1 - \sum iC_2\right) RT$$

solvent flows toward the side with the larger $\sum iC$; count every ion

ISOTONIC SOLUTIONS

$$\pi_1 = \pi_2$$

0.9% NaCl (saline) matches blood; hypertonic outside shrinks a cell (plasmolysis), hypotonic swells it



pressure above π reverses the flow: desalination

REVERSE OSMOSIS

- Apply a pressure **greater than** π on the solution side and the solvent flows the other way, out of the solution.
- Used to desalinate sea water. The membrane is a polymer film (cellulose acetate).
- Osmotic pressure is the colligative property of choice for polymers and proteins: even a very dilute solution gives a π that can be read as a column height h ($\pi = h\rho g$).

WHY IT WORKS

Solvent molecules cross the membrane in both directions, but more cross from the pure solvent (higher solvent "concentration", higher vapour pressure) into the solution. The pressure π needed to stop it is the same as the pressure $\pi = iCRT$ of an ideal gas of the solute at the same C and T.

QUICK CHECK

0.2 M glucose is separated by a membrane from 0.05 M NaCl at 300 K. Net osmotic pressure?

Answer: NaCl gives $0.05 \times 2 = 0.10$ M of particles; net $= (0.20 - 0.10) \times 0.0821 \times 300 = 2.46$ atm, solvent flows into the glucose side.

5 van't Hoff factor: dissociation and association

VAN'T HOFF FACTOR i The ratio of the observed colligative property to the value calculated assuming no dissociation or association. It corrects the formulas for solutes that split into ions ($i > 1$) or clump into larger units ($i < 1$). $i = 1$ for non-electrolytes in water.

DEFINITION

$$i = \frac{\text{observed}}{\text{calculated}} = \frac{M_{normal}}{M_{obs}}$$

more particles raise every colligative effect; the molar mass found from them goes down

DISSOCIATION INTO n IONS

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

α = degree of dissociation; complete dissociation $\alpha = 1$ gives $i = n$

ASSOCIATION OF n MOLECULES

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

dimer: $i = 1 - \frac{\alpha}{2}$; complete dimerisation $i = 0.5$

PARTICLE COUNT AND I

SOLUTE (COMPLETE IONISATION)	PARTICLES	i
glucose, urea, sucrose	molecules	1
NaCl, KCl, HCl	$\mathrm{M^+ + X^-}$	2
$\mathrm{CaCl_2}$, $\mathrm{Na_2SO_4}$, $\mathrm{K_2SO_4}$	3 ions	3
$\mathrm{K_3[Fe(CN)_6]}$, $\mathrm{FeCl_3}$, $\mathrm{AlCl_3}$	4 ions	4
$\mathrm{K_4[Fe(CN)_6]}$, $\mathrm{Al_2(SO_4)_3}$	5 ions	5
acetic or benzoic acid in benzene	dimers (hydrogen bonded)	≈ 0.5

KEY IDEA

For equal molality the order of every colligative property follows i: $\mathrm{Al_2(SO_4)_3} > \mathrm{K_3[Fe(CN)_6]} > \mathrm{CaCl_2} \approx \mathrm{Na_2SO_4} > \mathrm{NaCl} >$ glucose. Highest boiling point, lowest freezing point, lowest vapour pressure, highest π: the largest $i\,m$. A real electrolyte has i below the ideal integer because of ion pairing, closer to it on dilution.

TRAP

Do not apply i to the molality of the solvent. For a weak electrolyte i comes from α; for a strong one use the integer unless the question gives α. Association makes the observed molar mass **larger** and $i < 1$.

QUICK CHECK

$\mathrm{A_2B}$ is 30% ionised in water. Find i.

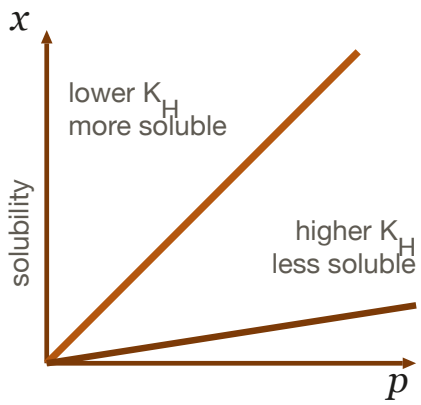
Answer: $\mathrm{A_2B} \longrightarrow 2\,\mathrm{A^+} + \mathrm{B^{2-}}$, $n = 3$: $i = 1 + 2(0.3) = 1.6$.

QUICK CHECK

Normal and observed molar masses of $\mathrm{MX_2}$ are 164 and 65.6. Percent ionisation?

Answer: $i = \frac{164}{65.6} = 2.5$; $\alpha = \frac{2.5-1}{3-1} = 0.75$, i.e. 75%.

6 Henry's law: solubility of gases



slope of each line $= 1/K_H$: a larger K_H, a less soluble gas

HENRY'S LAW At a given temperature the partial pressure of a gas above a solution is proportional to the mole fraction of the gas dissolved in it: $p = K_H\, x_{gas}$. A larger K_H means a **less** soluble gas at a given pressure.

SOLUBILITY

$$x_{gas} = \frac{p}{K_H}$$

K_H in bar or kbar; O_2 in water at 298 K: $K_H \approx 35$ kbar, so air at 0.2 bar of O_2 gives $x \approx 5.7 \times 10^{-6}$

FACTS AND USES

- K_H **rises** with temperature, so a gas is less soluble in hot water (warm soda goes flat, aquatic life suffers in warm water).
- Soda is bottled under high CO_2 pressure; opening it lowers p and the gas escapes as bubbles.
- Scuba divers use helium-oxygen mixtures because N_2 dissolves at depth and bubbles out as the bends on rising.
- At high altitude the partial pressure of O_2 falls, so less dissolves in blood: anoxia, with weakness and poor thinking.

TRAP

$K_H = p/x$, so K_H and solubility move in **opposite** directions. On a p against x plot, the line with the larger slope is the less soluble gas. On a $\log p$ against $\log x$ plot the slope is 1 and the intercept $\log K_H$. Henry's law is reached from the Equilibrium unit in some syllabus lists: both sheets keep it.

QUICK CHECK

At 298 K the Henry constants of gases w, x, y, z in water are $0.5, 2, 35, 40$ kbar. Which is most soluble, and what is the order?

Answer: $x = p/K_H$: smallest K_H dissolves most. Solubility: w $>$ x $>$ y $>$ z.

QUICK CHECK

A gas with $K_H = 40$ kbar is at 2 bar over water. Mole fraction dissolved?

Answer: $x = \dfrac{2}{40000} = 5 \times 10^{-5}$.

7 Worked examples

RAOULT WITH TWO LIQUIDS

At 300 K a solution of A and B ($x_A = 0.5$) has $p_{total} = 80$ torr; at $x_A = 0.25$ it is 70 torr. Find p°_A and p°_B.

$p = p^\circ_B + (p^\circ_A - p^\circ_B)x_A$: $0.5(p^\circ_A - p^\circ_B) + p^\circ_B = 80$ and $0.25(p^\circ_A - p^\circ_B) + p^\circ_B = 70$; subtract: $0.25(p^\circ_A - p^\circ_B) = 10$, so $p^\circ_A - p^\circ_B = 40$, $p^\circ_B = 60$, $p^\circ_A = 100$ torr

RELATIVE LOWERING

18 g of glucose ($M = 180$) in 178.2 g of water. Relative lowering of vapour pressure?

$n_2 = 0.1$, $n_1 = 9.9$: $x_2 = \dfrac{0.1}{10} = 0.01$, so $p^\circ - p = 0.01\, p^\circ$ (a 1% fall)

BOILING AND FREEZING

ΔT_b and ΔT_f for 18 g of glucose in 1 kg of water ($K_b = 0.52$, $K_f = 1.86$)?

$m = 0.1$: $\Delta T_b = 0.052$ K, $\Delta T_f = 0.186$ K; freezes at -0.186°C, boils at 100.052°C

MOLAR MASS

1.5 g of a non-electrolyte in 50 g of benzene ($K_f = 5.12$) lowers the freezing point by 0.85 K. M?

$$M = \frac{1000 \times 5.12 \times 1.5}{0.85 \times 50} = 181 \text{ g mol}^{-1}$$

OSMOTIC MOLAR MASS

0.5 g of a polymer in 200 mL gives $\pi = 2.0 \times 10^{-3}$ atm at 300 K. M?

$$M = \frac{wRT}{\pi V} = \frac{0.5 \times 0.0821 \times 300}{0.002 \times 0.2} = 3.08 \times 10^4 \text{ g/mol}$$

ELECTROLYTE

ΔT_f of 0.1 m NaCl if it is completely ionised?

$i = 2$: $\Delta T_f = 2 \times 1.86 \times 0.1 = 0.372$ K; a real value of $i \approx 1.9$ would give 0.35 K

CONSTANT FROM ENTHALPY

K_b of water from $\Delta_{vap}H = 40.66$ kJ mol^{-1} at 373.15 K?

$$K_b = \frac{8.314 \times 373.15^2 \times 18}{1000 \times 40660} = 0.512 \text{ K kg mol}^{-1}$$

ORDER OF BOILING POINTS

Arrange 0.1 m NaCl, $\mathrm{Na_2SO_4}$, glucose, $\mathrm{K_3[Fe(CN)_6]}$ by boiling point.

i: 2, 3, 1, 4; $\Delta T_b \propto i$: glucose < NaCl < $\mathrm{Na_2SO_4}$ < $\mathrm{K_3[Fe(CN)_6]}$

WEAK ELECTROLYTE

A 0.1 m solution of a weak monobasic acid HA is 2% ionised. ΔT_f ($K_f = 1.86$)?

$n = 2$: $i = 1 + (2-1)(0.02) = 1.02$; $\Delta T_f = 1.02 \times 1.86 \times 0.1 = 0.19$ K

ASSOCIATION

Acetic acid ($M = 60$) dimerises completely in benzene. Observed molar mass from freezing-point data?

$i = 1 - \frac{1}{2}(1) = 0.5$; $M_{obs} = \frac{M_{normal}}{i} = \frac{60}{0.5} = 120$ g mol^{-1}

8 Last-minute checklist

BEFORE YOU ANSWER

Molality for ΔT, molarity for π? Is the solute volatile? Is it an electrolyte (find i)? Does the freezing point go down? Which units of R and K?

- $p_A = x_A p_A^\circ$; $p = x_A p_A^\circ + x_B p_B^\circ$; $y_A = p_A/p$; non-volatile solute: $\frac{p^\circ - p}{p^\circ} = x_2$.
- $\Delta T_b = iK_b m$; $\Delta T_f = iK_f m$ (new $T_f = T_f^\circ - \Delta T_f$); $M_2 = \frac{1000 K w_2}{\Delta T w_1}$; $K = \frac{RT^2 M_1}{1000 \Delta H}$.
- $\pi = iCRT$; $M_2 = \frac{w_2 RT}{\pi V}$; net $\pi = (\sum iC_1 - \sum iC_2)RT$; reverse osmosis needs $p > \pi$.
- $i = 1 + (n-1)\alpha$ (dissociation); $i = 1 - \alpha(1 - 1/n)$ (association); $i = M_{normal}/M_{obs}$; order of every colligative effect follows i.
- Positive deviation: weaker A–B, $\Delta H, \Delta V > 0$, minimum-boiling azeotrope (ethanol + water); negative: stronger A–B, maximum-boiling azeotrope (chloroform + acetone, $\mathrm{HNO_3}$ + water).
- $p = K_H x$: larger K_H, less soluble; K_H rises with T; vapour is richer in the more volatile component.

Now test it. Practise this chapter with past-paper and bank questions on Prep Vault. **Practice this chapter →**