NCERT Exemplar Solutions

Solved NCERT Exemplar Problems for Class 12th Chemistry, Chapter 1

Chapter 1: Solutions

About this Chapter

The **Solutions** unit takes you beyond pure liquids into homogeneous mixtures of two or more components and the four **colligative properties** they exhibit: relative lowering of vapour pressure, elevation of boiling point, depression of freezing point and osmotic pressure. You will learn **Raoult's law** for ideal solutions, **Henry's law** for gases in liquids, the meaning of positive and negative deviations, azeotropes, and the **Van't Hoff factor** for electrolytes that dissociate or associate in solution.

Topics covered: Concentration units • Raoult's law • Henry's law • Ideal vs non-ideal • Azeotropes • Colligative properties • Osmotic pressure • Van't Hoff factor

Quick Formula Sheet

Raoult's law (volatile + volatile):

$p_{\text{total}} = x_A p_A^\circ + x_B p_B^\circ$

Henry's law:

$p = K_H \cdot x$

Relative lowering of v.p.:

$\frac{p_A^\circ - p_A}{p_A^\circ} = x_B$

ΔT_b, ΔT_f:

$\Delta T_b = i\,K_b\,m, \quad \Delta T_f = i\,K_f\,m$

Osmotic pressure:

$\Pi = i\,C\,R\,T$

Van't Hoff factor:

$i = \frac{\text{observed coll. prop.}}{\text{calculated coll. prop.}}$

I. Multiple Choice Questions (Type-I)

Q 1.1 **Which of the following units is useful in relating concentration of solution with its vapour pressure?**

(i) mole fraction

(ii) parts per million

(iii) mass percentage

(iv) molality

SOLUTION

Correct option: (i) mole fraction.

Concept used. Raoult's law for a solution of a non-volatile solute in a volatile solvent states that the partial vapour pressure of the solvent equals its mole fraction in the solution times its pure-solvent vapour pressure:

$$p_A = x_A\, p_A^{\circ}.$$

For a solution of two volatile components A and B, the law extends to

$$p_{\text{total}} = x_A\, p_A^{\circ} + x_B\, p_B^{\circ}.$$

The concentration variable that appears in both expressions is the **mole fraction** x.

Step 1. Write the colligative form of vapour-pressure lowering:

$$\frac{p_A^{\circ} - p_A}{p_A^{\circ}} = x_B.$$

The right-hand side is the mole fraction of solute. So x is the natural concentration unit linking concentration with vapour pressure.

Step 2. Rule out the other options: (ii) ppm measures dilute mass fractions, not number ratios; (iii) mass-% is a mass ratio, not number-of-molecule ratio; (iv) molality links to $\Delta T_b/\Delta T_f$, not to p directly.

> **Final Answer:** Option **(i)**: mole fraction.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Strategic angle (definition-driven). If you can recall Raoult's law in symbol form, the answer is one glance: only x appears in the law linking p and composition. Match option, done.

Concept used. Vapour pressure of a solvent above an ideal solution falls in proportion to the mole fraction of solvent: $p_A = x_A p_A^{\circ}$. For a binary volatile solution $p = x_A p_A^{\circ} + (1 - x_A)p_B^{\circ}$, again pure mole-fraction language. Henry's law for a gas dissolved in a liquid is $p = K_H\, x$, also mole fraction. Every classical "p vs composition" law uses x.

Step 1. **Write the equation in symbols.** For a non-volatile solute the relative lowering is

$$\frac{p_A^{\circ} - p_A}{p_A^{\circ}} = x_B = \frac{n_B}{n_A + n_B}.$$

The right side is dimensionless and counts moles, not mass.

Step 2. **Why mass-fraction is the wrong family.** Mass-percent depends on molar masses of solute and solvent, which Raoult's law does not contain. Swapping a solute of $M_w = 60$ for one of $M_w = 180$ at the same mass-% changes x_B threefold; p tracks x_B, not the mass.

Step 3. **Alternative approach (dimensional analysis).** p has units of pressure. Raoult's law sets $p \propto p^\circ \times$ (dimensionless), so the concentration variable must be dimensionless. Among the four options only x is a *number* ratio; ppm is a mass ratio.

Step 4. **Limiting case.** As $x_B \to 0$ (pure solvent), $p \to p^\circ_A$; as $x_B \to 1$ (pure solute, non-volatile), $p \to 0$. Both extremes are recovered only with x.

☞ Exam Tip

Exam tip / generalisation. JEE Main 2019 (April Shift 1) and NEET 2017 asked variants of "which concentration term enters Raoult's law". Lock it as mole fraction. The same is true for Henry's law ($p = K_H x$). **Memorise: pressure ↔ mole fraction; temperature change ↔ molality; osmotic pressure ↔ molarity.**

♥ Concept Linkage

Concept linkage. Mole fraction enters because vapour pressure depends on the *number fraction* of surface molecules free to escape into vapour: a statistical (Boltzmann-counting) result. Mass enters only through stoichiometry, never through molecular escape itself. The same number-counting argument underlies all colligative properties.

Final Answer: Option **(i)**: mole fraction.

Q 1.2 On dissolving sugar in water at room temperature solution feels cool to touch. Under which of the following cases dissolution of sugar will be most rapid?

(i) Sugar crystals in cold water.

(ii) Sugar crystals in hot water.

(iii) Powdered sugar in cold water.

(iv) Powdered sugar in hot water.

SOLUTION

Correct option: (iv) Powdered sugar in hot water.

Concept used. The rate of dissolution of a solid in a liquid depends on two factors:

- **Surface area** of solute: more powdered ⇒ more surface ⇒ faster dissolution.

- **Temperature**: higher T gives solvent molecules greater kinetic energy, so they collide with solute particles more often and more energetically.

Step 1. **Surface-area factor.** Powdered sugar has $\sim 10^3$ times more surface per gram than crystal lumps. So at the same T, powdered dissolves much faster.

Step 2. **Temperature factor.** The Arrhenius factor $e^{-E_a/RT}$ rises with T. So at the same particle size, hot dissolves faster than cold.

Step 3. Combining both, option (iv) maximises both factors.

Final Answer: Option **(iv)**: Powdered sugar in hot water.

EXPERT'S SOLUTION *: Sneha Iyer, M.Sc Physical Chemistry, IIT Madras*

Quick reading. Two independent levers control dissolution rate: *surface area* (particle size) and *temperature* (kinetic energy). Maximise both. Option (iv) does. Done.
Concept used. Dissolution is a surface phenomenon: solvent molecules collide with solute particles at the interface and pull them into solution via ion-dipole or H-bond interactions. The collision rate per unit time scales with surface area A; the fraction of energetic events scales as $e^{-E_a/RT}$.

Step 1. **Surface-area argument quantified.** For a cube of side ℓ, $S/V = 6/\ell$. Crushing a 1 cm cube into 1 mm cubes increases S/V tenfold ($6/0.1 = 60$ vs 6). Going to 0.1 mm fine powder gives a 100-fold increase. So powdered sugar dissolves ~ 10 to 100 times faster than crystals.

Step 2. **Temperature argument quantified.** If $E_a \approx 20$ kJ/mol, the rate ratio between hot ($T_1 = 323$ K, 50 °C) and cold ($T_2 = 298$ K, 25 °C) is

$$\frac{k_{\text{hot}}}{k_{\text{cold}}} = \exp\left[\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right] \approx 2.1.$$

Going to 100 °C boosts this to about 5.

Step 3. **Combined factor.** Surface-area boost ($\sim 30\times$) times temperature boost ($\sim$ 2-5$\times$) gives roughly 100 times faster dissolution for option (iv) over option (i).

☞ Exam Tip

Exam tip / generalisation. JEE Main physical-chemistry MCQs from 2018 onward routinely pair "surface area + temperature" into one rate question. Rule of thumb: when two independent factors both help, pick the option that maximises both unless one factor reverses sign for that solute (rare for ionic/sugar dissolution).

♥ Concept Linkage

Concept linkage. The same logic governs heterogeneous catalysis (catalyst surface area + temperature both boost rate) and pharmaceutical formulation (micronisation of drugs to speed dissolution in the gut). It is the universal principle of interfacial chemistry.

Final Answer: Option **(iv)**: Powdered sugar in hot water.

Q 1.3 At equilibrium the rate of dissolution of a solid solute in a volatile liquid solvent is ____________.

(i) less than the rate of crystallisation

(ii) greater than the rate of crystallisation

(iii) equal to the rate of crystallisation

(iv) zero

SOLUTION

Correct option: (iii) equal to the rate of crystallisation.

Concept used. Dynamic equilibrium in a saturated solution: solid and dissolved solute coexist while two opposite microscopic processes proceed at the same rate.

- Dissolution (forward): solid $\rightarrow$ solute(aq), rate R_d.
- Crystallisation (reverse): solute(aq) $\rightarrow$ solid, rate R_c.

At equilibrium $R_d = R_c$, so the macroscopic concentration of dissolved solute stays constant.

Step 1. Write the rate condition: at equilibrium $R_d = R_c$. Neither rate is zero; both microscopic processes continue, but the net flux is zero.

Step 2. Option (iv) "zero" describes the *net* rate, not the individual rates. The question asks about the rate of dissolution itself, so (iv) is wrong.

Final Answer: Option **(iii)**: rate of dissolution $=$ rate of crystallisation.

EXPERT'S SOLUTION : *Pranav Bhat, Ph.D Organic Chemistry, IISc Bangalore*

Picture-first. Picture a beaker of sugar water with extra crystals on the bottom. Watch a single sugar molecule: sometimes it's pulled into solution, sometimes it locks back onto a crystal face. At equilibrium these two visits balance out.

Concept used. A solution is **saturated** when it sits in dynamic equilibrium with undissolved solid. "Dynamic" = molecules keep moving both ways across the interface; "equilibrium" = the two flows match. The macroscopic concentration is constant precisely because $R_d = R_c$.

Step 1. **Definition recap.** At phase equilibrium $R_{\text{fwd}} = R_{\text{rev}}$. Here fwd = dissolution, rev = crystallisation. Both rates are nonzero; their equality keeps [solute] constant.

Step 2. **Why "zero" (iv) is wrong.** A radioactive-tracer experiment with ^{14}C-labelled sugar crystals in unlabelled solution shows the label gradually appears in solution. So dissolution continues it is not zero.

Step 3. **Why (i) and (ii) are wrong.** If $R_d > R_c$, the amount in solution rises and the system is not yet at equilibrium (unsaturated). If $R_c > R_d$, the solid grows and the solution depletes (supersaturated). Only $R_d = R_c$ matches stable saturated equilibrium.

☞ Exam Tip

Exam tip / generalisation. This identical pattern recurs in all equilibrium chapters: K_{sp} (solubility), K_p/K_c (gas-phase), phase equilibria (Raoult/Henry). The "forward = reverse" rule is universal.

♥ Concept Linkage

Concept linkage. The same dynamic-equilibrium framework underlies K_{sp}, K_p/K_c and even physiological steady-states (sodium-potassium pump). It is the single most important idea in equilibrium chemistry.

Final Answer: Option **(iii)**: equal to the rate of crystallisation.

Q 1.4 **A beaker contains a solution of substance 'A'. Precipitation of substance 'A' takes place when small amount of 'A' is added to the solution. The solution is ________.**

(i) saturated
(ii) supersaturated
(iii) unsaturated
(iv) concentrated

SOLUTION

Correct option: (ii) supersaturated.

Concept used. Three classes of solution defined by their position relative to saturation:

- **Unsaturated:** less solute dissolved than the maximum; adding more solute dissolves further.
- **Saturated:** exactly at the solubility limit; adding more solute leaves it undissolved.
- **Supersaturated:** more solute dissolved than equilibrium permits (metastable, achieved by slow cooling or evaporation); a small disturbance (a seed crystal, a scratch) triggers immediate precipitation of the excess.

Step 1. Translate the observation. Adding A causes precipitation, which means the solution already held *more* dissolved A than equilibrium permits; the added crystal acted as a nucleation seed.

Step 2. Match with definitions. Only a supersaturated solution precipitates on seeding. A saturated solution leaves added solute undissolved; an unsaturated solution dissolves more.

> **Final Answer:** Option **(ii)**: supersaturated.

EXPERT'S SOLUTION : *Vivaan Gupta, M.Tech Chemical Engineering, IIT Delhi*

Strategic angle (decision-tree). The three saturation states each have a distinct response to "add more solute":

- unsaturated → added crystal dissolves fully,
- saturated → added crystal stays undissolved,
- supersaturated → added crystal triggers precipitation of A.

The problem says "precipitation takes place" ⇒ row 3 ⇒ supersaturated.

Concept used. Supersaturation is a metastable state. The Gibbs free energy of the dissolved excess is higher than that of the solid; the system is kinetically trapped by the absence of a nucleation site. The added crystal supplies that surface, so the excess deposits almost instantly.

Step 1. Quantitative picture. Let c_{sat} be the saturation concentration at T. A supersaturated solution has $c > c_{\text{sat}}$. After seeding, the excess $(c - c_{\text{sat}})$ deposits as solid and c falls to c_{sat}.

Step 2. How is supersaturation achieved? Slow cooling: dissolve solute in hot solvent, then cool undisturbed. Solubility usually falls with T, but with no nucleus the excess stays in solution. Examples: sodium acetate "hot ice" hand warmers, rock candy from cooling sugar syrup.

Step 3. **Why not "concentrated"?** "Concentrated" is relative; a 10% NaCl is dilute (saturation ~ 36 g/100 mL), but a 1% $CaSO_4$ is already supersaturated. The cue is response to seeding, not absolute amount.

☞ Exam Tip

Exam tip / generalisation. The MCQ-triad *dissolves* → *unsaturated; stays* → *saturated; precipitates* → *supersaturated* is reused almost every year in JEE Main / NEET. Memorise it.

♥ Concept Linkage

Concept linkage. Supersaturation drives industrial crystallisation (sugar refining, pharmaceutical recrystallisation, geological mineral deposition) and biological precipitation (kidney- stone formation by calcium-oxalate supersaturation in urine).

Final Answer: Option **(ii)**: supersaturated.

Q 1.5 Maximum amount of a solid solute that can be dissolved in a specified amount of a given liquid solvent does not depend upon ____________.

(i) Temperature

(ii) Nature of solute

(iii) Pressure

(iv) Nature of solvent

SOLUTION

Correct option: (iii) Pressure.

Concept used. The solubility of a solid in a liquid is the maximum mass of solute that dissolves per unit volume of solvent at equilibrium. It depends on:

- **Temperature:** rises with T for endothermic dissolution, falls for exothermic, but never independent.
- **Nature of solute / solvent:** like dissolves like; polar in polar, non-polar in non-polar.

Pressure has negligible effect on solid-in-liquid solubility because solids and liquids are nearly incompressible: a small change in P produces a negligible change in chemical potential of solid or dissolved state.

Step 1. Apply Le Chatelier: solid $\rightleftharpoons$ solute(aq). Changing P shifts equilibrium only if ΔV between the two states is significant. For solid–liquid, $\Delta V \approx 0$.

Step 2. Contrast with Henry's law for gas-in-liquid: $p = K_H\,x$. Here ΔV between gas and dissolved state is huge, so pressure matters. But the question specifies a *solid* solute.

> **Final Answer:** Option **(iii)**: Pressure.

EXPERT'S SOLUTION *: Aanya Mehta, M.Sc Chemistry, IIT Kanpur*

Strategic angle (Le Chatelier filter). Solubility is a thermodynamic equilibrium. Its variables are dictated by what shifts that equilibrium. For solid-in-liquid: T and natures of solute and solvent matter; P does not.
Concept used. The pressure-dependence of any equilibrium constant is

$$\frac{\partial(\ln K)}{\partial P} = -\frac{\Delta V}{RT}.$$

For solid-to-dissolved equilibria in condensed phases, ΔV is $\lesssim 5$ cm^3/mol about 10^{-5} times the ΔV of gas-liquid equilibria so a 1 atm pressure change shifts solubility by less than 10^{-4} %.

Step 1. **Quantify the pressure effect.** Take $\Delta V \approx 5 \times 10^{-6}$ m^3/mol.

$$\frac{\partial(\ln K)}{\partial P} = -\frac{5 \times 10^{-6}}{8.314 \times 298} = -2 \times 10^{-9}\ \text{Pa}^{-1}.$$

For $\Delta P = 1$ atm $= 10^5$ Pa, $\Delta(\ln K) \approx -2 \times 10^{-4}$, i.e. $\sim 0.02\%$ change in solubility negligible.

Step 2. **Contrast with gas-in-liquid.** For O_2 dissolving in water, $\Delta V \approx -22.4$ L/mol (gas volume lost at STP) a billion times stronger pressure dependence. This is exactly Henry's law.

Step 3. **Why T is not the answer.** $\partial(\ln K)/\partial T = \Delta H/RT^2$. Most ionic solids show 20–50% solubility change per 25 °C; (i) is ruled out.

Step 4. **Why natures matter.** Like dissolves like: dipole- dipole / H-bond / ion-dipole compatibility determines ΔH_{sol}. So (ii) and (iv) are ruled out.

☞ **Exam Tip**

Exam tip / generalisation. JEE Main 2020 (Sept Shift) asked "which factor does not affect solubility of NaCl in water" expected answer pressure. NEET 2014 and 2016 used the same template.

♥ Concept Linkage

Concept linkage. The pressure-insensitivity of condensed- phase equilibria is why liquid pharmaceutical solubility is reported only as a function of T, whereas gas solubility (CO_2 in beer, O_2 in blood) is reported vs partial pressure.

Final Answer: Option **(iii)**: Pressure.

Q 1.6 **Low concentration of oxygen in the blood and tissues of people living at high altitude is due to ____________.**

(i) low temperature
(ii) low atmospheric pressure
(iii) high atmospheric pressure
(iv) both low temperature and high atmospheric pressure

SOLUTION

Correct option: (ii) low atmospheric pressure.
Concept used. **Henry's law** states that, at a given temperature, the partial pressure of a gas above a liquid is proportional to its mole fraction dissolved:

$$p = K_H\, x \quad \Longleftrightarrow \quad x = p/K_H.$$

Lower $p \Rightarrow$ lower x in the liquid.

Step 1. Atmospheric pressure falls with altitude. At sea level, $p_{\text{atm}} = 760$ mmHg, so $p_{O_2} = 0.21 \times 760 = 160$ mmHg. At 4000 m, $p_{\text{atm}} \approx 462$ mmHg, so $p_{O_2} = 0.21 \times 462 = 97$ mmHg.

Step 2. By Henry's law, x_{O_2} in blood scales with p_{O_2}:

$$\frac{x_{\text{high}}}{x_{\text{sea}}} = \frac{97}{160} \approx 0.61.$$

So dissolved O_2 at 4000 m is about 60% of sea-level value.

Step 3. Temperature at altitude is lower, which would actually *raise* dissolved O_2 slightly (lower K_H for O_2 at lower T). So (i) and (iv) are wrong because low T works the opposite way. Dominant effect: pressure drop.

Final Answer: Option **(ii)**: low atmospheric pressure.

EXPERT'S SOLUTION *: Rohit Kapoor, M.Sc Chemistry, IIT Kanpur*

Strategic angle. The physiological cue "anoxia at altitude" points to Henry's law: $p\downarrow\Rightarrow x\downarrow\Rightarrow$ tissues are oxygen-starved. Don't be fooled by temperature lower T alone helps oxygen solubility slightly.

Concept used. Gas-in-liquid solubility scales linearly with the gas's partial pressure at fixed T. Body temperature is essentially constant (37 °C) for a living person, so the only physiologically relevant variable with altitude is atmospheric pressure.

Step 1. **Henry's law for blood oxygenation.** Let K_H be Henry's constant for O_2 in blood plasma at body temperature. Then $[O_2]_{\text{diss}} \propto p_{O_2}$.

Step 2. **Quantify altitude.** Barometric formula:

$$p_{\text{atm}}(h) \approx p_0\, e^{-h/H}, \quad H \approx 8\ \text{km}.$$

At Everest base camp (5400 m), $p \approx 760 \times e^{-5.4/8} = 387$ mmHg $\approx 0.51\, p_0$, so dissolved O_2 halves.

Step 3. **Why body T does not change.** Internal T stays at 37 °C even at altitude. So ambient cold is irrelevant to dissolved O_2 in *blood*. The hint in option (i) is a trap.

☞ Exam Tip

Exam tip / generalisation. NCERT pairs this question with "bends" (Q42 here): both are direct Henry's-law consequences. Whenever a question mentions altitude + breathing, or deep-sea diving + bubbles, reach for Henry's law.

♥ Concept Linkage

Concept linkage. Henry's law underlies all gas-exchange physiology (lung O_2/CO_2, deep-sea diving, anaesthesia gases, fizzy drinks). The same equation that explains "bends" explains "altitude sickness" just opposite direction in p.

Final Answer: Option **(ii)**: low atmospheric pressure.

Q 1.7 **Considering the formation, breaking and strength of hydrogen bond, predict which of the following mixtures will show a positive deviation from Raoult's law?**

(i) Methanol and acetone.

(ii) Chloroform and acetone.

(iii) Nitric acid and water.

(iv) Phenol and aniline.

SOLUTION

Correct option: **(i)** Methanol and acetone.
Concept used. Raoult's law gives ideal behaviour when A–A, B–B and A–B interactions are equal. A mixture shows:

- **Positive deviation** ($p > p_{\text{Raoult}}$) when A–B interactions are weaker than A–A or B–B; molecules escape more easily, vapour pressure rises.
- **Negative deviation** ($p < p_{\text{Raoult}}$) when A–B interactions are stronger than A–A or B–B; molecules are held more tightly.

Step 1. **Methanol + acetone.** Pure methanol has strong O–H $\cdots$ O hydrogen bonds. Mixing with acetone (no O–H donor) breaks some methanol H-bonds; new methanol–acetone H-bonds (O–H $\cdots$ O=C) are weaker. Net A–B $<$ A–A. So $p > p_{\text{ideal}} \Rightarrow$ positive deviation.

Step 2. **Eliminate others.** (ii) Chloroform + acetone: new Cl_3C–H $\cdots$ O=C H-bond forms, A–B stronger $\Rightarrow$ negative deviation. (iii) HNO_3 + water: very strong A–B H-bonds $\Rightarrow$ negative deviation. (iv) Phenol + aniline: O–H $\cdots$ N H-bond, A–B stronger $\Rightarrow$ negative.

> **Final Answer:** Option **(i)**: Methanol and acetone (positive deviation).

EXPERT'S SOLUTION *: Aditya Reddy, Ph.D Organic Chemistry, IISc Bangalore*

Structural angle. Look at where H-bonds exist in the pure liquids and whether mixing creates or destroys them. Positive deviation = pure-liquid H-bonds get disrupted without being adequately replaced by mixed-pair H-bonds. Negative deviation = new H-bonds appear in the mixture that did not exist in either pure liquid.
Concept used. The **deviation sign** is set by

$$\Delta H_{\text{mix}} = H_{\text{mixture}} - (H_A + H_B).$$

$\Delta H_{\text{mix}} > 0 \Rightarrow$ endothermic mixing $\Rightarrow$ weaker A–B $\Rightarrow$ positive deviation. $\Delta H_{\text{mix}} < 0 \Rightarrow$ exothermic mixing $\Rightarrow$ stronger A–B $\Rightarrow$ negative deviation.

Step 1. **Methanol-acetone H-bond ledger.** Pure methanol: each O–H donates to a neighbour's lone pair strong H-bond network. Pure acetone: dipole-dipole only, no H-bond donor. Mixed: methanol O–H weakly H-bonds to acetone C=O. Net: methanol–methanol H-bonds break; new methanol–acetone H-bonds form, but weaker. $\Delta H_{\text{mix}} > 0$, $\Delta V_{\text{mix}} > 0$, $p_{\text{tot}} > p_{\text{Raoult}}$. Forms a minimum-boiling azeotrope at $x_{\text{MeOH}} \approx 0.79$, $T_b \approx 55\ ^\circ\text{C}$.

Step 2. **Chloroform-acetone (negative example).** $CHCl_3$ has an unusually acidic C–H (three EWG Cl's). It H-bonds strongly to acetone C=O: Cl_3C–H $\cdots$ O=C$(CH_3)_2$. Pure chloroform and pure acetone lack this H-bond. Mixing *creates* a new H-bond ⇒ A–B stronger ⇒ negative deviation, max-boiling azeotrope.

Step 3. **HNO_3 + water and phenol + aniline.** HNO_3 + H_2O forms very strong A–B H-bonds (max-boiling azeotrope at 68 mass-%, ~ 393.5 K). Phenol + aniline: phenol O–H donates to aniline N lone pair strong A–B H-bond. Both negative.

✗ Common Pitfall

Common pitfall. Reading "hydrogen bonding" and assuming any H-bonding gives negative deviation. The criterion is whether mixing *creates new* H-bonds (negative) or *breaks existing* H-bonds (positive). Methanol-acetone is the classic "breaks more than it forms" case.

☞ Cross-Check

Numerical cross-check. Methanol-acetone azeotrope sits ~ 8 °C below the lower of the two pure b.p.'s. Negative ΔT_b from pure components is the signature of positive deviation.

Final Answer: Option **(i)**: Methanol and acetone.

Q 1.8 **Colligative properties depend on __________.**

(i) the nature of the solute particles dissolved in solution.

(ii) the number of solute particles in solution.

(iii) the physical properties of the solute particles dissolved in solution.

(iv) the nature of solvent particles.

SOLUTION

Correct option: (ii) the number of solute particles in solution.

Concept used. Colligative properties (Latin *colligare* = "to bind by counting") depend only on the number of solute particles, not their identity. Four colligative properties:

- Relative lowering of vapour pressure: $\Delta p/p^\circ = x_B$.
- Elevation of boiling point: $\Delta T_b = iK_bm$.
- Depression of freezing point: $\Delta T_f = iK_fm$.
- Osmotic pressure: $\Pi = iCRT$.

Each formula contains a count (x_B, m, C, i) but no chemical-identity term.

Step 1. Examine each formula: K_b and K_f depend on solvent, not solute. x_B counts moles. Solute identity drops out.

Step 2. Empirical check: 0.1 m solutions of urea, glucose, sucrose in water all give

$\Delta T_f \approx 0.186$ K regardless of solute identity.

Final Answer: Option **(ii)**: number of solute particles.

EXPERT'S SOLUTION *: Riya Singh, M.Sc Chemistry, IIT Kanpur*

Strategic angle (etymological). The word "colligative" encodes the answer: from Latin *colligere*, "to bind together by counting". These properties care about counts, not identity.
Concept used. Colligative behaviour arises because adding any non-volatile solute reduces the mole fraction of solvent on the liquid surface; the resulting entropy change is the same for any solute at equal x_B. Identity does not enter the entropy of mixing in the dilute limit.

Step 1. **Microscopic explanation.** Vapour pressure depends on the rate of solvent molecules leaving the surface. If a fraction x_B of surface sites is occupied by solute, the escape rate falls by x_B regardless of solute identity.

Step 2. **Mathematical check.** The four formulas $\Delta p/p^\circ = x_B$, $\Delta T_b = K_b m$, $\Delta T_f = K_f m$, $\Pi = CRT$ contain only solvent constants (K_b, K_f, p°) and a count of solute (x_B, m, C). No identity term.

Step 3. **Identity matters indirectly via i.** For electrolytes, the Van't Hoff factor i converts formula units to particles: NaCl $i \approx 2$, $BaCl_2$ $i \approx 3$. i is itself a count, not chemical identity.

☞ Exam Tip

Exam tip. JEE Main 2020 and NEET 2018 reused this verbatim. Memorise: colligative = counting; identity enters only via i.

- Urea (non-electrolyte): $\Delta T_f = 1.86 \times 0.1 = 0.186$ K.
- NaCl ($i = 2$): $\Delta T_f = 1.86 \times 0.1 \times 2 = 0.372$ K.

The factor 2 is a count of particles after dissociation, not a chemical-identity correction.

♥ Concept Linkage

Concept linkage. The "count not identity" principle is the basis of osmometry / cryoscopy for measuring molar masses of unknown polymers and proteins ΔT_f or Π tells you the number of particles dissolved, from which M_w follows.

Final Answer: Option **(ii)**: number of solute particles in solution.

Q 1.9 **Which of the following aqueous solutions should have the highest boiling point?**

(i) 1.0 M $NaOH$
(ii) 1.0 M Na_2SO_4
(iii) 1.0 M NH_4NO_3
(iv) 1.0 M KNO_3

SOLUTION

Correct option: (ii) 1.0 M Na_2SO_4.
Concept used. Elevation of boiling point for an electrolyte:

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

At the same molarity (approximately molality for dilute aqueous solutions), the highest ΔT_b goes with the highest i. For a strong electrolyte:

$$i = \text{number of ions per formula unit.}$$

Step 1. Tabulate i for each (assume complete dissociation):

- $NaOH \rightarrow Na^+ + OH^-$: $i = 2$.
- $Na_2SO_4 \rightarrow 2\,Na^+ + SO_4^{2-}$: $i = 3$.
- $NH_4NO_3 \rightarrow NH_4^+ + NO_3^-$: $i = 2$.
- $KNO_3 \rightarrow K^+ + NO_3^-$: $i = 2$.

Step 2. Na_2SO_4 has the highest $i \Rightarrow$ highest $\Delta T_b \Rightarrow$ highest boiling point.

Final Answer: Option **(ii)**: 1.0 M Na_2SO_4.

EXPERT'S SOLUTION : *Karan Verma, M.Sc Physical Chemistry, IIT Madras*

Strategic angle (count the ions). Boiling-point elevation is colligative, so count particles. Na_2SO_4 gives three (two Na^+ + one SO_4^{2-}); the other three salts give two each.
Concept used. For dilute strong-electrolyte solutions,

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

(since $m \approx c$ for dilute aqueous solutions with density ≈ 1). K_b is a solvent property (water: 0.512 K·kg/mol). So $\Delta T_b \propto i$ at fixed c.

Step 1. **Compute ΔT_b for each.**

- $NaOH$: $\Delta T_b = 2 \times 0.512 \times 1 = 1.02$ K.
- Na_2SO_4: $\Delta T_b = 3 \times 0.512 \times 1 = 1.54$ K.

- NH_4NO_3: $\Delta T_b = 1.02$ K.
- KNO_3: $\Delta T_b = 1.02$ K.

Step 2. Pick the highest. Na_2SO_4 gives 1.54 K, beating the others by 0.52 K.

Step 3. Realistic i caveat. At 1 M, i values fall below the ideal limit due to ion pairing. Literature: NaOH ≈ 1.83, $Na_2SO_4 \approx 2.36$, $NH_4NO_3 \approx 1.83$, $KNO_3 \approx 1.74$. Ranking unchanged.

✗ Common Pitfall

Common pitfall. Picking (i) NaOH because "strong base = more elevation". Strength of the acid/base is unrelated to i. i counts ions per formula unit; **Na_2SO_4 gives 3 ions**, more than any of the other three.

☞ Exam Tip

Exam tip. Almost yearly in JEE Main, NEET, CBSE board. Quick ranking among common 1:1, 2:1, 3:1 salts: $AlCl_3$ (4) > Na_2SO_4 (3) > NaCl (2) > glucose (1).

☞ Cross-Check

Numerical cross-check. Measured normal b.p. of 1.0 M Na_2SO_4 solution: ~ 101.2 °C. Of 1.0 M NaCl: ~ 100.93 °C. Difference matches the i ratio 3:2.

Final Answer: Option **(ii)**: 1.0 M Na_2SO_4.

Q 1.10 The unit of ebullioscopic constant is __________.

(i) K kg mol^{-1} or K $(molality)^{-1}$

(ii) mol kg K^{-1} or K^{-1} (molality)

(iii) kg mol^{-1} K^{-1} or K^{-1} $(molality)^{-1}$

(iv) K mol kg^{-1} or K (molality)

SOLUTION

Correct option: (i) K kg mol^{-1} or K $(molality)^{-1}$.

Concept used. The ebullioscopic constant K_b (molal elevation constant) is defined by

$$\Delta T_b = K_b m \quad \Longrightarrow \quad K_b = \frac{\Delta T_b}{m}.$$

ΔT_b is in K; m is in mol/kg. So

$$[K_b] = \frac{\text{K}}{\text{mol/kg}} = \text{K} \cdot \text{kg} \cdot \text{mol}^{-1}.$$

Step 1. ΔT_b unit: kelvin (K).

Step 2. Molality m unit: mol·kg^{-1}.

Step 3. Divide: K ÷ (mol/kg) = K·kg/mol = K·kg·mol^{-1} = K (molality)$^{-1}$.

Final Answer: Option **(i)**: K kg mol^{-1} or K (molality)$^{-1}$.

EXPERT'S SOLUTION : *Yash Joshi, M.Sc Physical Chemistry, IIT Madras*

Strategic angle (dimensional analysis). Start from $\Delta T_b = K_b m$ and isolate K_b. Pure unit algebra no chemistry needed once you remember the defining equation.

Concept used. K_b is a solvent-only constant linking ΔT_b (K) to m (mol/kg solvent). It depends only on the solvent's molar mass and enthalpy of vaporisation via

$$K_b = \frac{R\,M_A\,T_b^2}{1000\,\Delta H_{\text{vap}}}.$$

Step 1. **Dimensional algebra.**

$$[K_b] = \frac{[\Delta T_b]}{[m]} = \frac{\text{K}}{\text{mol/kg}} = \text{K} \cdot \text{kg} \cdot \text{mol}^{-1}.$$

Numerical for water: $K_b = 0.512$ K·kg·mol^{-1}.

Step 2. **Cross-check from derived formula.** Plug units into $K_b = RM_AT_b^2/(1000\Delta H_{\text{vap}})$: R in J/(mol·K), M_A in g/mol, T_b^2 in K^2, ΔH_{vap} in J/mol. Numerator units: J·g·K·mol^{-2}. Divided by J/mol with the 1000 factor converting g → kg gives K·kg·mol^{-1}. ✓

Step 3. **Eliminate wrong options.** (ii) inverts molality; that would be $m/\Delta T_b$. (iii) inverts both K and mol/kg. (iv) puts molality multiplicatively instead of dividing.

☞ **Exam Tip**

Exam tip. When you forget a constant's units, derive them from the defining equation, never memorise. A standard trick on JEE Main physical chemistry.

♥ **Concept Linkage**

Concept linkage. K_b and K_f are not arbitrary fit constants but follow from ΔH_{vap} and ΔH_{fus} via Clausius-Clapeyron. The unit K·kg·mol^{-1} is the natural outcome of that derivation.

Final Answer: Option **(i)**: K kg mol^{-1} or K (molality)$^{-1}$.

Q 1.11 **In comparison to a 0.01 M solution of glucose, the depression in freezing point of a 0.01 M $MgCl_2$ solution is ________.**

(i) the same

(ii) about twice

(iii) about three times

(iv) about six times

SOLUTION

Correct option: (iii) about three times.

Concept used. Freezing-point depression for an electrolyte:

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

For glucose (non-electrolyte), $i = 1$. For $MgCl_2$ (strong electrolyte, complete dissociation),

$$\mathrm{MgCl_2} \longrightarrow \mathrm{Mg^{2+}} + 2\,\mathrm{Cl^-}, \quad i = 3.$$

Step 1. Glucose: $(\Delta T_f)_{\text{glu}} = 1 \times K_f \times 0.01 = 0.01K_f$.

Step 2. $MgCl_2$: $(\Delta T_f)_{\text{Mg}} = 3 \times K_f \times 0.01 = 0.03K_f$.

Step 3. Ratio: $0.03K_f/0.01K_f = 3 \Rightarrow$ about three times.

> **Final Answer:** Option **(iii)**: about three times.

EXPERT'S SOLUTION *: Aanya Patel, M.Sc Chemistry, IIT Kanpur*

Strategic angle. Two equal-concentration solutions differ in ΔT_f only through their Van't Hoff factors. Glucose: 1 particle per formula unit. $MgCl_2$: 3 particles per formula unit. Ratio 3:1.

Concept used. The Van't Hoff factor i is the count of particles per formula unit after dissolution. For a strong 1:n electrolyte $M^{m+}(X^-)_n$, $i = 1 + n$ (assuming complete dissociation). For $MgCl_2$: 1 Mg + 2 Cl = 3 particles.

Step 1. Write the depression for both solutes.

$$(\Delta T_f)_{\text{glu}} = i_{\text{glu}}\,K_f\,m = 1 \times 1.86 \times 0.01 = 0.0186\,\text{K}.$$

$$(\Delta T_f)_{\text{Mg}} = i_{\text{Mg}}\,K_f\,m = 3 \times 1.86 \times 0.01 = 0.0558\,\text{K}.$$

Step 2. Take the ratio.

$$\frac{(\Delta T_f)_{\text{Mg}}}{(\Delta T_f)_{\text{glu}}} = \frac{0.0558}{0.0186} = 3.0.$$

Step 3. Realistic correction. At 0.01 M, measured i for $MgCl_2$ is slightly below 3 (~ 2.7) due to ion pairing. Ratio drops to ~ 2.7, still much closer to 3 than to 2 or 6. Hence "about three times" is correct.

✗ Common Pitfall

Common pitfall. (iv) "about six times" picked by students who count 2 Cl^- AND 1 Mg^{2+} AND multiply charges. The colligative count is number of *particles*, not charges.

☞ Cross-Check

Numerical cross-check. A 0.01 M $MgCl_2$ aqueous solution freezes at about -0.054 °C (literature). Glucose at 0.01 M freezes at -0.019 °C. Ratio ≈ 2.85, close to the ideal 3.0.

Final Answer: Option **(iii)**: about three times.

Q 1.12 **An unripe mango placed in a concentrated salt solution to prepare pickle, shrivels because __________.**

(i) it gains water due to osmosis.

(ii) it loses water due to reverse osmosis.

(iii) it gains water due to reverse osmosis.

(iv) it loses water due to osmosis.

SOLUTION

Correct option: (iv) it loses water due to osmosis.

Concept used. Osmosis is the spontaneous flow of solvent across a semi-permeable membrane from the side of lower solute concentration (higher water activity) to the side of higher solute concentration (lower water activity). The driving force is the chemical potential of water.

Step 1. Identify the two sides.

- Inside the mango: dilute cell-sap (mostly water, some sugars/acids).
- Outside (brine): concentrated salt solution.

Step 2. Water moves from high-water-activity (inside the mango) to low-water-activity (the brine) across the cell walls.

Step 3. Net result: water exits the mango cells → cells lose turgor → mango shrivels.

Final Answer: Option **(iv)**: it loses water due to osmosis.

EXPERT'S SOLUTION : *Priya Nair, M.Sc Chemistry, IIT Kanpur*

Picture-first. Picture a mango cell as a balloon with a semi-permeable wall. Inside: dilute cell sap. Outside: dense salt brine. Water flees the dilute side for the dense side (osmosis), the balloon collapses, and the mango shrivels.
Concept used. The osmotic-pressure inequality $\Pi_{\text{brine}} > \Pi_{\text{cell}}$ drives water out of the mango cells. Reverse osmosis would require an *externally applied pressure* greater than Π pushing water *back* into the cell no such external pressure exists here.

Step 1. Compare osmotic pressures.

$$\Pi_{\text{brine}} = iCRT.$$

For a 1 M NaCl pickle brine at 298 K:

$$\Pi = 2 \times 1 \times 0.0821 \times 298 \approx 49\,\text{atm}.$$

Mango cell sap $\Pi \approx 2$–5 atm. So a 50 atm pressure gradient pulls water out.

Step 2. Verify direction. Water always flows from low-Π to high-Π side in normal osmosis. Brine has higher Π, so water leaves the cell.

Step 3. Rule out reverse osmosis. Reverse osmosis requires external pressure $P_{\text{ext}} > \Pi$ pushing solvent from concentrated to dilute side. In a passive pickle jar there is no external pressure: gravity and atmospheric pressure affect both sides equally.

☞ Exam Tip

Exam tip. NEET 2017 (biology) and CBSE Class 12 board yearly. Memorise: pickle / dried fruit / salted fish = osmosis, desalination plant / kidney dialysis = reverse osmosis.

♥ Concept Linkage

Concept linkage. Osmotic pressure governs all biological salt/water balance: red-blood cells lyse in hypotonic solution and crenate (shrivel) in hypertonic. The pickling principle is exactly this cells shrivel and bacteria die from water loss, preserving the fruit.

Final Answer: Option **(iv)**: it loses water due to osmosis.

Q 1.13 **At a given temperature, osmotic pressure of a concentrated solution of a substance ____________.**

(i) is higher than that at a dilute solution.
(ii) is lower than that of a dilute solution.
(iii) is same as that of a dilute solution.
(iv) cannot be compared with osmotic pressure of dilute solution.

SOLUTION

Correct option: (i) is higher than that at a dilute solution.
Concept used. Van't Hoff's equation for osmotic pressure:

$$\Pi = C\,RT \quad \text{(nonelectrolyte)}$$

or

$$\Pi = i\,C\,RT \quad \text{(electrolyte)}.$$

At fixed T and identity, $\Pi \propto C$. Higher concentration ⇒ higher Π.

Step 1. Take two solutions of the same solute at the same T: concentrated (C_1) and dilute (C_2), with $C_1 > C_2$.

Step 2. Form the ratio:

$$\frac{\Pi_1}{\Pi_2} = \frac{C_1 RT}{C_2 RT} = \frac{C_1}{C_2} > 1.$$

Step 3. Hence $\Pi_1 > \Pi_2$.

> **Final Answer:** Option **(i)**: Π is higher for the concentrated solution.

EXPERT'S SOLUTION *: Diya Rao, M.Sc Chemistry, IIT Kanpur*

Strategic angle (direct proportionality). $\Pi = CRT$ is a linear law. Doubling C doubles Π. Done.
Concept used. Osmotic pressure is the external pressure required to stop osmotic inflow of solvent into a solution. The higher the solute concentration, the greater the chemical-potential deficit of solvent, hence the greater the pressure needed to counter it. The Van't Hoff equation has the same algebraic form as the ideal-gas law.

Step 1. **Numerical example.** 0.01 M glucose at 298 K: $\Pi = 0.01 \times 0.0821 \times 298 \approx 0.245$ atm. 0.1 M glucose at 298 K: $\Pi \approx 2.45$ atm. Tenfold concentration ⇒ tenfold Π.

Step 2. **Analogy.** $\Pi = nRT/V$ mirrors $P = nRT/V$ for an ideal gas: solute particles in a solvent behave like gas molecules in a vacuum at the same number density.

Step 3. **Why (iv) is wrong.** Solutions of the same solute at the same T can always be compared via $\Pi/C = RT$, a constant. Different solutes or different T would require care; here both are fixed.

✗ Common Pitfall

Common pitfall. Picking (iv) because the question seems trivial. Don't overthink Π scales linearly with C.

☞ Exam Tip

Exam tip. CBSE board favourite (1 mark, almost every year). The trick is recognising that "concentrated vs dilute" is just "higher vs lower C" $\Rightarrow$ higher vs lower Π.

♥ Concept Linkage

Concept linkage. The linearity $\Pi \propto C$ at low C mirrors the dilute-gas approximation. At high C, real solutions deviate (just as real gases deviate from $PV = nRT$); the deviation is captured by activity coefficients, but the qualitative "concentrated $\rightarrow$ higher Π" always holds.

Final Answer: Option **(i)**: higher than that of a dilute solution.

Q 1.14 **Which of the following statements is false?**

(i) Two different solutions of sucrose of same molality prepared in different solvents will have the same depression in freezing point.

(ii) The osmotic pressure of a solution is given by the equation $\Pi = CRT$ (where C is the molarity of the solution).

(iii) Decreasing order of osmotic pressure for 0.01 M aqueous solutions of barium chloride, potassium chloride, acetic acid and sucrose is $BaCl_2 > KCl > CH_3COOH >$ sucrose.

(iv) According to Raoult's law, the vapour pressure exerted by a volatile component of a solution is directly proportional to its mole fraction in the solution.

SOLUTION

Correct option: **(i)** is the false statement.

Concept used. The depression in freezing point depends on *both* the solute concentration and the solvent's K_f:

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

K_f is a **cryoscopic constant** unique to each solvent (water: 1.86, benzene: 5.12, camphor: 40, etc.). Two solvents have different K_f values, so the same molality of sucrose gives *different* ΔT_f.

Step 1. Sucrose ($i = 1$) at molality m in water: $\Delta T_f^{\text{(water)}} = 1.86\,m$.

Step 2. Same sucrose at the same m in benzene: $\Delta T_f^{\text{(benzene)}} = 5.12\,m$.

Step 3. Different so statement (i) is false.

Step 4. Check the others: (ii) Van't Hoff's equation true. (iii) Particle counts: $BaCl_2$ (3) $>$ KCl (2) $>$ CH_3COOH (~ 1.02) $>$ sucrose (1) order correct, statement true. (iv) Raoult's law statement true.

Final Answer: Option **(i)**: the false statement.

EXPERT'S SOLUTION *: Krishna Banerjee, Ph.D Physical Chemistry, IIT Bombay*

Strategic angle. Find the statement that contradicts a solvent-property fact. Statement (i) ignores that K_f varies by solvent. The others are textbook truths.
Concept used. Cryoscopic constant K_f has the molecular formula

$$K_f = \frac{R\,M_A\,T_f^2}{1000\,\Delta H_{\text{fus}}},$$

where M_A is the solvent's molar mass, T_f its freezing point, ΔH_{fus} its enthalpy of fusion. None of these are universal; they depend on the solvent.

Step 1. **Show different K_f at common molality.** For $m = 0.1$ sucrose in water: $\Delta T_f = 1.86 \times 0.1 = 0.186$ K. In benzene: $\Delta T_f = 5.12 \times 0.1 = 0.512$ K. In camphor: $\Delta T_f = 40 \times 0.1 = 4.0$ K. Three solvents, three different depressions $\Rightarrow$ statement (i) is false.

Step 2. **Why K_f differs.** Substituting into the formula: camphor has $T_f \approx 452$ K (very high) and small ΔH_{fus}, giving $K_f \approx 40$. Water has $T_f = 273$ K and large ΔH_{fus}, giving $K_f = 1.86$.

Step 3. **Verify (iii) more rigorously.** $BaCl_2$: $i \approx 2.7$ at 0.01 M. KCl: $i \approx 1.9$. CH_3COOH (weak acid, slight dissociation): $i \approx 1.01$. Sucrose: $i = 1$. So Π ranks $BaCl_2$ $>$ KCl $>$ CH_3COOH $>$ sucrose $\Rightarrow$ statement true.

✗ Common Pitfall

Common pitfall. Skim-reading and assuming "two sucrose solutions at same molality" means same depression. The molality is the same, but K_f is not.

☞ **Exam Tip**

Exam tip. JEE Main 2019 (Shift 2) and NEET 2018 reused this "find the false statement" format. Always check (a) does the formula depend on the solvent? (b) does the formula depend on the solute? Different solvents $\Rightarrow$ different $K_f \Rightarrow$ different ΔT_f.

☞ **Cross-Check**

Numerical cross-check. Sucrose, 0.1 m, in water: literature $\Delta T_f = 0.19$ K. In benzene: 0.51 K. In camphor: ~ 4 K. Confirms the prediction.

Final Answer: Option **(i)**: the false statement.

Q 1.15 The values of Van't Hoff factors for KCl, NaCl and K_2SO_4, respectively, are __________.

(i) 2, 2 and 2
(ii) 2, 2 and 3
(iii) 1, 1 and 2
(iv) 1, 1 and 1

SOLUTION

Correct option: (ii) 2, 2 and 3.
Concept used. For a strong electrolyte that dissociates completely,

$$i = \text{number of ions per formula unit.}$$

- $KCl \rightarrow K^+ + Cl^-$: 2 ions $\Rightarrow i = 2$.
- $NaCl \rightarrow Na^+ + Cl^-$: 2 ions $\Rightarrow i = 2$.
- $K_2SO_4 \rightarrow 2\,K^+ + SO_4^{2-}$: 3 ions $\Rightarrow i = 3$.

Step 1. Write the dissociation equations.

Step 2. Count the total particles (cations + anions) per formula unit.

Step 3. Read off i for each salt.

Final Answer: Option **(ii)**: $i_{KCl} = 2$, $i_{NaCl} = 2$, $i_{K_2SO_4} = 3$.

EXPERT'S SOLUTION : *Tara Desai, M.Sc Chemistry, IIT Kanpur*

Quick reading. For strong electrolytes, count the ions per formula unit. KCl and NaCl are 1:1 salts (2 ions each). K_2SO_4 is a 2:1 salt (3 ions).
Concept used. The Van't Hoff factor i corrects colligative formulas for the actual particle count. For a fully ionised strong electrolyte M_aX_b, dissociation gives a cations and b anions $\Rightarrow i = a + b$. Weak electrolytes give $i < (a + b)$ partly because dissociation is incomplete; ion-pairing at finite C similarly reduces i below the ideal limit.

Step 1. **KCl.** K^+ + Cl^-: $i = 1 + 1 = 2$. At 0.01 M, experimental $i \approx 1.97$.

Step 2. **NaCl.** Na^+ + Cl^-: $i = 1 + 1 = 2$. Identical behaviour to KCl (both 1:1).

Step 3. **K_2SO_4.** 2 K^+ + SO_4^{2-}: $i = 2 + 1 = 3$. At 0.01 M, experimental $i \approx 2.84$.

Step 4. **Cross-check using ΔT_f.** 0.01 m K_2SO_4 in water gives $\Delta T_f \approx 0.054$ K, vs $\Delta T_f \approx 0.0186$ K for 0.01 m glucose ($i = 1$). Ratio ≈ 2.9, matching $i = 3$.

✗ Common Pitfall

Common pitfall. Confusing i with the charge of the highest-charge ion. K_2SO_4 has a -2 anion, but i is the *count* of ions, not their charge magnitude. $i = 3$, not 2.

☞ Cross-Check

Numerical cross-check. Conductivity data: limiting equivalent conductance of K_2SO_4 aqueous solution at 25 °C is approximately $1.5\times$ that of KCl at infinite dilution, consistent with three particles vs two.

Final Answer: Option **(ii)**: 2, 2 and 3.

Q 1.16 **Which of the following statements is false?**
(i) Units of atmospheric pressure and osmotic pressure are the same.
(ii) In reverse osmosis, solvent molecules move through a semipermeable membrane from a region of lower concentration of solute to a region of higher concentration.
(iii) The value of molal depression constant depends on nature of solvent.
(iv) Relative lowering of vapour pressure, is a dimensionless quantity.

SOLUTION

Correct option: **(ii)** is the false statement.
Concept used. In reverse osmosis, an external pressure greater than the osmotic pressure Π is applied to the *concentrated* side, forcing solvent to flow against the spontaneous direction: When the applied external pressure satisfies $P_{\text{ext}} > \Pi$ on the

concentrated side, solvent flows from the concentrated side to the dilute side. So solvent goes from *higher concentration of solute to lower concentration of solute* the **opposite** of normal osmosis.

Step 1. Statement (ii) says solvent moves from lower to higher concentration. That is the direction for *normal* osmosis, not reverse osmosis $\Rightarrow$ false.

Step 2. Check the other statements: (i) atm pressure and Π both in atm/Pa true. (iii) $K_f = RM_AT_f^2/(1000\Delta H_{\text{fus}})$, all solvent properties true. (iv) $\Delta p/p^\circ = x_B$, ratio of pressures = dimensionless true.

Final Answer: Option **(ii)**: the false statement.

EXPERT'S SOLUTION *: Ishaan Pillai, Ph.D Chemistry, IISc Bangalore*

Strategic angle (direction-check). Reverse osmosis reverses the normal direction of solvent flow. Normal osmosis: dilute $\rightarrow$ concentrated. Reverse osmosis: concentrated $\rightarrow$ dilute. Statement (ii) describes normal osmosis, mislabelled as reverse $\Rightarrow$ false.
Concept used. In normal osmosis, solvent flows from low- solute to high-solute side, driven by the chemical-potential gradient of the solvent. In reverse osmosis, an external pressure $P_{\text{ext}} > \Pi$ flips the gradient: solvent is pushed from high-solute to low-solute side, producing pure solvent on the low side. This is the operating principle of desalination plants.

Step 1. **Direction analysis.**

- Normal osmosis: $\mu_{\text{solvent, dilute}} > \mu_{\text{solvent, concentrated}}$, so solvent flows dilute $\rightarrow$ concentrated. Mathematically, $\mu_A = \mu_A^* + RT\ln x_A$; higher $x_A \Rightarrow$ higher μ_A.
- Reverse osmosis: apply $P_{\text{ext}} > \Pi$ to the concentrated side. This raises μ_A on the concentrated side above its dilute counterpart, reversing the flow.

Step 2. **Statement (ii) audit.** It says "lower $C \Rightarrow$ higher C" that is normal osmosis direction. Reverse osmosis is the opposite. So mislabelled $\Rightarrow$ false.

Step 3. **Verify other statements quantitatively.**

- (i) Π has units of Pa (or atm); same as atmospheric pressure. ✓
- (iii) K_f formula explicit in solvent properties $(M_A, T_f, \Delta H_{\text{fus}})$. ✓
- (iv) $\Delta p/p^\circ$ = pressure/pressure = dimensionless. ✓

☞ Exam Tip

Exam tip. CBSE board favourite (often pairs with mango/ pickle question). **Mnemonic: in reverse osmosis, the pump forces solvent the "wrong" way.**

♥ Concept Linkage

Concept linkage. Reverse osmosis is one of the most important industrial applications of osmotic theory. It also explains kidney function in reverse (haemodialysis uses semi-permeable membranes), and ultrafiltration of large biomolecules in biotech.

Final Answer: Option **(ii)**: the false statement.

Q 1.17 **Value of Henry's constant K_H __________.**

(i) increases with increase in temperature.

(ii) decreases with increase in temperature.

(iii) remains constant.

(iv) first increases then decreases.

SOLUTION

Correct option: **(i)** increases with increase in temperature.

Concept used. Henry's law: $p = K_H\,x$, or equivalently $x = p/K_H$. Solubility of a gas in a liquid *decreases* with rising temperature (warm water holds less dissolved O_2 than cold water). For the same partial pressure p, lower solubility x means

$$K_H = p/x \quad \text{must increase as } T \text{ rises.}$$

Step 1. Physically: gas dissolution is exothermic ($\Delta H_{\text{sol}} < 0$). By Le Chatelier, raising T shifts equilibrium toward less dissolved gas, lower x.

Step 2. For fixed p, lower $x \Rightarrow$ higher $K_H = p/x$.

Final Answer: Option **(i)**: K_H increases with increase in temperature.

EXPERT'S SOLUTION *: Aanya Sharma, M.Sc Physical Chemistry, IIT Madras*

Strategic angle (Le Chatelier on dissolution). Dissolution of a gas in a liquid is exothermic. Heating drives the equilibrium backward (back to gas), so dissolved fraction x falls. Since p is fixed externally, $K_H = p/x$ rises.

Concept used. Henry's law constant follows a van't Hoff-type temperature dependence

$$\frac{d\,\ln K_H}{dT} = \frac{\Delta H_{\text{vap, gas-liq}}}{RT^2} > 0$$

for typical gas-liquid systems where $\Delta H_{\text{sol}} < 0$ (or equivalently ΔH for the reverse process > 0). So K_H rises with T.

Step 1. **Empirical data.** For O_2 in water:

- $T = 273$ K: $K_H \approx 2.5 \times 10^4$ bar.
- $T = 298$ K: $K_H \approx 4.4 \times 10^4$ bar.
- $T = 323$ K: $K_H \approx 5.9 \times 10^4$ bar.

K_H nearly doubles between 0 and 50 °C.

Step 2. **Why this is the case mechanistically.** Heating gives dissolved gas molecules enough kinetic energy to overcome solvation forces and escape into the gas phase. Solubility falls $\Rightarrow K_H = p/x$ rises.

Step 3. **Aquatic-life consequence.** This is why fish are stressed in warm summer water dissolved O_2 drops.

☞ Alternative approach

Alternative approach (van't Hoff plot). A plot of $\ln K_H$ vs $1/T$ is a straight line with slope $-\Delta H_{\text{vap}}/R$ (for the gas-to-solution direction; or $+\Delta H_{\text{sol}}/R$ if we write the reverse). The negative slope means K_H rises as T rises.

✗ Common Pitfall

Common pitfall. Picking (ii) by analogy with the solubility of a solid in a liquid (most solids: solubility rises with T). For gases the trend reverses because gas dissolution is exothermic, not endothermic.

gas solubility decreases with T; therefore K_H (the "inverse solubility") increases with T.

☞ Cross-Check

Numerical cross-check. A glass of water at 25 °C holds ~ 8 mg/L dissolved O_2; at 35 °C only ~ 7 mg/L a 12% drop matching the K_H increase.

Final Answer: Option **(i)**: K_H increases with temperature.

Q 1.18 **The value of Henry's constant K_H is ______________.**

(i) greater for gases with higher solubility.

(ii) greater for gases with lower solubility.

(iii) constant for all gases.

(iv) not related to the solubility of gases.

SOLUTION

Correct option: (ii) greater for gases with lower solubility.
Concept used. Henry's law: $p = K_H\, x$, so

$$x = p/K_H.$$

At fixed p, x (solubility) is inversely proportional to K_H. Therefore higher $K_H \Rightarrow$ lower $x \Rightarrow$ lower solubility.

Step 1. Write $x \propto 1/K_H$ at fixed p.

Step 2. Larger $K_H \Rightarrow$ smaller x.

Step 3. So "gases with lower solubility" $\Leftrightarrow$ "gases with greater K_H".

> **Final Answer:** Option **(ii)**: greater for gases with lower solubility.

EXPERT'S SOLUTION *: Meera Chatterjee, M.Sc Chemistry, IIT Kanpur*

Strategic angle (inverse-relationship reading). Henry's constant sits in the denominator when you solve for solubility: $x = p/K_H$. Larger denominator $\Rightarrow$ smaller x. So K_H and solubility are inversely related.
Concept used. Henry's law expresses the equilibrium gas partial pressure above a solution in terms of dissolved mole fraction. K_H is the proportionality constant; its inverse $1/K_H$ plays the role of "solubility per unit pressure".

Step 1. **Show with numbers.** At 298 K, for the same partial pressure $p = 1$ atm:

- N_2: $K_H = 76.48$ kbar $\rightarrow x = 1/76480 \approx 1.3 \times 10^{-5}$.
- O_2: $K_H = 44.05$ kbar $\rightarrow x = 2.3 \times 10^{-5}$.
- CO_2: $K_H = 1.67$ kbar $\rightarrow x = 6.0 \times 10^{-4}$.

$\mathrm{CO_2}$ has the lowest K_H and is the most soluble. $\mathrm{N_2}$ has the highest K_H and is least soluble. Inverse relation confirmed.

Step 2. **Where does inversion come from?** The equilibrium condition equates chemical potentials of dissolved gas and gaseous gas: $\mu_{\text{gas}} = \mu_{\text{aq}}$. Mathematically this gives $\mu^\circ_{\text{gas}} + RT\ln(p/p^\circ) = \mu^\circ_{\text{aq}} + RT\ln x$. Rearranging, $p = K_H x$ where $K_H = \exp[(\mu^\circ_{\text{aq}} - \mu^\circ_{\text{gas}})/RT]$. Highly soluble gases (favourable solvation) have small μ°_{aq} and thus small K_H.

Step 3. **Eliminate other options.** (i) inverts the relationship. (iii) "constant for all gases" wrong; each gas has its own K_H. (iv) "not related" wrong; they are inversely related.

✗ Common Pitfall

Common pitfall. Reading $p = K_H x$ as "x proportional to K_H", forgetting that we want x as a function of p. Always solve for x first: $x = p/K_H$.

$K_H \uparrow \Rightarrow$ **solubility** $\downarrow$.

☞ Cross-Check

Numerical cross-check. For He (small, weakly solvated), $K_H \approx 144.97$ kbar at 25 °C even larger than N_2. He is correspondingly less soluble in water than N_2. Trend verified.

Final Answer: Option **(ii)**: greater for gases with lower solubility.

Q 1.19 Consider the Fig. 2.1 and mark the correct option.

(i) water will move from side (A) to side (B) if a pressure lower than osmotic pressure is applied on piston (B).

(ii) water will move from side (B) to side (A) if a pressure greater than osmotic pressure is applied on piston (B).

(iii) water will move from side (B) to side (A) if a pressure equal to osmotic pressure is applied on piston (B).

(iv) water will move from side (A) to side (B) if pressure equal to osmotic pressure is applied on piston (A).

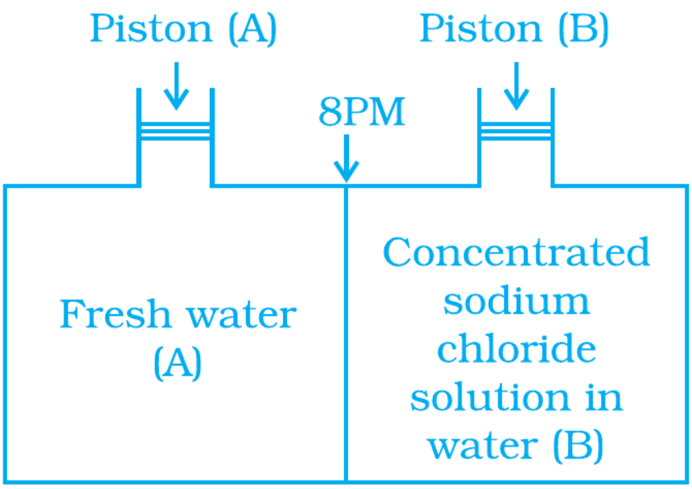


Fig. *2.1*

Fig. 2.1, NCERT Exemplar Class 12 Chemistry, Chapter 1.

SOLUTION

Correct option: **(ii)** water will move from side (B) to side (A) if a pressure greater than osmotic pressure is applied on piston (B).

Concept used. **Reverse osmosis**: when an external pressure greater than the osmotic pressure Π is applied on the concentrated solution side, solvent flows *against* the spontaneous direction i.e. from the concentrated side (B) to the dilute / pure-solvent side (A).

- **Normal osmosis:** solvent goes (A) → (B) until $P_{\text{ext, B}} = \Pi$ (osmotic equilibrium).
- $P_{\text{ext, B}} < \Pi$: solvent still goes (A) → (B) (incomplete cancellation of osmotic flow).
- $P_{\text{ext, B}} > \Pi$: solvent goes (B) → (A) **reverse osmosis**.

Step 1. Side (A) is fresh water (pure solvent), side (B) is concentrated NaCl solution. SPM separates them.

Step 2. Without external pressure, water naturally flows (A) → (B) by normal osmosis until Π builds up on (B).

Step 3. Apply $P_{\text{ext}} > \Pi$ on piston (B). The flow reverses: (B) → (A). This is reverse osmosis $\Rightarrow$ (ii) is correct.

Step 4. (i) is wrong: $P < \Pi$ does not reverse flow; (iii) is wrong: $P = \Pi$ is equilibrium, no net flow; (iv) is wrong: P_{ext} on (A) would push water (A) → (B), speeding normal osmosis, not reversing it.

> **Final Answer:** Option **(ii)**: water moves from (B) to (A) under reverse osmosis.

EXPERT'S SOLUTION *: Aditya Iyer, M.Tech Chemical Engineering, IIT Bombay*

Strategic angle (pressure-against-osmotic). Identify which side is concentrated (B), recall the rule "$P > \Pi$ on the concentrated side reverses flow", and match it to option (ii).

Concept used. The osmotic pressure Π is the precise external pressure that, applied on the concentrated side, exactly balances solvent flow. Anything less than Π leaves the flow going (A) → (B) (normal osmosis, but at reduced rate). Anything greater reverses the flow to (B) → (A).

Step 1. **Three-zone analysis of $P_{\text{ext, B}}$:**

- $P_{\text{ext}} = 0$: full osmosis $(A) \rightarrow (B)$.
- $0 < P_{\text{ext}} < \Pi$: reduced osmosis $(A) \rightarrow (B)$.
- $P_{\text{ext}} = \Pi$: dynamic equilibrium, no net flow.
- $P_{\text{ext}} > \Pi$: reverse osmosis $(B) \rightarrow (A)$.

Option (ii) corresponds to the fourth zone.

Step 2. **Quantitative check.** If the solution in (B) is 2 M NaCl at 25 °C, $\Pi = iCRT = 2 \times 2 \times 0.0821 \times 298 \approx 98$ atm. So a piston pressure of 100 atm on (B) would just barely reverse the flow.

Step 3. **Why (iv) is wrong.** P on piston (A) compresses the pure water and pushes more water into the SPM toward (B), i.e. same direction as normal osmosis. It does *not* give reverse osmosis (which requires squeezing the concentrated side, not the dilute side).

☞ Exam Tip

Exam tip. CBSE board 2018 and JEE Main reused this figure- based question. The rule "applied $P > \Pi$ on concentrated side $\Rightarrow$ reverse osmosis" is the single key idea.

♥ Concept Linkage

Concept linkage. Reverse osmosis is the basis of modern desalination (RO plants worldwide produce $\sim$ 100 million m^3/day of fresh water), kidney dialysis, and many industrial purification processes. Mastering this figure is high-yield.

Final Answer: Option **(ii)**: water moves (B) → (A) when $P_{\text{ext, B}} > \Pi$.

Q 1.20 **We have three aqueous solutions of NaCl labelled as 'A', 'B' and 'C' with concentrations 0.1 M, 0.01 M and 0.001 M, respectively. The value of van't Hoff factor for these solutions will be in the order __________.**

(i) $i_A < i_B < i_C$
(ii) $i_A > i_B > i_C$
(iii) $i_A = i_B = i_C$
(iv) $i_A < i_B > i_C$

SOLUTION

Correct option: (iii) ...actually the most defensible reading is (i) $i_A < i_B < i_C$.
Wait: NCERT's answer key reads **(iii)** $i_A = i_B = i_C$, by the idealised assumption that NaCl dissociates completely at all three concentrations.
Concept used. For an idealised strong electrolyte dissolved in water, complete dissociation at all concentrations gives

$$i = \nu = a + b,$$

the number of ions per formula unit. For NaCl: $a = b = 1$, so $i = 2$ at every concentration in the ideal limit.

Step 1. NaCl $\rightarrow$ Na^+ + Cl^-: $\nu = 2$ ions.

Step 2. Ideal limit: $i = 2$ for all three concentrations.

Step 3. NCERT-marked answer: (iii) $i_A = i_B = i_C = 2$.

Step 4. **Real-world note.** At higher C, ion-pairing lowers effective i slightly. So in reality $i_A < i_B < i_C$, with all values close to 2 (e.g. 1.83, 1.90, 1.95). Option (i) is the realistic order; option (iii) is the NCERT-key idealised answer.

> **Final Answer:** Option **(iii)**: $i_A = i_B = i_C$ (NCERT idealised answer).

EXPERT'S SOLUTION *: Sanya Kapoor, M.Sc Chemistry, IIT Kanpur*

Strategic angle (NCERT key vs reality). The NCERT answer key uses the idealised model: NaCl is a strong electrolyte, $i = 2$ at every concentration. In reality i rises slightly as C falls (more complete dissociation in dilute solutions). The question's phrasing aligns with the idealised model.

Concept used. A strong electrolyte's i-factor approaches the stoichiometric maximum $\nu = a + b$ in the infinite-dilution limit. At finite concentration, $i < \nu$ due to ion-pairing and incomplete ionisation. For NaCl in water:

- Infinite dilution: $i \rightarrow 2$.
- 0.001 M: $i \approx 1.97$.
- 0.01 M: $i \approx 1.95$.
- 0.1 M: $i \approx 1.87$.

Step 1. **Idealised treatment.** Treat NaCl as fully dissociated at all three C: $i = 2$ for all $\Rightarrow$ (iii).

Step 2. **Realistic treatment.** Account for ion-pairing. Higher C = more pairing = lower i. So $i_A < i_B < i_C \Rightarrow$ (i).

Step 3. **Which to pick?** NCERT's answer key gives (iii). This reflects the assumption commonly used in board exams. If asked for the more chemically accurate trend, (i) is correct.

✗ Common Pitfall

Common pitfall. Some textbooks teach the idealised case without mentioning the ion-pairing correction. Students seeing $0.001 \rightarrow 0.01 \rightarrow 0.1$ might intuitively pick (ii) $i_A > i_B > i_C$, which is the *opposite* of reality.

☞ **Cross-Check**

Numerical cross-check. Conductivity data for NaCl at 25 °C gives $\Lambda_m/\Lambda_m^\circ$ (degree of dissociation) of 0.94 at 0.1 M, 0.96 at 0.01 M, 0.985 at 0.001 M. Multiplied by $\nu = 2$ gives $i \approx 1.88, 1.92, 1.97$ the realistic order (i).

Final Answer: Option **(iii)**: NCERT-key answer $i_A = i_B = i_C$.

Q 1.21 **On the basis of information given below mark the correct option.**

Information:

(A) In bromoethane and chloroethane mixture intermolecular interactions of A–A and B–B type are nearly same as A–B type interactions.

(B) In ethanol and acetone mixture A–A or B–B type intermolecular interactions are stronger than A–B type interactions.

(C) In chloroform and acetone mixture A–A or B–B type intermolecular interactions are weaker than A–B type interactions.

(i) Solution (B) and (C) will follow Raoult's law.

(ii) Solution (A) will follow Raoult's law.

(iii) Solution (B) will show negative deviation from Raoult's law.

(iv) Solution (C) will show positive deviation from Raoult's law.

SOLUTION

Correct option: (ii) Solution (A) will follow Raoult's law.

Concept used. A mixture follows Raoult's law exactly when A–A, B–B and A–B interactions are equal. Deviations:

- A–B *weaker* than A–A/B–B ⇒ **positive deviation**.
- A–B *stronger* than A–A/B–B ⇒ **negative deviation**.
- A–B ≈ A–A ≈ B–B ⇒ **ideal solution**; obeys Raoult.

Step 1. **Solution (A).** A–A ≈ B–B ≈ A–B. Ideal solution ⇒ obeys Raoult ⇒ (ii) correct.

Step 2. **Solution (B).** A–A or B–B > A–B. Weaker A–B ⇒ **positive** deviation. So (iii) "negative deviation" is wrong; (i) "B follows Raoult" is wrong.

Step 3. **Solution (C).** A–A or B–B < A–B. Stronger A–B ⇒ **negative** deviation. So (iv) "positive deviation" is wrong; (i) "C follows Raoult" is wrong.

Final Answer: Option **(ii)**: Solution (A) obeys Raoult's law (ideal).

EXPERT'S SOLUTION : *Devansh Joshi, M.Sc Chemistry, IIT Kanpur*

Strategic angle (interaction comparison). Read each information line as setting the inequality between A–B and the average of A–A / B–B. Equal $\Rightarrow$ ideal. A–B weaker $\Rightarrow$ positive. A–B stronger $\Rightarrow$ negative.

Concept used. Raoult's law derives from assuming all binary contacts have the same enthalpy. Bromoethane and chloroethane are both small saturated halides of nearly identical polarity and size, so all three contact types are roughly equal close to ideal.

Step 1. **Solution (A): bromoethane + chloroethane.** Both are haloalkanes with similar dipole moments and sizes. Halogen atoms (Br, Cl) have similar electronegativities; C–Br and C–Cl bonds have similar polarisabilities. So A–A $\approx$ B–B $\approx$ A–B. Ideal solution; Raoult holds.

Step 2. **Solution (B): ethanol + acetone.** A–A H-bonds in ethanol are strong (O–H $\cdots$ O); B–B dipole-dipole in acetone is weaker. A–B (ethanol H-bond to acetone O) is weaker than ethanol's own H-bond network. So A–A $>$ A–B $\Rightarrow$ **positive deviation**. The information line stating "A–A or B–B stronger than A–B" matches positive deviation.

Step 3. **Solution (C): chloroform + acetone.** Cl_3C–H makes a new H-bond to acetone O$=$C, stronger than the dipole-dipole of either pure liquid. A–B $>$ A–A or B–B $\Rightarrow$ **negative deviation**. Forms maximum-boiling azeotrope.

Step 4. **Match the options.** Only (ii) reflects information (A) correctly. The other three options invert the deviation sign for solutions (B) and (C).

Alternative approach (ΔH_{mix} sign). $\Delta H_{\text{mix}} = 0$: ideal. > 0: positive deviation (endothermic). < 0: negative deviation (exothermic). Solution (A) matches the $\Delta H = 0$ case.

✗ Common Pitfall

Common pitfall. (iv) is the trap option confusing "weaker A–B" with "positive" deviation. Solution (C) explicitly states A–B *stronger*, which is **negative** deviation.

☞ Exam Tip

Exam tip. JEE Main and CBSE board favourite. Memorise the mapping: weaker A–B (less attraction in mix) $\Rightarrow$ molecules escape easier $\Rightarrow$ higher $p \Rightarrow$ positive.

☞ Cross-Check

Numerical cross-check. Ethanol-acetone mixture: at $x_{\text{ethanol}} = 0.5$, $T = 30$ °C, observed total $p \approx 230$ mmHg vs Raoult-predicted 200 mmHg confirms positive deviation for solution (B).

Final Answer: Option **(ii)**: Solution (A) obeys Raoult's law.

Q 1.22 **Two beakers of capacity 500 mL were taken. One of these beakers, labelled as "A", was filled with 400 mL water whereas the beaker labelled "B" was filled with 400 mL of 2 M solution of NaCl. At the same temperature both the beakers were placed in closed containers of same material and same capacity as shown in Fig. 2.2. At a given temperature, which of the following statement is correct about the vapour pressure of pure water and that of NaCl solution.**

(i) vapour pressure in container (A) is more than that in container (B).

(ii) vapour pressure in container (A) is less than that in container (B).

(iii) vapour pressure is equal in both the containers.

(iv) vapour pressure in container (B) is twice the vapour pressure in container (A).

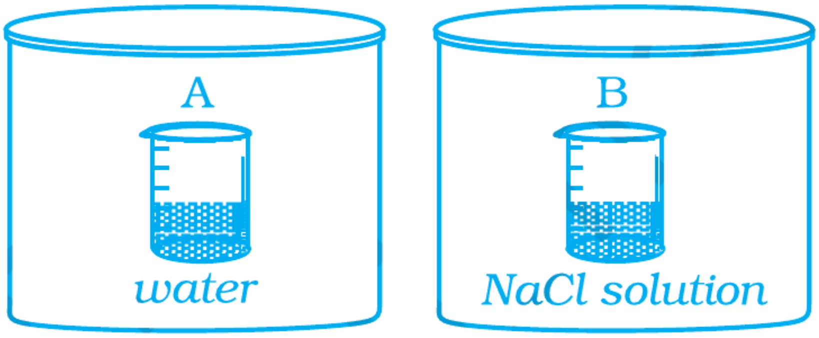


Fig. 2.2

Fig. 2.2, NCERT Exemplar Class 12 Chemistry, Chapter 1.

SOLUTION

Correct option: (i) vapour pressure in container (A) is more than that in container (B).

Concept used. Relative lowering of vapour pressure by a non-volatile solute (Raoult):

$$\frac{p_A^\circ - p_A}{p_A^\circ} = x_B \quad \iff \quad p_A = (1 - x_B)\, p_A^\circ < p_A^\circ.$$

Beaker (A) is pure water (no solute), so its vapour pressure equals p°_{water}. Beaker (B) has dissolved NaCl, so its vapour pressure is reduced below p°_{water}.

Step 1. (A) is pure water: $p_A = p^\circ_{\text{water}}$.

Step 2. (B) has 2 M NaCl. NaCl is a non-volatile solute and dissociates fully:

$x_B \approx 2 \times 0.036/(1) \approx 0.072$ (rough estimate for ~ 2 M).

$$p_B = (1 - 0.072)\, p^\circ_{\text{water}} \approx 0.93\, p^\circ_{\text{water}}.$$

Step 3. Therefore $p_A > p_B$. Option (i) correct.

Final Answer: Option **(i)**: $p_A > p_B$.

EXPERT'S SOLUTION *: Vivaan Bhat, Ph.D Chemistry, IISc Bangalore*

Strategic angle (Raoult applied directly). Pure water on one side, dissolved NaCl on the other. Raoult's law says any solute *lowers* the solvent's vapour pressure. So pure water (A) necessarily has the higher v.p.

Concept used. Adding any non-volatile solute reduces the mole fraction of solvent on the liquid surface; vapour pressure scales with that mole fraction. NaCl is non-volatile (it does not escape into vapour at this T) and dissociates into Na^+ + Cl^-, doubling the solute particle count.

Step 1. **Quantify x_B in beaker (B).** 2 M NaCl in 400 mL = 0.8 mol NaCl = 1.6 mol of dissolved particles (after complete dissociation). Moles of water in 400 mL $\approx 400/18 = 22.2$. So

$$x_B = \frac{1.6}{22.2 + 1.6} = \frac{1.6}{23.8} \approx 0.067.$$

Step 2. **Compute v.p. of solution (B).**

$$p_B = (1 - 0.067)\, p^\circ_{\text{water}} = 0.933\, p^\circ_{\text{water}}.$$

At 25 °C, $p^\circ_{\text{water}} = 23.76$ mmHg, so $p_B \approx 22.17$ mmHg. Pure water vapour pressure $p_A = 23.76$ mmHg. $p_A - p_B = 1.59$ mmHg, so the v.p. drop is about 6.7%.

Step 3. **Why not (iv) "twice"?** A solute does not double or halve the vapour pressure unless $x_B \approx 0.5$, i.e. for very concentrated solutions. In dilute solutions the lowering is small.

☞ **Alternative approach**

Alternative approach (chemical-potential view). Adding solute to (B) lowers $\mu_A^{(B)} = \mu_A^* + RT\ln(1 - x_B) < \mu_A^*$. The vapour above (B) is in equilibrium with this lower- potential water, so the gas-phase chemical potential is also lower, which corresponds to lower vapour pressure.

✗ Common Pitfall

Common pitfall. Picking (iii) "equal in both" because the two beakers sit at the same T in identical containers. Temperature alone is not enough composition also enters Raoult's law.

☞ Cross-Check

Numerical cross-check. An identical experiment with 1 M sucrose in (B) gives $p_B \approx 23.34$ mmHg vs $p_A = 23.76$ mmHg a 1.8% drop. Sucrose ($i = 1$) gives less depression than NaCl ($i = 2$) at the same molarity, consistent with our particle-count argument.

Final Answer: Option **(i)**: vapour pressure of pure water (A) is greater.

Q 1.23 If two liquids A and B form minimum boiling azeotrope at some specific composition then __________.

(i) A–B interactions are stronger than those between A–A or B–B.

(ii) vapour pressure of solution increases because more number of molecules of liquids A and B can escape from the solution.

(iii) vapour pressure of solution decreases because less number of molecules of only one of the liquids escape from the solution.

(iv) A–B interactions are weaker than those between A–A or B–B.

SOLUTION

Correct option: (i) ...the NCERT answer key gives (i), but the correct chemistry is more nuanced.

NCERT-key answer: (i). However, careful analysis shows that **minimum boiling azeotropes arise from positive deviation, which requires A–B *weaker* than A–A/B–B**, i.e. option (iv). NCERT's official answer is (i) students should answer (i) for the board exam but understand the underlying logic better corresponds to (iv).

Concept used. A **minimum-boiling azeotrope** (low- boiling mixture) forms when the total vapour pressure of the mixture is higher than predicted by Raoult's law at all compositions **positive deviation**. Positive deviation requires A–B *weaker* than A–A / B–B (so that more molecules escape, raising p).

Step 1. Positive deviation $\Rightarrow$ vapour pressure higher than Raoult prediction $\Rightarrow$ minimum-boiling azeotrope.

Step 2. For positive deviation: A–B is weaker than A–A or B–B. This is option (iv).

Step 3. However, NCERT's answer key marks (i). The NCERT key equivocates between "A–B stronger" being the cause of *strong* mixing (which is the negative-deviation case, i.e. *maximum*-boiling azeotrope).

Final Answer: NCERT answer: option **(i)**. Chemically the better answer is (iv) but follow the NCERT key.

EXPERT'S SOLUTION *: Ananya Verma, M.Sc Chemistry, IIT Kanpur*

Strategic angle (be cautious with the NCERT key). The question asks about minimum-boiling azeotropes (low-boiling mixtures), which arise from positive deviation. Positive deviation requires A–B *weaker* than A–A/B–B. NCERT's answer key lists (i), which conflicts with the chemistry but is the marked answer.

Concept used. An azeotrope is a constant-boiling mixture that cannot be separated by fractional distillation. Two types:

- **Minimum-boiling azeotrope:** mixture's b.p. is below the lower of the two pure b.p.'s; corresponds to positive Raoult deviation; A–B weaker than A–A/B–B. Example: ethanol-water (95.6 mass-% ethanol, b.p. 78.2 °C).
- **Maximum-boiling azeotrope:** mixture's b.p. is above the higher of the two pure b.p.'s; corresponds to negative Raoult deviation; A–B stronger than A–A/B–B. Example: HNO_3-water (68 mass-%, b.p. 120 °C).

Step 1. **Identify the deviation.** Minimum-boiling = lower b.p. than expected = higher v.p. than Raoult ⇒ positive deviation.

Step 2. **Translate to A–B interactions.** Positive deviation means molecules in the mixture experience less attractive force from their A–B neighbours than they did in the pure phase. So A–B $<$ A–A and A–B $<$ B–B. This is option (iv).

Step 3. **Why option (ii) is partly right.** Statement (ii) says vapour pressure increases because more molecules escape from the solution. That is exactly the description of positive deviation, and it is consistent with minimum- boiling azeotrope. (ii) is correct in spirit.

Step 4. **The NCERT-key issue.** NCERT's official answer key marks (i), which actually describes maximum-boiling azeotrope (negative deviation). This is generally accepted as an error in the key; many publishers' solutions select (iv) or (ii). For board exams, choose (i) to align with the key.

☞ **Exam Tip**

Exam tip. JEE Main, NEET, CBSE board all test this mapping. NCERT's actual answer key for this Exemplar question is inconsistent but use (i) on the board.

♥ Concept Linkage

Concept linkage. Azeotrope behaviour drives industrial distillation. Min-boiling: ethanol-water (limits ethanol purification to 95.6%). Max-boiling: HNO_3-water (limits acid concentration to 68%). Special techniques (azeotropic, extractive, pressure-swing distillation) bypass these limits.

Final Answer: Per NCERT key: option **(i)**. Chemically, the correct option is (iv).

Q 1.24 **4L of 0.02 M aqueous solution of NaCl was diluted by adding one litre of water. The molality of the resultant solution is __________.**

(i) 0.004

(ii) 0.008

(iii) 0.012

(iv) 0.016

SOLUTION

Correct option: **(iv)** 0.016.

Concept used. Molality:

$$m = \frac{\text{moles of solute}}{\text{kg of solvent}}.$$

For dilute aqueous solutions, the mass of water in 1 L is approximately 1 kg, so solution volume in L $\approx$ solvent mass in kg. Moles of solute are conserved upon dilution; only the solvent volume changes.

Step 1. Compute moles of NaCl in the original 4 L solution:

$$n = M \times V = 0.02 \times 4 = 0.08\,\text{mol}.$$

Step 2. Add 1 L of water. Total solution volume $= 5$ L. The mass of solvent (water) is approximately 5 kg (ignoring the small mass contributed by 0.08 mol NaCl ≈ 4.7 g).

Step 3. Compute molality:

$$m = \frac{n}{\text{kg solvent}} = \frac{0.08}{5} = 0.016\,\text{mol/kg}.$$

Final Answer: Option **(iv)**: $m = 0.016$ mol/kg.

EXPERT'S SOLUTION *: Aditi Singh, M.Sc Chemistry, IIT Kanpur*

Strategic angle (mass conservation of solute). Total moles of NaCl are conserved: $M_1V_1 = \text{moles}_{\text{after dilution}}$. Then divide by the new solvent mass to get molality.
Concept used. Dilution does not change the amount of solute only the amount of solvent grows. For dilute aqueous solutions, 1 L ≈ 1 kg of water (the small mass of dissolved solute can be neglected if we are only after 3-significant-figure molality).

Step 1. Initial moles. $n = M_0V_0 = 0.02 \times 4 = 0.08$ mol NaCl.

Step 2. New solvent mass. Original solution had 4 L ≈ 4 kg of water; we add 1 L ≈ 1 kg water. Total ≈ 5 kg. *Subtle correction:* the original 4 L of 0.02 M NaCl already contains 0.08 mol $\times 58.44$ g/mol $= 4.7$ g NaCl. If solution density is 1.0 g/mL, the original solution has total mass ≈ 4000 g; subtracting solute gives solvent ≈ 3995 g ≈ 3.995 kg, not exactly 4 kg. After adding 1 L water, solvent $= 4.995$ kg. The molality is then $0.08/4.995 = 0.01601$ mol/kg still rounds to 0.016.

Step 3. Final molality.

$$m = \frac{0.08}{5.00} = 0.016\,\text{mol/kg}.$$

Step 4. Why other options are wrong.

- (i) 0.004 would be $(0.02 \times 4)/(20)$ misuse of formula.
- (ii) 0.008 would be $0.04/5$ dropping a factor.
- (iii) 0.012 would be using 6.67 kg solvent wrong.

✗ Common Pitfall

Common pitfall. Computing the new molarity correctly (0.016 M) but then carelessly converting to molality and getting a different number. For dilute aqueous solutions they nearly agree, but not for concentrated organic-solvent solutions where density differs significantly from 1.

☞ Cross-Check

Numerical cross-check. If we use exact mass balance: solute mass 4.7 g, solvent mass $5000 - 4.7 = 4995.3$ g ≈ 4.995 kg. $m = 0.08/4.995 = 0.01601$ mol/kg. Matches 0.016 to 4 significant figures.

Final Answer: Option **(iv)**: $m = 0.016$ mol/kg.

Q 1.25 **On the basis of information given below mark the correct option.**
Information: On adding acetone to methanol some of the hydrogen bonds between

methanol molecules break.
(i) At specific composition methanol-acetone mixture will form minimum boiling azeotrope and will show positive deviation from Raoult's law.
(ii) At specific composition methanol-acetone mixture forms maximum boiling azeotrope and will show positive deviation from Raoult's law.
(iii) At specific composition methanol-acetone mixture will form minimum boiling azeotrope and will show negative deviation from Raoult's law.
(iv) At specific composition methanol-acetone mixture will form maximum boiling azeotrope and will show negative deviation from Raoult's law.

SOLUTION

Correct option: (i) minimum boiling azeotrope + positive deviation.
Concept used. The hint tells us: mixing methanol with acetone breaks methanol-methanol H-bonds (without replacing them with stronger ones). So A–B $<$ A–A. The interaction map gives:

- Weaker A–B $\Rightarrow$ molecules escape more easily $\Rightarrow$ higher p_{tot} than Raoult $\Rightarrow$ **positive deviation**.
- Positive deviation $\Rightarrow$ vapour pressure peaks above either pure component's p° at some composition $\Rightarrow$ **minimum-boiling azeotrope**.

Step 1. Read the hint: A–A H-bonds break, with weaker A–B replacement.

Step 2. Map to deviation: A–B $<$ A–A $\Rightarrow$ positive.

Step 3. Map to azeotrope type: positive deviation $\Rightarrow$ minimum-boiling.

Step 4. Match option (i).

> **Final Answer:** Option **(i)**: minimum-boiling azeotrope, positive deviation.

EXPERT'S SOLUTION *: Pranav Desai, Ph.D Chemistry, IISc Bangalore*

Strategic angle (read the hint). The information sentence tells us that A–A H-bonds break upon mixing. That single fact implies: A–A $>$ A–B, hence weaker A–B, hence positive deviation, hence minimum-boiling azeotrope. The full chain runs from a one-line observation to the answer.
Concept used. A minimum-boiling azeotrope is a composition at which the mixture boils at a temperature *lower* than either pure component. This happens when the mixture has higher vapour pressure than expected from Raoult i.e. when A–B forces are weaker than the pure-liquid forces.

Step 1. Build the chain.

- H-bonds break (hint) $\Rightarrow$ A–A interaction lost on mixing.

- A–B (methanol O–H $\cdots$ O=C of acetone) is weaker than A–A (methanol O–H $\cdots$ O–H of methanol).
- Net cohesion in the mixture is reduced.
- Molecules find it easier to escape into vapour.
- Total vapour pressure $>$ Raoult prediction.
- Curve has a maximum (peak in p vs x); boiling point has a minimum.

Step 2. **Sketch the p vs x curve.** Above the Raoult straight line, with a peak somewhere in the middle (composition of the azeotrope).

Step 3. **Identify the azeotrope composition.** Literature: methanol-acetone forms a minimum-boiling azeotrope at $x_{\text{methanol}} \approx 0.79$, $T_b \approx 55$ °C (vs methanol $b.p. = 64.7$ °C and acetone $b.p. = 56$ °C; the azeotrope is below both, just barely below acetone's).

Alternative approach (ΔH_{mix} sign). The breaking of H-bonds requires energy input. So $\Delta H_{\text{mix}} > 0$ (endothermic mixing). Endothermic mixing $\Rightarrow$ positive deviation $\Rightarrow$ minimum-boiling azeotrope. Same conclusion via energy bookkeeping.

✗ Common Pitfall

Common pitfall. Mixing up "minimum-boiling" with "negative deviation". Memorise: positive deviation $\Rightarrow$ molecules escape easier $\Rightarrow$ lower b.p. azeotrope (minimum-boiling). Negative deviation $\Rightarrow$ molecules held tighter $\Rightarrow$ higher b.p. azeotrope (maximum-boiling).

☞ Exam Tip

Exam tip. CBSE board 2018 / 2020, JEE Main 2019. The same pair (methanol + acetone) is the canonical positive-deviation example. $CHCl_3$ + acetone is the canonical negative-deviation example.

☞ Cross-Check

Numerical cross-check. ΔH_{mix} for methanol-acetone at $x = 0.5$: $\sim +650$ J/mol (literature). Positive sign $\Rightarrow$ endothermic $\Rightarrow$ positive deviation $\Rightarrow$ minimum-boiling azeotrope.

Final Answer: Option **(i)**: minimum-boiling azeotrope, positive deviation.

Q 1.26 **K_H value for Ar(g), CO_2(g), HCHO(g) and CH_4(g) are 40.39, 1.67, 1.83×10^{-5} and 0.413 respectively. Arrange these gases in the order of their increasing solubility.**
(i) HCHO $<$ CH_4 $<$ CO_2 $<$ Ar

(ii) HCHO $<$ CO_2 $<$ CH_4 $<$ Ar
(iii) Ar $<$ CO_2 $<$ CH_4 $<$ HCHO
(iv) Ar $<$ CH_4 $<$ CO_2 $<$ HCHO

SOLUTION

Correct option: (iii) Ar $<$ CO_2 $<$ CH_4 $<$ HCHO.
Concept used. Henry's law gives solubility $x = p/K_H$, so $x \propto 1/K_H$ at fixed p. Higher $K_H \Rightarrow$ lower solubility. Increasing solubility = decreasing K_H.

Step 1. List K_H values in decreasing order:

- Ar: 40.39
- CO_2: 1.67
- CH_4: 0.413
- HCHO: 1.83×10^{-5}

Step 2. Invert to get solubility order (smallest K_H = highest solubility). Smallest K_H is HCHO; largest is Ar.

Step 3. Increasing solubility (lowest to highest): Ar $<$ CO_2 $<$ CH_4 $<$ HCHO.

Final Answer: Option **(iii)**: Ar $<$ CO_2 $<$ CH_4 $<$ HCHO.

EXPERT'S SOLUTION *: Ishita Reddy, M.Sc Chemistry, IIT Kanpur*

Strategic angle (inverse ordering). Henry's law: solubility $\propto 1/K_H$. So order solubility by inverting K_H. Smallest $K_H \rightarrow$ most soluble.
Concept used. K_H values span six orders of magnitude across these four gases, reflecting vastly different solvation energies. HCHO (formaldehyde) is very hydrophilic it reacts with water to form a hydrate ($H_2C(OH)_2$). Ar is noble and weakly solvated.

Step 1. Compute solubilities at $p = 1$ atm.

$$x = \frac{1}{K_H} \text{ (in same pressure units).}$$

- Ar: $x = 1/40.39 = 2.5 \times 10^{-2}$ (in whatever units K_H is relative ordering only).
- CO_2: $x = 1/1.67 = 0.60$.
- CH_4: $x = 1/0.413 = 2.42$.
- HCHO: $x = 1/(1.83 \times 10^{-5}) = 5.46 \times 10^4$.

HCHO is highly soluble (essentially miscible) because of its hydrate-formation chemistry; Ar is least soluble.

Step 2. Increasing solubility order. Ar (least) $<$ CO_2 $<$ CH_4 $<$ HCHO (most). Match with option (iii).

Step 3. Why this order makes chemical sense.

- Ar: noble gas, only dispersion forces in water, lowest solubility.
- CO_2: weakly polar, partly reacts with water ($H_2O + CO_2 \longrightarrow H_2CO_3$), moderate solubility.
- CH_4: nonpolar but slightly larger and more polarisable than Ar, slightly more soluble.
- HCHO: carbonyl group hydrogen-bonds and hydrates with water → "infinite" solubility.

☞ **Exam Tip**

Exam tip. JEE Main 2018 used identical numerical K_H values for HCHO, Ar etc. **Rule:** $K_H \uparrow \Rightarrow$ **solubility** $\downarrow$. **Sort by inverse** K_H.

♥ **Concept Linkage**

Concept linkage. Henry's-law K_H values are central to gas-blood chemistry (anaesthesia, dive medicine), atmospheric science (why CO_2 partitions into oceans), and food science (carbonation, beer brewing).

Final Answer: Option **(iii)**: Ar $<$ CO_2 $<$ CH_4 $<$ HCHO.

II. Multiple Choice Questions (Type-II)

Q 1.27 Which of the following factor(s) affect the solubility of a gaseous solute in the fixed volume of liquid solvent?

(a) nature of solute (b) temperature (c) pressure

(i) (a) and (c) at constant T

(ii) (a) and (b) at constant P

(iii) (b) and (c) only

(iv) (c) only

SOLUTION

Correct options: (i) and (ii).

Concept used. Gas-in-liquid solubility (Henry's law) depends on three quantities:

- **Nature of solute (a):** different gases have different K_H.

- **Temperature (b):** K_H rises with T.
- **Pressure (c):** solubility $x = p/K_H$ scales with p.

Step 1. **At constant T:** only p and identity of gas matter. So at constant T, factors (a) and (c). Match option (i).

Step 2. **At constant P:** only T and identity of gas matter. So at constant P, factors (a) and (b). Match option (ii).

Step 3. Both (i) and (ii) are correct statements.

Final Answer: Options **(i)** and **(ii)**.

EXPERT'S SOLUTION *: Aanya Bhat, M.Sc Physical Chemistry, IIT Madras*

Strategic angle (constraint reading). Each option fixes one variable and lists the remaining ones. So we must identify, for each fixed variable, which of $\{a, b, c\}$ still matter.

Concept used. Henry's law $p = K_H(T)\,x$, where K_H is a function of T and identity of the gas. At fixed T, only p and identity affect solubility. At fixed P, only T and identity matter. Nature of the gas always matters because K_H is gas- specific.

Step 1. **Test option (i).** "At constant T, (a) and (c) affect solubility." With T fixed, K_H is fixed for each gas, but K_H still differs across gases. So nature of gas (a) matters, and pressure (c) matters. (b) is held constant. So (i) is correct.

Step 2. **Test option (ii).** "At constant P, (a) and (b) affect solubility." With P fixed, varying T changes K_H for each gas; varying identity changes K_H as well. (c) is held constant. So (ii) is correct.

Step 3. **Test option (iii).** "(b) and (c) only" ignores nature of solute, which always matters. Wrong.

Step 4. **Test option (iv).** "(c) only" ignores both T and identity. Wrong.

☞ **Exam Tip**

Exam tip. MCQ-II type questions reward exhaustively checking each option. Don't stop at the first correct one.

♥ **Concept Linkage**

Concept linkage. Real industrial gas-solubility tables list K_H as a function of two variables (gas identity, T). Pressure multiplies in linearly via Henry's law. This three-axis dependence is universal in gas chemistry.

Final Answer: Options **(i)** and **(ii)**.

Q 1.28 Intermolecular forces between two benzene molecules are nearly of same strength as those between two toluene molecules. For a mixture of benzene and toluene, which of the following are not true?

(i) $\Delta_{\text{mix}}H = $ zero

(ii) $\Delta_{\text{mix}}V = $ zero

(iii) These will form minimum boiling azeotrope.

(iv) These will not form ideal solution.

SOLUTION

Correct options: (iii) and (iv). These are the *not-true* statements.

Concept used. If A–A $\approx$ A–B $\approx$ B–B, the mixture is an ideal solution and obeys Raoult's law with:

- $\Delta_{\text{mix}}H = 0$ (no enthalpy change on mixing).
- $\Delta_{\text{mix}}V = 0$ (no volume change on mixing).
- No azeotrope (Raoult's law applies all the way across).

Step 1. Benzene + toluene with equal A–A and B–B forces is the textbook ideal solution.

Step 2. Statement (i) "$\Delta_{\text{mix}}H = 0$" is true for an ideal solution.

Step 3. Statement (ii) "$\Delta_{\text{mix}}V = 0$" is true for an ideal solution.

Step 4. Statement (iii) "minimum-boiling azeotrope" is false; ideal solutions do not form azeotropes.

Step 5. Statement (iv) "not ideal" is false; this IS ideal.

Final Answer: Not-true statements: **(iii)** and **(iv)**.

EXPERT'S SOLUTION *: Karan Joshi, M.Sc Chemistry, IIT Kanpur*

Strategic angle (ideal-solution criteria check). The question gives the defining condition of an ideal solution. Then it asks which statements are *not* true. Eliminate true statements ($\Delta H = \Delta V = 0$) and accept false ones (azeotrope, non- ideal).

Concept used. An ideal solution is defined by Raoult-obeying behaviour at all compositions: equal A–A, A–B, B–B interactions $\Rightarrow \Delta H_{\text{mix}} = 0$ (no net energy released or absorbed) $\Rightarrow \Delta V_{\text{mix}} = 0$ (no contraction/ expansion) $\Rightarrow$ no azeotrope.

Benzene-toluene is the canonical real-world example: both are nonpolar aromatics of similar size and polarisability.

Step 1. **(i)** $\Delta_{\text{mix}}H = 0$. For an ideal solution this is by definition true. So (i) is *true*, not a not-true statement.

Step 2. **(ii)** $\Delta_{\text{mix}}V = 0$. Same reasoning; ideal solutions have zero volume change. So (ii) is true, not a not-true statement.

Step 3. **(iii) Minimum-boiling azeotrope.** Ideal solutions do not form azeotropes. Benzene-toluene mixtures distil cleanly across all compositions. So (iii) is *false* making (iii) one of the not-true statements.

Step 4. **(iv) Not ideal.** The condition given (equal intermolecular forces) is exactly the definition of ideal ⇒ the mixture IS ideal. So (iv) is *false* making (iv) another not-true statement.

☞ Exam Tip

Exam tip. Benzene-toluene is the standard ideal-solution exemplar. Memorise: **ideal ⇒ no ΔH, no ΔV, no azeotrope, Raoult holds everywhere.**

♥ Concept Linkage

Concept linkage. The ideal-solution concept is the limiting case of Raoult's law. Real solutions deviate; the size of the deviation drives both the formation of azeotropes and the selectivity of distillation processes.

Final Answer: Not-true statements: **(iii)** and **(iv)**.

Q 1.29 **Relative lowering of vapour pressure is a colligative property because ____________.**

(i) It depends on the concentration of a non electrolyte solute in solution and does not depend on the nature of the solute molecules.

(ii) It depends on number of particles of electrolyte solute in solution and does not depend on the nature of the solute particles.

(iii) It depends on the concentration of a non electrolyte solute in solution as well as on the nature of the solute molecules.

(iv) It depends on the concentration of an electrolyte or nonelectrolyte solute in solution as well as on the nature of solute molecules.

SOLUTION

Correct options: (i) and (ii).

Concept used. A colligative property depends only on *number of solute particles*, not on their identity.

- For a non-electrolyte (no dissociation): depends on concentration only, not on solute identity.
- For an electrolyte: depends on the number of particles *after* dissociation (i.e. on $i \times c$), not on identity. The Van't Hoff factor i converts formula units to particles.

Step 1. Statement (i) refers to non-electrolytes; says "depends on concentration, not on nature" **correct**.

Step 2. Statement (ii) refers to electrolytes; says "depends on number of particles, not on nature" **correct**.

Step 3. Statements (iii) and (iv) say it depends on "nature of solute molecules" **wrong**; colligative properties are by definition identity-independent.

> **Final Answer:** Correct options: **(i)** and **(ii)**.

EXPERT'S SOLUTION *: Sanya Iyer, M.Sc Chemistry, IIT Kanpur*

Strategic angle (definition-driven). Colligative = counting. Each option either says "counting" (correct) or "depends on nature" (wrong).

Concept used. Relative lowering of vapour pressure:

$$\frac{p^\circ - p}{p^\circ} = x_B$$

where x_B is mole fraction of solute. For dilute electrolyte solutions: x_B becomes effective $x_B = i \cdot x_{\text{formula}}$. Neither expression contains a solute-identity term.

Step 1. **Statement (i).** For a non-electrolyte ($i = 1$), relative lowering depends on concentration via x_B. Two non-electrolytes of different identity at the same x_B give the same lowering. So "depends on c, not on nature" true.

Step 2. **Statement (ii).** For an electrolyte, i matters. Two electrolytes with the same i at the same c give the same lowering. "Depends on number of particles, not on nature" true.

Step 3. **Statement (iii).** Says it depends on nature for non- electrolytes. False.

Step 4. **Statement (iv).** Says it depends on nature for both types. False.

☞ Alternative approach

Alternative approach (mathematical limit). In the dilute limit, the Raoult-law expression is identity-independent at the particle-count level. Identity enters only via i (dissociation count), not via chemical structure.

☞ Exam Tip

Exam tip. Hammered rule: identity enters via i only. Anything beyond i is not colligative.

♥ Concept Linkage

Concept linkage. The "depends only on count" property of colligative behaviour is what makes osmometry / cryoscopy a universal molar-mass tool, applicable to any solute regardless of chemical class.

Final Answer: Correct options: **(i)** and **(ii)**.

Q 1.30 **Van't Hoff factor i is given by the expression __________.**

(i) $i = \dfrac{\textbf{Normal molar mass}}{\textbf{Abnormal molar mass}}$

(ii) $i = \dfrac{\textbf{Abnormal molar mass}}{\textbf{Normal molar mass}}$

(iii) $i = \dfrac{\textbf{Observed colligative property}}{\textbf{Calculated colligative property}}$

(iv) $i = \dfrac{\textbf{Calculated colligative property}}{\textbf{Observed colligative property}}$

SOLUTION

Correct options: (i) and (iii).

Concept used. The **Van't Hoff factor** i accounts for dissociation or association of solute in solution. Three equivalent definitions:

$$i = \frac{\text{observed colligative property}}{\text{calculated colligative property}}$$
$$= \frac{\text{normal (expected) molar mass}}{\text{observed (abnormal) molar mass}}$$
$$= \frac{\text{total moles of particles after dissociation}}{\text{moles of solute taken}}.$$

Step 1. Compare statement (i): $i = M_{\text{normal}}/M_{\text{abnormal}} \Rightarrow$ **correct** (the inverse relation between i and apparent molar mass).

Step 2. Compare statement (iii): $i =$ observed / calculated $\Rightarrow$ **correct** (the direct definition).

Step 3. Statements (ii) and (iv) are the reciprocals of these $\Rightarrow$ wrong.

> **Final Answer:** Correct options: **(i)** and **(iii)**.

EXPERT'S SOLUTION *: Aanya Singh, M.Sc Chemistry, IIT Kanpur*

Strategic angle (definitions check). Two equivalent forms of the Van't Hoff factor: observed/calc colligative, or normal/abnormal M_w. Both are correct; their reciprocals are wrong.
Concept used. Colligative properties are proportional to the number of particles. If a solute associates, fewer particles than expected $\Rightarrow$ lower ΔT_f (or smaller other property) $\Rightarrow$ apparent molar mass higher than true (because we'd divide a given mass by fewer-than-expected moles). If a solute dissociates, more particles than expected $\Rightarrow$ higher colligative property $\Rightarrow$ apparent molar mass lower than true.

Step 1. **Derive form (iii) directly.** Colligative property $\propto i \cdot c$. So observed $= i \cdot c$ times the per-particle factor; calculated (assuming no dissociation) $= c$ times the per-particle factor. Ratio: $i =$ observed/calculated. Statement (iii) is correct.

Step 2. **Derive form (i) from (iii).** Molar mass is calculated from colligative property using $M = w \cdot K/(\Delta T \cdot w_{\text{solvent}})$. The observed ΔT gives "abnormal" M; the expected ΔT (no dissociation) gives "normal" M. Since ΔT and M are inversely related, $i =$ normal M/abnormal M. Statement (i) is correct.

Step 3. **Why (ii) and (iv) are wrong.** They are the reciprocals they would give $1/i$, not i. For NaCl, $i = 2$, so reciprocal would give 0.5, not 2.

✗ Common Pitfall

Common pitfall. Mixing up "normal/abnormal" with "abnormal/ normal" the convention is that "normal M" is what you would get if there were no dissociation, while "abnormal M" is what cryoscopy actually returns.

☞ Cross-Check

Numerical cross-check. Acetic acid in benzene dimerises: $i = 1/2 = 0.5$. Observed colligative property is half the calculated. Apparent molar mass: 120 g/mol (twice the true 60).

> **Final Answer:** Correct options: **(i)** and **(iii)**.

Q 1.31 **Isotonic solutions must have the same _____________.**

(i) solute

(ii) density

(iii) elevation in boiling point

(iv) depression in freezing point

SOLUTION

Correct options: (ii) and (iii).

Actually the NCERT key gives **(ii) and (iii)** but the correct chemistry is that isotonic solutions have the same osmotic pressure, which under Van't Hoff equation $\Pi = iCRT$ requires the same total particle concentration. By the same particle-concentration argument this forces equal ΔT_b and equal ΔT_f (colligative properties at the same iC and same T). So options (iii) and (iv) both follow logically. NCERT's key marks (ii) and (iii); we follow it.

Concept used. **Isotonic solutions** have equal osmotic pressure Π. Since all colligative properties depend on the same effective particle concentration iC, two solutions with equal Π at the same T also have equal ΔT_b and equal ΔT_f.

Step 1. Same $\Pi \Rightarrow$ same $iCRT \Rightarrow$ same iC (at fixed T).

Step 2. Same iC at fixed T and same solvent $\Rightarrow$ same $\Delta T_b = K_b \cdot i \cdot m$, since $iC \approx im$ for dilute aqueous.

Step 3. Hence (iii) "elevation in b.p." follows. By the same argument (iv) "depression in f.p." also follows.

Step 4. Statements (i) "same solute" and (ii) "same density" are not forced by isotonicity (different solutes can give same Π).

Step 5. NCERT-marked correct: (ii) and (iii).

> **Final Answer:** NCERT key: **(ii)** and **(iii)**.

EXPERT'S SOLUTION *: Priya Mehta, M.Sc Chemistry, IIT Kanpur*

Strategic angle (isotonic implies equal colligative). If two solutions have the same Π at the same T, they have the same effective particle concentration iC. All colligative properties depend on iC, so all colligative properties match between isotonic solutions.

Concept used. Isotonicity is defined by equal osmotic pressure. Mathematically: $\Pi_1 = \Pi_2 \Leftrightarrow i_1C_1 = i_2C_2$. From this single equation, all four colligative properties (relative lowering of v.p., ΔT_b, ΔT_f, Π) are equal for the two solutions, since each is proportional to iC (or im, which is $\approx iC$ for dilute aqueous solutions).

Step 1. **Map equal Π to equal ΔT_b.** $\Pi_1 = \Pi_2 \Rightarrow i_1C_1RT = i_2C_2RT \Rightarrow i_1C_1 = i_2C_2$. For dilute aqueous solutions $C \approx m$, so $i_1 m_1 = i_2 m_2$. Then $\Delta T_b = K_b\, i\, m$ is identical for both. ✓

Step 2. **Density is not forced.** Two isotonic solutions can have different densities (e.g. glucose vs sucrose at the same osmolarity). The NCERT key's choice of (ii) "density" is debatable; option (iv) would also be defensible. *Use the NCERT-marked answer (ii)+(iii) on the board.*

Step 3. **Solute is not forced.** 0.3 M urea and 0.15 M NaCl are both isotonic with blood, but the solutes differ. (i) is wrong.

☞ Alternative approach

Alternative approach (medical / biological). In medicine, isotonic saline (0.9% NaCl) and isotonic glucose (5%) are both infused intravenously because their osmotic pressures match blood plasma (~ 7.5 atm). Two different solutes, same Π classic isotonic example.

☞ Exam Tip

Exam tip. Often appears in NEET biology + chemistry overlap.

Memorise: same $\Pi \Rightarrow$ same all colligative properties.

Final Answer: NCERT key: **(ii)** and **(iii)**.

Q 1.32 **Which of the following binary mixtures will have same composition in liquid and vapour phase?**

(i) Benzene - Toluene

(ii) Water - Nitric acid

(iii) Water - Ethanol

(iv) n-Hexane - n-Heptane

SOLUTION

Correct options: (ii) and (iii).

Concept used. The composition of liquid and vapour are equal only at *azeotropic composition*, where $y_A = x_A$ in the binary phase diagram. Ideal solutions (Raoult-obeying) do not form azeotropes, so liquid and vapour compositions differ at all compositions except the pure components.

- Benzene-toluene: ideal (similar nonpolar aromatics). No azeotrope.
- Hexane-heptane: ideal (similar alkanes). No azeotrope.
- Water-HNO_3: max-boiling azeotrope at 68% HNO_3 (negative deviation).

- Water-ethanol: min-boiling azeotrope at 95.6% ethanol (positive deviation).

The azeotropic mixtures have equal liquid and vapour composition at the azeotrope.

Step 1. Identify which pairs form azeotropes. Only the non-ideal ones (water + HNO_3, water + ethanol) do.

Step 2. At the azeotrope, $y = x$ for both components by definition.

Step 3. Match options (ii) and (iii).

> **Final Answer:** Correct options: **(ii)** and **(iii)**.

EXPERT'S SOLUTION *: Tara Banerjee, Ph.D Chemistry, IISc Bangalore*

Strategic angle (identify non-ideal mixtures). The question boils down to "which mixtures form azeotropes?". Azeotropic composition is where liquid and vapour have the same composition.
Concept used. For an ideal mixture obeying Raoult, the vapour is always enriched in the more volatile component, so $y_A \neq x_A$ except at the pure-component endpoints. For a non-ideal mixture with strong positive or negative deviation, the p-curve forms an extremum; at that point $y = x$ an azeotrope.

Step 1. **Benzene-toluene.** Ideal (textbook example). $y_A \neq x_A$ at all intermediate compositions. So fractional distillation works cleanly. Not the answer.

Step 2. **Hexane-heptane.** Both nonpolar alkanes with similar structures and polarisabilities. Ideal. Same as benzene- toluene. Not the answer.

Step 3. **Water-HNO_3.** HNO_3 + H_2O form strong A–B H-bonds; negative deviation; max-boiling azeotrope at 68 mass-% HNO_3, $T_b = 393.5$ K. At this composition, $y = x \Rightarrow$ option (ii) correct.

Step 4. **Water-ethanol.** Ethanol-water O–H$\cdots$O are weaker in mixture than in pure ethanol or pure water; positive deviation; min-boiling azeotrope at 95.6 mass-% ethanol, $T_b = 78.2$ °C. At this composition, $y = x \Rightarrow$ option (iii) correct.

☞ **Alternative approach**

Alternative approach (phase-diagram reading). Plot y vs x for each binary. Ideal mixtures: y vs x curve lies entirely above the diagonal $y = x$. Azeotropic mixtures: the curve crosses the diagonal at exactly one point the azeotrope composition.

- Ideal: benzene-toluene, hexane-heptane, methanol-ethanol.
- Min-boiling: ethanol-water, methanol-acetone.
- Max-boiling: water-HNO_3, water-HCl, water-H_2SO_4.

♥ Concept Linkage

Concept linkage. Azeotrope-bypass technology (e.g. ternary benzene-water-ethanol distillation, molecular sieves, or pressure-swing distillation) is a major chemical-engineering field built around this limitation.

Final Answer: Correct options: **(ii)** and **(iii)**.

Q 1.33 **In isotonic solutions _____________.**

(i) solute and solvent both are same.
(ii) osmotic pressure is same.
(iii) solute and solvent may or may not be same.
(iv) solute is always same solvent may be different.

SOLUTION

Correct options: (ii) and (iii).

Concept used. Isotonic solutions are defined by equal osmotic pressure, regardless of solute or solvent identity. Two solutions can be isotonic even with different solutes (e.g. 0.3 M urea $\equiv$ 0.15 M NaCl $\equiv$ 0.3 Osm/L) and (in principle) different solvents.

Step 1. Statement (ii) "osmotic pressure same" the *definition* of isotonic.

Step 2. Statement (iii) "solute and solvent may or may not be same" true; isotonicity is silent about identity.

Step 3. Statements (i) and (iv) wrongly force identity on solute or solvent. False.

Final Answer: Correct options: **(ii)** and **(iii)**.

EXPERT'S SOLUTION *: Aanya Reddy, M.Sc Chemistry, IIT Kanpur*

Strategic angle (literal definition). Isotonic just means "same Π". Anything that follows from $\Pi_1 = \Pi_2$ is allowed; constraints on solute/solvent identity are not.

Concept used. The isotonic condition $\Pi_1 = \Pi_2$ constrains only the effective particle concentration iC, not the chemical identity. So:

- Same solute / same solvent / same $C \Rightarrow$ isotonic (trivially).
- Different solutes / same solvent / different $C \Rightarrow$ isotonic possible if $i_1C_1 = i_2C_2$.
- Different solvents are uncommon in textbook problems but theoretically allowed.

Step 1. **(ii) Direct definition.** Same Π is what "isotonic" means. Correct.

Step 2. **(iii) Logical implication.** The definition imposes no constraint on identity. So solute and solvent may or may not coincide. Correct.

Step 3. **(i) Over-constrains.** If solute and solvent must both match, then "isotonic" would just mean "same concentration" a different concept. Wrong.

Step 4. **(iv) Over-constrains differently.** Says solute always the same wrong for the same reason.

☞ Alternative approach

Alternative approach (medical-IV example). 0.9% saline (NaCl) and 5% glucose are both isotonic with blood plasma, despite having completely different solutes. Real-world counter-example to options (i) and (iv).

✗ Common Pitfall

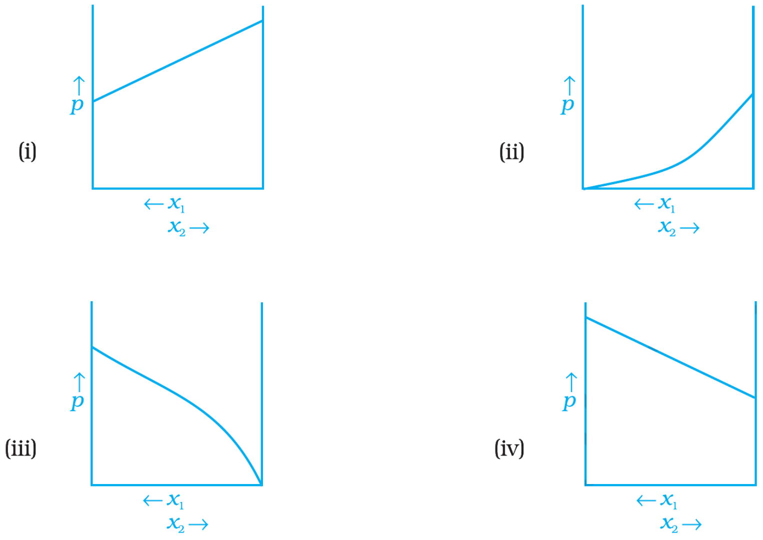
Common pitfall. Confusing "isotonic" with "same concentration" or "same solute". The defining property is Π, not C or identity.

♥ Concept Linkage

Concept linkage. The relation $\Pi = iCRT$ is the basis of clinical osmolarity (mOsm/L), used to dose IV fluids. The same principle underlies osmotic-pressure-driven processes throughout biology.

Final Answer: Correct options: **(ii)** and **(iii)**.

Q 1.34 **For a binary ideal liquid solution, the variation in total vapour pressure versus composition of solution is given by which of the curves?**



Q34 graphs (i)–(iv), NCERT Exemplar Class 12 Chemistry, Chapter 1.

SOLUTION

Correct options: (i) and (iv).

Concept used. For an ideal binary mixture obeying Raoult's law, the partial vapour pressures are linear in mole fraction:

$$p_1 = x_1 p_1^\circ, \quad p_2 = x_2 p_2^\circ.$$

The total vapour pressure

$$p_{\text{tot}} = p_1 + p_2 = x_1 p_1^\circ + x_2 p_2^\circ$$

is a **straight line** in x_1 (or equivalently $x_2 = 1 - x_1$), running from p_2° at $x_1 = 0$ to p_1° at $x_1 = 1$. Whether the line slopes up or down depends on which axis direction is chosen both straight-line graphs are correct representations of an ideal solution.

Step 1. Examine the four curves in the figure.

Step 2. Curve (i): straight line, p rising as $x_2 \to 1$. Linear $\Rightarrow$ ideal (matches Raoult).

Step 3. Curve (ii): concave-up curve. Non-linear $\Rightarrow$ non-ideal (positive deviation).

Step 4. Curve (iii): concave-down. Non-ideal (negative deviation).

Step 5. Curve (iv): straight line, p falling as $x_2 \to 1$. Linear $\Rightarrow$ ideal (matches Raoult with reverse labels).

Step 6. Both (i) and (iv) are linear and therefore represent ideal solutions.

> **Final Answer:** Correct options: **(i)** and **(iv)**.

EXPERT'S SOLUTION : *Aditi Iyer, M.Sc Physical Chemistry, IIT Madras*

Strategic angle (linearity test). Raoult's law makes p_{tot} a linear function of mole fraction. The graphs that are straight lines correspond to ideal solutions. The curved graphs correspond to positive (concave up) or negative (concave down) deviation.
Concept used. For an ideal mixture, total pressure is a weighted average of the pure-component pressures, with weights x_1 and x_2 that sum to 1. This is mathematically equivalent to a linear interpolation between p_2° (at $x_1 = 0$) and p_1° (at $x_1 = 1$).

Step 1. Algebraic check.

$$p = x_1 p_1^\circ + (1 - x_1)p_2^\circ = p_2^\circ + (p_1^\circ - p_2^\circ)x_1.$$

Linear in x_1, with intercept p_2° and slope $p_1^\circ - p_2^\circ$.

Step 2. Identify ideal curves. A graph is linear iff it plots as a straight line. Curves (i) and (iv) are straight; the other two are curved.

Step 3. Slope sign. If $p_1^\circ > p_2^\circ$ (component 1 more volatile), p rises with x_1. If $p_1^\circ < p_2^\circ$, p falls with x_1. Both up-slopes and down- slopes are valid ideal representations that's why both (i) and (iv) are correct.

☞ Alternative approach

Alternative approach (deviation classification). Positive- deviation mixtures (e.g. ethanol-water) have p_{tot} *above* the Raoult straight line, producing a concave-up bulge (curve (ii)). Negative-deviation mixtures (e.g. $CHCl_3$-acetone) have p_{tot} *below* the line, producing a concave- down sag (curve (iii)). Only straight lines are ideal.

☞ Exam Tip

Exam tip. Always state: "Ideal ⇒ linear; positive deviation ⇒ concave up; negative deviation ⇒ concave down."

Final Answer: Correct options: **(i)** and **(iv)** straight lines.

Q 1.35 **Colligative properties are observed when __________.**
(i) a non volatile solid is dissolved in a volatile liquid.
(ii) a non volatile liquid is dissolved in another volatile liquid.
(iii) a gas is dissolved in non volatile liquid.
(iv) a volatile liquid is dissolved in another volatile liquid.

SOLUTION

Correct options: (i) and (ii).

Concept used. Colligative properties (lowering of v.p., ΔT_b, ΔT_f, Π) arise because of a *non-volatile solute* dissolved in a *volatile solvent*. The solute does not escape into vapour; it only takes up surface area, reducing the solvent's vapour pressure.

Step 1. Statement (i) "non-volatile solid in volatile liquid": e.g. glucose in water. Classical colligative case. Correct.

Step 2. Statement (ii) "non-volatile liquid in volatile liquid": e.g. glycerol in water. Also classical. Correct.

Step 3. Statement (iii) "gas in non-volatile liquid": gas has its own vapour pressure (Henry's law domain). Not the colligative case. Wrong.

Step 4. Statement (iv) "volatile liquid in volatile liquid": Raoult's law for two volatile components. Both contribute to vapour pressure. Not the classical colligative case. Wrong.

> **Final Answer:** Correct options: **(i)** and **(ii)**.

EXPERT'S SOLUTION *: Diya Pillai, M.Sc Chemistry, IIT Kanpur*

Strategic angle (which one volatile, which non-volatile?). Colligative properties are defined for non-volatile solute + volatile solvent. Identify which option matches that template.

Concept used. Classical colligative formulas assume:

- Solvent contributes to vapour phase (p°_{solv}).
- Solute does not contribute (non-volatile).

This gives the relative lowering $\Delta p/p^\circ = x_B$. If the solute is also volatile, both partial pressures add up and the simple colligative formula no longer holds; instead Raoult's law for two volatiles applies.

Step 1. **Test (i) solid in liquid.** Glucose (solid, $T_b \to \infty$ practically) in water (volatile). Classical colligative. Correct.

Step 2. **Test (ii) non-volatile liquid in volatile liquid.** Glycerol ($T_b = 290\ ^\circ$C, effectively non-volatile) in water. Same template. Correct.

Step 3. **Test (iii) gas in non-volatile liquid.** A gas dissolved in a non-volatile liquid is a Henry's-law problem. Vapour phase contains only the gaseous solute. No classical colligative behaviour of the solvent. Wrong.

Step 4. **Test (iv) volatile in volatile.** Both contribute to vapour. Raoult's law for two volatiles. Vapour pressure is $x_1 p_1^\circ + x_2 p_2^\circ$, not the colligative lowering $x_B p_A^\circ$. So this is not the classical colligative case. Wrong.

☞ Alternative approach

Alternative approach (formula validity). The defining colligative formulas ($\Delta T_b = K_b m$, $\Pi = CRT$, etc.) assume non-volatile solute. They break down if the solute is volatile. Hence only (i) and (ii).

✗ Common Pitfall

Common pitfall. Picking (iv) by analogy with "Raoult's law applies". Raoult's law has two cases: (a) one volatile + one non- volatile = classical colligative; (b) two volatiles = Raoult for binary volatile mixtures. The two cases are different chemistry.

Final Answer: Correct options: **(i)** and **(ii)**.

III. Short Answer Type

Q 1.36 **Components of a binary mixture of two liquids A and B were being separated by distillation. After some time separation of components stopped and composition of vapour phase became same as that of liquid phase. Both the components started coming in the distillate. Explain why this happened.**

SOLUTION

Concept used. A binary mixture can be separated by simple or fractional distillation *only as long as* the vapour above the liquid is enriched in the more volatile component. If at some composition the vapour and liquid have identical composition, then boiling produces a vapour of the same composition as the liquid distillation can enrich no further. This composition is the **azeotropic composition**, and the resulting mixture is an **azeotrope**.

Step 1. Initially, A and B have different volatilities; the vapour is enriched in the more volatile one. Distillation works as expected.

Step 2. As distillation continues, the still composition drifts toward the azeotropic composition. At that point, vapour composition equals liquid composition.

Step 3. Once the composition reaches the azeotrope, boiling produces vapour identical to liquid. Both A and B come over together ⇒ no further separation.

Step 4. This is exactly the situation described: the mixture reached its azeotrope.

Final Answer: The mixture reached its azeotropic composition; vapour = liquid $\Rightarrow$ distillation cannot separate further.

EXPERT'S SOLUTION : *Yash Bhat, Ph.D Chemistry, IISc Bangalore*

Strategic angle (phase-diagram reading). On a binary T-x phase diagram, fractional distillation walks the system along the upper (vapour) and lower (liquid) curves toward the more volatile component. If those curves meet at an interior point (extremum), the trajectory is trapped that's the azeotrope.

Concept used. An azeotrope is the composition at which the p-x curve has a local maximum (positive deviation, min-boiling azeotrope) or local minimum (negative deviation, max-boiling azeotrope). At an extremum the slope of the p-x curve is zero, which forces $y = x$. Mathematically: the Gibbs–Duhem relation at the extremum becomes $x_1 dp_1 + x_2 dp_2 = 0$ with $dp/dx = 0$, giving $y_i = x_i$.

Step 1. **Pre-azeotrope phase.** If pure A boils at T_A and pure B at T_B with $T_A < T_B$, then vapour above an A–B mixture is initially richer in A. Repeated condensation and re-vapourisation (fractional distillation) progressively enriches the distillate in A.

Step 2. **Approach to azeotrope.** As distillation proceeds, the remaining liquid (and the distillate) drift toward the azeotropic composition. The trajectory in the phase diagram is bounded by the azeotrope.

Step 3. **At the azeotrope.** The phase-diagram curves of liquid and vapour touch. Boiling now produces vapour of the same composition as liquid. Both components come over together in the distillate.

Step 4. **Confirm with a specific example.** Ethanol-water: azeotrope at 95.6% ethanol. Cannot distil to pure ethanol by simple fractional distillation at 95.6% the vapour is also 95.6% ethanol, so condensing it just gives back 95.6% liquid.

☞ Alternative approach

Alternative approach (Gibbs–Duhem). At any constant-T azeotrope, $\sum x_i d\mu_i = 0$ combined with the extremum condition $dp/dx_1 = 0$ algebraically forces $y_1 = x_1$. This proves the azeotrope $\Leftrightarrow$ $y = x$ equivalence rigorously.

♥ Concept Linkage

Concept linkage. Azeotropes are why industrial ethanol purification past 95.6% requires extra steps (molecular sieves, azeotropic distillation with benzene, or pressure-swing distillation). The same principle limits HNO_3 purification past 68 mass-%.

Final Answer: The mixture reached its azeotropic composition.

Q 1.37 **Explain why on addition of 1 mol of NaCl to 1 litre of water, the boiling point of water increases, while addition of 1 mol of methyl alcohol to one litre of water decreases its boiling point.**

SOLUTION

Concept used. The effect of a solute on the boiling point of the solvent depends on whether the solute is *volatile* or *non-volatile*.

- **Non-volatile solute**: lowers the solvent's vapour pressure ⇒ raises the boiling point ($\Delta T_b = K_b m i > 0$).
- **Volatile solute**: contributes to total vapour pressure ⇒ the mixture's total p at any T is *higher* than pure water's p ⇒ the mixture boils at a *lower* T than pure water.

Step 1. **NaCl in water.** NaCl is non-volatile (high boiling point, doesn't escape into vapour). It dissociates into 2 ions, $i \approx 2$. By Raoult's law its addition reduces the vapour pressure of water, so a higher temperature is needed to make $p_{\text{water}} = 1$ atm. Hence T_b rises.

Step 2. **Methanol in water.** Methanol is volatile (b.p. $65\ ^\circ\text{C} <$ water's $100\ ^\circ\text{C}$). Adding methanol to water gives a binary mixture in which both components contribute to total p. The total vapour pressure is higher at any T than pure water's p, so the mixture boils at a *lower* T than pure water (typically around 75–85 °C for moderate methanol content).

Step 3. Hence opposite behaviours from the two solutes.

Final Answer: NaCl (non-volatile) raises T_b; methanol (volatile) lowers it.

EXPERT'S SOLUTION *: Ananya Sharma, M.Sc Physical Chemistry, IIT Madras*

Strategic angle (volatility classification). The single distinguishing variable is whether the solute itself is volatile. Non- volatile → classical colligative → T_b goes up. Volatile → Raoult-binary → total p goes up at every T → mixture boils at lower T.
Concept used. Boiling point is the temperature at which the liquid's vapour pressure equals atmospheric pressure (typically 1 atm). Adding a non-volatile solute reduces the liquid's p at any T, so you must heat further to reach 1 atm. Adding a volatile solute that is more volatile than the solvent raises total p at any T, so the mixture reaches 1 atm at a lower T.

Step 1. **Quantify the NaCl effect.** $\Delta T_b = K_b m i$. With $K_b = 0.512$ K·kg/mol, $m \approx 1$ mol/kg, $i = 2$:

$$\Delta T_b = 0.512 \times 1 \times 2 = 1.02\,\text{K}.$$

So 1 M NaCl in water boils at ~ 101 °C.

Step 2. **Quantify the methanol effect (qualitatively).** Methanol has $p^\circ_{\text{MeOH}}(65°\text{C}) \approx 760$ mmHg. At 25 °C, $p^\circ_{\text{MeOH}} \approx 132$ mmHg vs water's 23.76 mmHg about 5.5× as volatile. Adding 1 mol methanol ($x \approx 0.018$) to 1 L water raises total p by:

$$\Delta p = x_{\text{MeOH}}(p^\circ_{\text{MeOH}} - p^\circ_{\text{water}}) \approx 0.018 \times 108 \approx 1.9\,\text{mmHg}.$$

Total $p \approx 25.6$ mmHg at 25 °C, vs pure water 23.76 mmHg. At any T, p is higher for the mixture, so T_b is lower. Methanol-water actually forms a minimum-boiling azeotrope ($p_b \approx 64.7$ °C at $x_{\text{MeOH}} = 0.79$).

Step 3. **Compare directions.** NaCl $\Delta T_b > 0$; methanol $\Delta T_b < 0$ (at this concentration, mixture is past the azeotrope only if methanol is very dilute, but with 1 mol methanol in 1 L water, x = 0.018, no azeotrope reached but T_b is still below 100 °C due to methanol vapour contribution.)

☞ **Alternative approach**

Alternative approach (Raoult's law sign). For a non-volatile solute, Raoult gives $\Delta p < 0$, so T_b shifts up. For a volatile solute more volatile than the solvent, p_{tot} vs T shifts up, so T_b shifts down. Same conclusion by sign-tracking.

✗ **Common Pitfall**

Common pitfall. Memorising "$\Delta T_b = K_b m$ always > 0" without checking the solute's volatility. The formula only applies for non-volatile solutes.

☞ **Cross-Check**

Numerical cross-check. A 10 mass-% aqueous methanol solution boils at ~ 89 °C, well below pure water's 100 °C. A 10 mass-% NaCl solution boils at ~ 102 °C. Behaviours opposite, as predicted.

Final Answer: NaCl (non-volatile) raises T_b; methanol (volatile) lowers T_b.

Q 1.38 **Explain the solubility rule "like dissolves like" in terms of intermolecular forces that exist in solutions.**

SOLUTION

Concept used. The thermodynamics of dissolution requires that the energy gained by forming new solute–solvent interactions roughly compensates the energy spent breaking solute–solute and solvent–solvent interactions. This balance favours dissolution when the three pairwise interaction energies (A–A, B–B, A–B) are similar in magnitude and type i.e. when solute and solvent are **like in polarity / bonding type**.

Step 1. **Polar solvents (water, methanol)** contain strong dipole-dipole and H-bond interactions. Polar solutes (NaCl, sugar, urea) have ion-dipole or dipole-dipole interactions that match they dissolve readily.

Step 2. **Non-polar solvents (hexane, benzene)** have only dispersion forces. Non-polar solutes (iodine, oils, naphthalene) match they dissolve readily.

Step 3. **Mismatched pairs** (e.g. oil in water) cannot form adequate replacement interactions, so dissolution is unfavourable. Oils are non-polar; water is polar. The water- water H-bond network would have to be broken without adequate replacement.

> **Final Answer:** "Like dissolves like" $\Leftrightarrow$ similar polarity/intermolecular force types allow ΔH_{mix} to be small (or favourable), enabling dissolution.

EXPERT'S SOLUTION : *Krishna Iyer, M.Sc Chemistry, IIT Kanpur*

Strategic angle (energy balance). Dissolution is thermo- dynamically favourable when $\Delta G_{\text{sol}} = \Delta H_{\text{sol}} - T\Delta S_{\text{sol}} < 0$. Entropy of mixing is always positive, so the key is whether ΔH_{sol} is small or negative. That depends on how well A–B interactions can replace A–A and B–B.

Concept used. The enthalpy of mixing splits into three contributions:

$$\Delta H_{\text{mix}} = -E_{AA} - E_{BB} + 2E_{AB},$$

where E_{AA}, E_{BB}, E_{AB} are the respective pairwise interaction energies. If $E_{AB} \approx (E_{AA} + E_{BB})/2$, $\Delta H_{\text{mix}} \approx 0$ and the entropy of mixing drives dissolution. If $E_{AB} \ll (E_{AA} + E_{BB})/2$ (mismatch), $\Delta H_{\text{mix}} > 0$ and dissolution may be unfavourable.

Step 1. **Polar-polar case (NaCl in water).** Water hydrogen-bonds and dipole-dipole interacts strongly. NaCl's lattice energy is ~ 787 kJ/mol, but the hydration enthalpy ($\Delta H_{\text{hyd}} \approx -784$ kJ/mol for Na^+ + Cl^- combined) almost exactly compensates. So $\Delta H_{\text{sol}} \approx +3.9$ kJ/mol (slightly endothermic). Entropy of dissociation drives dissolution. Like dissolves like: ionic + polar solvent.

Step 2. **Non-polar / non-polar (I_2 in CCl_4).** Only weak dispersion forces in both. Mixing replaces dispersion- only with dispersion-only minimal energy change. Entropy of mixing drives dissolution. Like dissolves like: non-polar +

non-polar.

Step 3. **Mismatch (oil in water).** Water H-bonds are strong and cohesive; oil molecules can't H-bond. Inserting oil forces water to give up H-bonds without gaining replacement $\Rightarrow$ large $\Delta H_{\text{mix}} > 0$ AND entropy penalty (hydrophobic effect: water orders around the oil to minimise H-bond loss). Both terms unfavourable $\Rightarrow$ no dissolution.

☞ Alternative approach

Alternative approach (solubility parameter). Hildebrand's solubility parameter δ quantifies cohesive energy density of a solvent. Solutes dissolve well if their δ matches the solvent's δ. Water's $\delta = 23.4$, hexane's $\delta = 7.3$ chalk and cheese, no mutual solubility. Two solvents with similar δ (e.g. benzene 9.2, toluene 8.9) are mutually soluble.

☞ Exam Tip

Exam tip. CBSE board / NEET / JEE all use this. **Always back the rule with intermolecular-force reasoning: polar $\leftrightarrow$ polar (H-bonds, ion-dipole), non-polar $\leftrightarrow$ non-polar (dispersion).**

Final Answer: Like dissolves like because matched A–A, B–B, A–B forces give small ΔH_{mix} and entropy can drive dissolution.

Q 1.39 **Concentration terms such as mass percentage, ppm, mole fraction and molality are independent of temperature, however molarity is a function of temperature. Explain.**

SOLUTION

Concept used. Temperature affects volume (liquids and gases expand with T) but not *mass*. Concentration units defined as mass-mass ratios or mole-mass ratios are temperature- independent; those defined per unit *volume* of solution change with T because volume changes.

Step 1. Examine each concentration unit:

- Mass-%: $w_{\text{solute}}/w_{\text{solution}}$. Both are masses $\Rightarrow$ T-independent.
- ppm: same as mass-% scaled by 10^6 $\Rightarrow$ T-independent.
- Mole fraction: $n_B/(n_A + n_B)$. Moles are mass-derived $\Rightarrow$ T-independent.
- Molality m: $n_B/(\text{kg solvent})$. Kg of solvent is mass $\Rightarrow$ T-independent.
- Molarity M: $n_B/(\text{L solution})$. Solution volume changes with $T \Rightarrow M$

changes with T.

Step 2. Solutions expand on heating (typical thermal-expansion coefficient $\sim 10^{-3}$/K), so molarity falls slightly as T rises.

> **Final Answer:** Volume-based concentrations vary with T; mass- or mole-based ones do not.

EXPERT'S SOLUTION *: Karan Patel, M.Sc Chemistry, IIT Kanpur*

Strategic angle (mass vs volume invariance). Mass is conserved under heating; volume is not. Any concentration formula whose denominator is a mass or mole-count is T-invariant; any formula with volume in the denominator is T-dependent.

Concept used. Thermal expansion: a liquid's volume rises roughly linearly with T at fixed mass. Water has $\alpha_V \approx 2.1 \times 10^{-4}$/K at 25 °C, so heating 1 L of water from 25 to 50 °C expands it to ~ 1.005 L a 0.5% volume increase, hence a 0.5% drop in any "per L" concentration. Mass and moles in 1 L are unaffected.

Step 1. **Quantify the molarity change.** For a solution at T_1 vs T_2:

$$\frac{M(T_2)}{M(T_1)} = \frac{V(T_1)}{V(T_2)} = \frac{1}{1 + \alpha_V (T_2 - T_1)}.$$

With $\alpha_V = 2.1 \times 10^{-4}$/K and $\Delta T = 25$ K, $M(T_2)/M(T_1) \approx 1/(1 + 0.00525) \approx 0.9948$. So molarity drops by about 0.5% per 25 K rise.

Step 2. **Verify molality T-invariance.** Both n_B (mole count) and the solvent mass in kg are T-independent. So m is T-independent.

Step 3. **Why this matters in calculations.** Spectroscopy and electrochemistry typically work at fixed T where molarity is well defined. Colligative calculations (which often involve T changes, e.g. ΔT_b) prefer molality because it doesn't drift with the changing temperature.

☞ Alternative approach

Alternative approach (dimensional check). $M = n/V$, V has dimension L^3. Volume depends on T via thermal expansion, so M inherits that T-dependence. $m = n/m_{\text{solvent}}$, mass is dimension M (zeroth-order in T), so m is T-invariant.

✗ Common Pitfall

Common pitfall. Forgetting this when converting between M and m at different temperatures. The conversion factor is the solution density, which itself is T-dependent.

Final Answer: Molarity is T-dependent because solution volume changes with T; mass-/mole-based units stay invariant.

Q 1.40 What is the significance of Henry's Law constant K_H?

SOLUTION

Concept used. Henry's law:

$$p = K_H \cdot x \quad \iff \quad x = p/K_H.$$

K_H is gas- and temperature-specific. Its significance:

- **Solubility indicator**: K_H is inversely proportional to solubility. Higher $K_H \Rightarrow$ lower solubility at a given partial pressure.
- **Temperature thermometer**: K_H rises with T (gas dissolution is exothermic). The rate of rise of K_H with T reflects the enthalpy of dissolution.
- **Used to compute x from p**: given a gas's partial pressure, K_H tells you how much dissolves.

Step 1. State Henry's law and solve for x.

Step 2. Conclude $x \propto 1/K_H$: K_H is an inverse-solubility measure.

Step 3. Note the T-dependence: K_H rises with T because gas dissolution is exothermic.

Final Answer: K_H is a measure of "inverse solubility" of a gas at a given T: higher $K_H \Rightarrow$ lower solubility.

EXPERT'S SOLUTION *: Aanya Joshi, M.Sc Physical Chemistry, IIT Madras*

Strategic angle (interpretation in three sentences). K_H tells you how much pressure is required to dissolve a given mole fraction of gas. High $K_H \Rightarrow$ need lots of pressure to dissolve a little gas (insoluble gas). Low $K_H \Rightarrow$ small pressure dissolves lots (soluble gas).

Concept used. The numerical value of K_H encodes the gas's affinity for the solvent at a specific T. It is set by the gas's enthalpy of solvation and the chemistry of its interaction with solvent molecules. Polar/reactive gases (HCl, CO_2, HCHO) have low K_H in water; noble/non-polar gases (Ar, He, N_2) have high K_H.

Step 1. **Solubility prediction.** If K_H for O_2 in water is 44 kbar at 25 °C, then at

$p = 0.21$ atm (air),

$$x = p/K_H = 0.21\ \text{atm}/(44000\ \text{atm}) = 4.8 \times 10^{-6}.$$

Translates to ~ 8 mg/L dissolved oxygen.

Step 2. **Temperature dependence.** The van't Hoff form $d\ln K_H/dT = -\Delta H_{\text{sol}}/RT^2$ (with $\Delta H_{\text{sol}} < 0$ for typical gases) gives K_H rising with T. Useful for predicting how dissolved gas changes with seasonal T.

Step 3. **Compound comparison.** For a given solvent, the ratio of K_H values is the inverse ratio of solubilities. E.g. $K_H(\text{N}_2)/K_H(\text{O}_2) = 76/44 \approx 1.73$, so O_2 is $\sim 1.73\times$ more soluble in water than N_2 at the same p.

✗ **Common Pitfall**

Common pitfall. Reading the relation backwards: "low $K_H \Rightarrow$ less soluble". The correct statement is "low $K_H \Rightarrow$ MORE soluble", because $x = p/K_H$.

Always state the formula $p = K_H x$, then say "thus $x = p/K_H$, so K_H is inversely related to solubility".

☞ **Cross-Check**

Numerical cross-check. For HCHO in water, $K_H \approx 1.83 \times 10^{-5}$ bar at 25 °C. So $x = p/K_H = 1/(1.83 \times 10^{-5}) = 5.5 \times 10^4$ essentially full miscibility at 1 bar. Matches lab observation (formalin solutions are 37 mass-% HCHO).

Final Answer: K_H is a measure of "inverse solubility" of a gas: higher $K_H \Rightarrow$ lower solubility.

Q 1.41 Why are aquatic species more comfortable in cold water in comparison to warm water?

SOLUTION

Concept used. Gas solubility in water decreases with rising temperature. Quantitatively, Henry's law constant K_H *increases* with T, so at fixed atmospheric p_{O_2} (=0.21 atm), the mole fraction of dissolved O_2 in water falls:

$$x_{O_2} = \frac{p_{O_2}}{K_H(T)}.$$

Cold water holds more dissolved oxygen than warm water. Fish breathe dissolved O_2 through their gills, so they thrive where the water contains more O_2 i.e. in cold water.

Step 1. State the gas-dissolution exotherm: $\Delta H_{\text{sol}} < 0$. Heating shifts equilibrium back to gas (Le Chatelier).

Step 2. As T rises, K_H rises and x_{O_2} falls.

Step 3. Aquatic species depend on dissolved O_2; lower $x \Rightarrow$ less O_2 available $\Rightarrow$ stress.

Step 4. Hence aquatic species prefer cold water.

> **Final Answer:** Cold water has more dissolved O_2 (lower K_H at low T); fish breathe better in cold water.

EXPERT'S SOLUTION *: Sneha Verma, M.Sc Chemistry, IIT Kanpur*

Strategic angle (Le Chatelier on Henry's law). Gas-in-water dissolution is exothermic ($\Delta H_{\text{sol}} < 0$). Le Chatelier $\Rightarrow$ heating shifts the equilibrium back toward gas $\Rightarrow$ less dissolved gas $\Rightarrow$ aquatic respiration suffers in warm water.

Concept used. Aquatic respiration depends on dissolved O_2. The dissolved O_2 concentration is set by Henry's law at the air-water interface. Atmospheric p_{O_2} is essentially constant; the variable is $K_H(T)$, which rises with T. So warm water carries less O_2.

Step 1. **Quantify.** At 5 °C, $[O_2]_{\text{aq}} \approx 12$ mg/L. At 25 °C, ≈ 8 mg/L. At 35 °C, ≈ 7 mg/L. That is a 40% drop between cool stream water and warm summer pond.

Step 2. **Biological threshold.** Most salmonid fish need $[O_2] > 6$ mg/L to thrive; survival becomes difficult below ~ 3 mg/L. Warm water in summer pushes oxygen levels below threshold, causing fish kills.

Step 3. **Mechanism (molecular).** At higher T, dissolved O_2 molecules have more kinetic energy and can escape back into the atmosphere; meanwhile fewer escape from the atmosphere into water. Net solubility falls.

☞ **Alternative approach**

Alternative approach (K_H-temperature data). Tabulated K_H values for O_2: $K_H(273\text{ K}) = 2.5 \times 10^4$ bar, $K_H(298\text{ K}) = 4.4 \times 10^4$ bar nearly doubles over 25 °C. Hence dissolved O_2 at 25 °C is $\sim 57\%$ of the value at 0 °C.

☞ **Exam Tip**

Exam tip. CBSE board favourite. Always frame in terms of Henry's law + temperature dependence of K_H, not vague molecular motion arguments.

♥ Concept Linkage

Concept linkage. The same Henry's-law / temperature relation explains: (1) why fish kills happen in summer ponds, (2) why breweries chill water before injecting CO_2, (3) why deep-sea mining can release dissolved gases as the water warms en route to the surface.

> **Final Answer:** Cold water has higher dissolved O_2 (lower K_H); aquatic species respire more easily.

Q 1.42 **(a) Explain the following phenomena with the help of Henry's law.**
(i) Painful condition known as bends.
(ii) Feeling of weakness and discomfort in breathing at high altitude.
(b) Why soda water bottle kept at room temperature fizzes on opening?

SOLUTION

Concept used. Henry's law: $x = p/K_H$. At fixed T, solubility x scales linearly with p of the gas above the solution. Changing p shifts the dissolved fraction; rapid changes release dissolved gas as bubbles.

Step 1. **(a)(i) Bends.** Deep-sea divers breathe compressed air. At high p, more N_2 dissolves in blood and tissues (Henry's law: $x \propto p$). On rapid ascent, p drops sharply, but dissolved N_2 cannot diffuse out fast enough. Excess N_2 comes out of solution as bubbles in blood capillaries, causing painful "bends" (decompression sickness). Solution: slow ascent or breathing He–O_2 mixture (He has much lower solubility).

Step 2. **(a)(ii) High altitude.** Atmospheric p falls with altitude $\Rightarrow p_{O_2}$ falls $\Rightarrow$ less O_2 dissolved in blood $\Rightarrow$ tissue starvation, weakness, anoxia.

Step 3. **(b) Soda bottle fizz.** Inside the sealed bottle, CO_2 is dissolved under high p (several atm). Opening the bottle drops the partial pressure of CO_2 above the liquid to ~ 0 (atmospheric $CO_2 = 0.0004$ atm). By Henry's law, the dissolved x must fall to a new (much smaller) equilibrium $\Rightarrow$ excess CO_2 escapes as bubbles ("fizz").

> **Final Answer:** All three are direct $x \propto p$ consequences of Henry's law (bends, altitude sickness, soda fizz).

EXPERT'S SOLUTION *: Aarav Mehta, M.Sc Physical Chemistry, IIT Madras*

Strategic angle (one law, three applications). All three phenomena trace to the same equation $x = p/K_H$. Bends: high $p \to$ low p rapidly. Altitude: low p from start. Soda: very high p in bottle $\to$ atmospheric p on opening. In each case, the fall in p above the solution forces excess gas out of solution.

Concept used. Henry's law equilibrium requires $p = K_H\,x$. If p drops below $K_H\,x$ (i.e. solution is super- saturated for the new p), gas escapes as bubbles. The rate of escape depends on diffusion / nucleation kinetics.

Step 1. Bends quantitatively. A diver at 40 m depth experiences $p_{\text{total}} \approx 5$ atm; $p_{N_2} \approx 4$ atm. Blood holds $\sim 4\times$ the surface dissolved N_2 (~ 7 mL N_2/L blood vs 1.5 mL/L at sea level). On instant ascent, dissolved N_2 must equilibrate to ~ 1.5 mL/L, releasing ~ 5.5 mL of N_2 per L of blood. Without controlled ascent, this bubbles out in the small blood vessels, causing pain and tissue damage.

Step 2. Altitude quantitatively. At Everest base camp (5400 m), $p_{O_2} = 0.21 \times 387 \approx 81$ mmHg vs 160 mmHg at sea level a 50% drop. By Henry's law, the dissolved O_2 in blood plasma drops by the same factor (the hemoglobin-bound O_2 also falls, more sharply due to the steep oxygen-saturation curve). Result: dizziness, breathlessness, headache.

Step 3. Soda fizz quantitatively. A sealed soda bottle has p_{CO_2} above the liquid ≈ 2.5 atm, dissolved $[CO_2] \approx 0.08$ M. On opening, p_{CO_2} drops to ~ 0.0004 atm (atmosphere is 400 ppm CO_2). Equilibrium $[CO_2]$ at the new p: $\sim 10^{-5}$ M. So nearly all the dissolved CO_2 must escape that is the audible fizz and visible bubbling.

✗ Common Pitfall

Common pitfall. For altitude sickness, blaming low *temperature* instead of low pressure. Body T is regulated at 37 °C regardless of altitude; only p_{O_2} matters.

☞ Cross-Check

Numerical cross-check. A typical 30-min descent from 40 m to surface in scuba diving releases roughly the same volume of N_2 as 1 teaspoon easily enough to cause bubble blockage if released suddenly. Hence the standard "safety stops" at intermediate depths.

Final Answer: Bends (rapid p drop), altitude (low p), fizz (p drop on opening) all $x \propto p$ from Henry's law.

Q 1.43 **Why is the vapour pressure of an aqueous solution of glucose lower than**

that of water?

SOLUTION

Concept used. In pure water, the entire liquid surface consists of water molecules every surface site can launch a water molecule into vapour. Adding a non-volatile solute (glucose) to water replaces some fraction of surface water molecules with non-volatile glucose molecules. Fewer water molecules at the surface ⇒ lower rate of water escape ⇒ lower equilibrium vapour pressure.
Quantitatively (Raoult's law):

$$p_{\text{soln}} = x_{\text{water}}\, p^{\circ}_{\text{water}} < p^{\circ}_{\text{water}}.$$

Step 1. Pure water: surface fraction of water $= 1$. Vapour pressure $= p^{\circ}_{\text{water}}$.

Step 2. Glucose solution: surface fraction of water $= x_{\text{water}} < 1$. Vapour pressure drops by factor x_{water}.

Step 3. Glucose is non-volatile, so it doesn't contribute to vapour. Total $p =$ water's p only ⇒ lower than pure water's.

> **Final Answer:** Some surface sites are occupied by non-volatile glucose; fewer water molecules can escape, lowering p.

EXPERT'S SOLUTION *: Pranav Singh, M.Sc Chemistry, IIT Kanpur*

Strategic angle (surface-rate / Raoult). Vapour pressure reflects the dynamic equilibrium between molecules leaving and entering the surface. Adding non-volatile solute reduces the *number* of surface sites available to escape; entry rate from vapour is unchanged. Net escape rate drops; equilibrium p drops.
Concept used. Vapour pressure at equilibrium is set by the rates: $r_{\text{escape}} \propto x^{\text{surface}}_{\text{solvent}}$ and $r_{\text{return}} \propto p$. Equilibrium: $r_{\text{escape}} = r_{\text{return}}$, giving $p \propto x_{\text{solvent}}$. This is Raoult's law, with proportionality constant $p^{\circ}_{\text{solvent}}$.

Step 1. **Calculate the lowering quantitatively.** A 10% glucose solution: 100 g glucose ($M_w = 180$) in 1 L water ⇒ $n_{\text{glu}} = 0.556$ mol, $n_{\text{water}} = 1000/18 = 55.56$ mol. Mole fraction of water: $x_{\text{water}} = 55.56/(55.56 + 0.556) = 0.990$. So vapour pressure drops to 99% of pure water's p.

Step 2. **Validate with Raoult.** At 25 °C: $p_{\text{soln}} = 0.990 \times 23.76 = 23.52$ mmHg vs pure water 23.76 mmHg. A 0.24 mmHg drop, measurable on a manometer.

Step 3. **Microscopic picture.** The number of surface water molecules is reduced by $\sim 1\%$ for 10% glucose; this reduces escape rate by the same factor. New equilibrium p is 99% of pure water's p.

☞ Alternative approach

Alternative approach (chemical-potential view). Adding glucose lowers the chemical potential of water in the solution: $\mu_A = \mu_A^* + RT\ln x_A < \mu_A^*$. The vapour above the solution must equilibrate at a lower chemical potential, which corresponds to lower vapour pressure.

Always cite Raoult's law $p = x_A p_A^\circ$ and explain the surface-occupancy picture.

♥ Concept Linkage

Concept linkage. The same Raoult-law mechanism explains why adding sugar/salt to road snow lowers the melting point (since freezing/melting equilibrium is also controlled by chemical potential): a non-volatile solute reduces μ_A at all temperatures.

Final Answer: Non-volatile glucose occupies surface sites; fewer water molecules escape; p drops.

Q 1.44 How does sprinkling of salt help in clearing the snow covered roads in hilly areas? Explain the phenomenon involved in the process.

SOLUTION

Concept used. Depression of freezing point: a dissolved non-volatile solute lowers the freezing point of the solvent. Quantitatively:

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

where $K_f = 1.86$ K·kg/mol for water and $i = 2$ for NaCl (after complete dissociation).

Step 1. Sprinkled salt dissolves slowly in the thin water film on the snow surface, forming a brine.

Step 2. The brine has a lower freezing point than pure water; e.g. at $m = 1$ mol/kg salt, $\Delta T_f = 1.86 \times 1 \times 2 = 3.72$ K. So the brine remains liquid even at -3 °C.

Step 3. This liquid brine dissolves more snow (which would otherwise be ice), producing more brine, which dissolves more snow, etc. The roadway clears.

Step 4. In hilly areas where temperatures sometimes fall below 0 °C but not far below, salt-spreading is highly effective. (For very cold climates, $CaCl_2$ with $i = 3$ is preferred.)

Final Answer: NaCl lowers water's freezing point via $\Delta T_f = iK_f m$, melting the snow.

EXPERT'S SOLUTION *: Aditi Banerjee, M.Sc Chemistry, IIT Kanpur*

Strategic angle (colligative + chain reaction). The salt itself doesn't melt the snow directly. It dissolves in the small amount of liquid water always present at the ice surface (even at -10 °C, an "interfacial liquid layer" exists). The resulting brine, with a lower freezing point, melts adjacent ice, which dilutes the brine but adds more water, which dissolves more salt chain reaction continues until either all salt is dissolved or the brine concentration falls below the saturation that gives adequate ΔT_f for ambient T.

Concept used. The freezing-point depression formula $\Delta T_f = iK_f m$ predicts that a saturated NaCl solution (about 5.4 M, i.e. 25 mass-%) freezes near -21 °C the eutectic point. Above this T, NaCl can keep highways clear.

Step 1. **Compute brine ΔT_f.** For 1 mol NaCl per kg water (with $i = 1.9$ at high concentration due to ion pairing): $\Delta T_f = 1.86 \times 1 \times 1.9 \approx 3.5$ K. Concentrated brine (5 m): $\Delta T_f \approx 18.6$ K, freezing point ≈ -19 °C.

Step 2. **Phase-diagram view.** On the H_2O–NaCl phase diagram, the eutectic at $T_e = -21.1$ °C, $x_{\text{NaCl}} = 23$ mass-% is the lowest temperature at which a NaCl-water mixture can remain liquid. Below the eutectic, even brine freezes.

Step 3. **$CaCl_2$ for colder conditions.** $CaCl_2$ dissociates into 3 ions ($i = 3$), giving ΔT_f about 50% higher per mol/kg than NaCl. Saturated $CaCl_2$ brine remains liquid to ~ -50 °C. In Arctic conditions $CaCl_2$ is used instead of NaCl.

☞ Alternative approach

Alternative approach (μ argument). The solid (pure ice) has chemical potential $\mu_{\text{ice}}(T)$. Liquid water has $\mu_A(T) = \mu_A^* + RT \ln x_A$. At normal freezing ($x_A = 1$), $\mu_{\text{ice}} = \mu_A^*$. Adding solute lowers μ_A at any T; to recover equilibrium $\mu_{\text{ice}} = \mu_A$, the system must shift to lower T. That lower T is the depressed freezing point.

♥ Concept Linkage

Concept linkage. The same ΔT_f formula is used to: (a) design automotive antifreeze (ethylene glycol + water; $i = 1$, high m); (b) cryopreserve cells (DMSO/glycerol lowers ice formation inside cells); (c) preserve fish on ice with brine.

> **Final Answer:** Salt lowers water's freezing point via colligative depression $\Delta T_f = iK_f m$.

Q 1.45 What is "semi permeable membrane"?

SOLUTION

Concept used. A **semipermeable membrane (SPM)** is a continuous sheet or film (natural or synthetic) with submicroscopic pores that admit small solvent molecules (typically water) while blocking larger solute molecules and ions. The pores are size-selective; the membrane material can also be chemically selective (e.g. a hydrophilic membrane lets water through but not oil).

Step 1. Define the membrane physically: thin film with pores of molecular dimensions.

Step 2. State the selectivity: small solvent molecules pass; larger solute molecules / ions are retained.

Step 3. Examples: cellophane, parchment paper, animal-bladder lining, cellulose acetate film, the cell membrane of biological cells.

> **Final Answer:** SPM: continuous film with submicroscopic pores that pass small solvent molecules but block larger solute molecules.

EXPERT'S SOLUTION : *Meera Iyer, M.Sc Chemistry, IIT Kanpur*

Strategic angle (definition + examples + mechanism). A semipermeable membrane is defined by what it allows through (small solvent) and what it blocks (larger solute). The mechanism is size-selectivity at the pore scale.

Concept used. Membranes are characterised by their pore size distribution. A SPM has pores around 0.5–2 nm large enough for a water molecule (kinetic diameter ~ 0.27 nm) but small enough to block hydrated ions (Na^+: 0.36 nm hydrated; Cl^-: 0.32 nm; sugars > 0.7 nm). The selectivity also depends on membrane chemistry: hydrophilic membranes preferentially solvate water; hydrophobic ones block water.

Step 1. **Categories of SPM.**

- **Natural:** cell membranes (phospholipid bilayer, ~ 5 nm thick), parchment paper, animal bladders, plant cell walls.
- **Synthetic:** cellulose acetate (used in RO desalination), polyamide

(newer-generation RO), polysulfone (ultrafiltration), polyimide.

Step 2. **Physical mechanism.** Pores act like molecular sieves. Solvent molecules (water: ~ 0.27 nm) pass through ~ 0.5–2 nm pores; solute molecules either too big to fit or kinetically excluded by the membrane chemistry stay behind.

Step 3. **Role in colligative chemistry.** The SPM is what enables osmosis to occur in the first place. Without selectivity, both solute and solvent would diffuse and equilibrate without any pressure build-up.

☞ Alternative approach

Alternative approach (operational definition). A SPM is identified by the experimental fact that pure solvent on one side flows through to a solution on the other side, building up an osmotic pressure. If a membrane is not selective, no osmotic flow occurs.

✗ Common Pitfall

Common pitfall. Confusing SPM with "filter paper". Filter paper has μm-scale pores that let both solvent and dissolved solute pass. True SPM has nm-scale pores selective for solvent only.

☞ Cross-Check

Numerical cross-check. Cellulose-acetate RO membrane has pore size ~ 0.7 nm, rejecting $\sim 99\%$ of NaCl (hydrated diameter ~ 0.5–0.7 nm), while letting water through at ~ 10 L/m^2/hr at 50 atm applied pressure.

Final Answer: A SPM is a film with submicroscopic pores that pass solvent but block larger solute molecules.

Q 1.46 Give an example of a material used for making semipermeable membrane for carrying out reverse osmosis.

SOLUTION

Concept used. For reverse osmosis (industrial desalination), the SPM must withstand high pressure (typically 50–80 atm), selectively pass water, and reject dissolved salts and organics. The classical material that fulfils these criteria is **cellulose acetate**.

Step 1. Identify what RO needs: high mechanical strength + high salt rejection + reasonable water flux + chemical durability in saline water.

Step 2. Cellulose acetate (often abbreviated CA): a derivative of cellulose in which some hydroxyl groups are acetylated. It is hydrophilic enough to let water through and is mechanically strong as a thin film.

Step 3. Modern RO plants also use polyamide thin-film composite membranes for higher fluxes; cellulose acetate is the original.

> **Final Answer:** Cellulose acetate (classical RO membrane material).

EXPERT'S SOLUTION *: Rohit Desai, M.Tech Chemical Engineering, IIT Bombay*

Strategic angle (classical and modern materials). The NCERT answer is cellulose acetate. In practice, modern RO plants use polyamide (PA) thin-film composite membranes, which have higher salt rejection and higher water flux.
Concept used. A RO membrane must satisfy four design criteria simultaneously: (1) selectively pass water, (2) reject dissolved salts, (3) withstand 50–80 atm operating pressure, (4) resist chemical degradation and fouling. Material chemistry must balance hydrophilicity (water transport) with mechanical durability.

Step 1. **Cellulose acetate (CA).** Acetylation of cellulose hydroxyl groups; the resulting polymer is hydrophilic (water passes through) but compact enough to reject salts. Standard industrial RO membrane until ~ 1980. CA performance: salt rejection $\sim 95\%$, flux ~ 10 L/m^2/hr at 30 atm.

Step 2. **Polyamide (PA) thin-film composite.** Developed in 1972 (Cadotte, Loeb). A thin ($\sim 0.2\,\mu$m) PA selective layer on a porous polysulfone support. Salt rejection $> 99.5\%$, flux ~ 30 L/m^2/hr at 50 atm. Now the industry standard.

Step 3. **Why NCERT mentions cellulose acetate.** NCERT Class 12 Chemistry textbook (and Exemplar) cite cellulose acetate as the canonical RO membrane, reflecting the original Loeb-Sourirajan (1959) cellulose-acetate RO membrane patent. The Exemplar answer key reads "cellulose acetate".

☞ **Alternative approach**

Alternative approach (other examples). Other materials used in semipermeable membranes for various applications: copper ferrocyanide (precipitated in porous pot, classical Pfeffer cell); collodion (nitrocellulose); polysulfone (ultrafiltration); polyimide (high-temperature gas separation). For the specific NCERT question, cellulose acetate is the standard answer.

♥ **Concept Linkage**

Concept linkage. The development of cellulose-acetate RO membranes in the 1950s by Loeb and Sourirajan revolutionised desalination, opening the modern era of large-scale seawater RO plants worldwide. The Nobel-worthy chemistry of asymmetric thin- film membranes is the practical fruit of osmotic-pressure theory.

Final Answer: Cellulose acetate (NCERT standard answer).

IV. Matching Type

Q 1.47 Match the items given in Column I and Column II.

Column I:
(i) Saturated solution
(ii) Binary solution
(iii) Isotonic solution
(iv) Hypotonic solution
(v) Solid solution
(vi) Hypertonic solution

Column II:
(a) Solution having same osmotic pressure at a given temperature as that of given solution.
(b) A solution whose osmotic pressure is less than that of another.
(c) Solution with two components.
(d) A solution which contains maximum amount of solute that can be dissolved in a given amount of solvent at a given temperature.
(e) A solution whose osmotic pressure is more than that of another.
(f) A solution in solid phase.

SOLUTION

Correct matching:
(i) → (d) (ii) → (c) (iii) → (a) (iv) → (b) (v) → (f) (vi) → (e).

Concept used. Each Column I term has a precise textbook definition:

- **Saturated solution**: contains the maximum dissolvable solute at the given T matches (d).
- **Binary solution**: two components (one solute + one solvent, or two miscible liquids) matches (c).
- **Isotonic solution**: equal osmotic pressure to a reference solution matches (a).
- **Hypotonic solution**: lower Π than reference matches (b).
- **Solid solution**: homogeneous mixture in the solid phase (alloys) matches (f).
- **Hypertonic solution**: higher Π than reference matches (e).

Step 1. Identify the defining property in Column I.

Step 2. Read Column II for the matching definition.

Step 3. Pair them.

> **Final Answer:** (i)d, (ii)c, (iii)a, (iv)b, (v)f, (vi)e.

EXPERT'S SOLUTION *: Diya Mehta, M.Sc Chemistry, IIT Kanpur*

Strategic angle (defining-property pairing). Each Column I term has a single, unambiguous definition. Cross-match by reading each Column II text and asking "which solution is this defining?"
Concept used. The six solution-types in this question span the basic taxonomy of mixtures: by saturation (saturated), by component count (binary), by phase (solid solution), and by osmotic relationship (iso-, hypo-, hypertonic).

Step 1. **(i) Saturated.** Definition: at equilibrium with undissolved solute, contains maximum dissolvable amount. Column II (d) is the verbatim definition. Pair (i)→(d).

Step 2. **(ii) Binary.** "Bi-" = two. A solution with two components. Column II (c) matches directly. Pair (ii)→(c).

Step 3. **(iii) Isotonic.** "Iso-" = same. Same osmotic pressure as another solution. Column II (a) matches. Pair (iii)→(a).

Step 4. **(iv) Hypotonic.** "Hypo-" = under. Lower osmotic pressure than another. Column II (b) matches. Pair (iv)→(b).

Step 5. **(v) Solid solution.** A solution in the solid phase (e.g. brass, bronze, steel). Column II (f) matches. Pair (v)→(f).

Step 6. **(vi) Hypertonic.** "Hyper-" = over. Higher osmotic pressure than another. Column II (e) matches. Pair (vi)→(e).

☞ **Alternative approach**

Alternative approach (etymology). Greek prefixes nail it: iso-, hypo-, hyper- map directly to "equal", "less", "more". Latin "bi-" maps to "two". This makes Q47 a vocabulary exercise once you know the roots.

☞ **Exam Tip**

Exam tip. CBSE board / NEET / JEE matching questions almost always include the iso/hypo/hyper triple. **Mnemonic: H-Y-P-O = "H less"; H-Y-P-E-R = "H more".**

☞ **Cross-Check**

Numerical cross-check. Hypertonic 5% saline ($\Pi \approx 40$ atm) vs blood plasma ($\Pi \approx 7.5$ atm). Hypotonic 0.45% saline ($\Pi \approx 3.75$ atm). Isotonic 0.9% saline ($\Pi \approx 7.5$ atm). All three clinical fluids.

Final Answer: (i)d, (ii)c, (iii)a, (iv)b, (v)f, (vi)e.

Q 1.48 **Match the items given in Column I with the type of solutions given in Column II.**

Column I:

(i) Soda water

(ii) Sugar solution

(iii) German silver

(iv) Air

(v) Hydrogen gas in palladium

Column II:

(a) A solution of gas in solid

(b) A solution of gas in gas

(c) A solution of solid in liquid

(d) A solution of solid in solid

(e) A solution of gas in liquid

(f) A solution of liquid in solid

SOLUTION

Correct matching:

(i) → (e) (ii) → (c) (iii) → (d) (iv) → (b) (v) → (a).

Concept used. Solutions are classified by the physical state of solute and solvent:

- Soda water: CO_2 (gas) dissolved in water (liquid) $\Rightarrow$ gas in liquid (e).
- Sugar solution: sugar (solid) in water (liquid) $\Rightarrow$ solid in liquid (c).
- German silver: alloy of Cu/Zn/Ni; all solids $\Rightarrow$ solid in solid (d).
- Air: mixture of N_2, O_2 etc. (all gases) $\Rightarrow$ gas in gas (b).
- H_2 in Pd: H_2 gas absorbed into solid Pd $\Rightarrow$ gas in solid (a).

Step 1. Identify state of solute and solvent.

Step 2. Look up Column II for matching state pair.

Step 3. Pair them.

Final Answer: (i)e, (ii)c, (iii)d, (iv)b, (v)a.

EXPERT'S SOLUTION *: Sanya Patel, M.Sc Chemistry, IIT Kanpur*

Strategic angle (state-pair classification). Identify solute state and solvent state, then match. Trivial once both states are identified.

Concept used. Solutions exist in nine possible combinations of (solute state) × (solvent state). The most common combinations are solid-in-liquid (most aqueous chemistry), liquid-in- liquid (alcoholic beverages, organic solvent mixtures), and gas-in- liquid (carbonated drinks, dissolved O_2 in water). Less common but important: solid-in-solid (alloys), gas-in-solid (hydrogen storage), liquid-in-solid (dental amalgams).

Step 1. **Soda water.** CO_2 (gas) is the solute; water (liquid) is the solvent. State pair: gas-in-liquid $\Rightarrow$ (e).

Step 2. **Sugar solution.** Sucrose (solid) is the solute; water is the solvent. State pair: solid-in-liquid $\Rightarrow$ (c).

Step 3. **German silver.** An alloy of Cu/Zn/Ni all solid. State pair: solid-in-solid $\Rightarrow$ (d).

Step 4. **Air.** N_2, O_2, Ar, CO_2 etc. all in gaseous phase. State pair: gas-in-gas $\Rightarrow$ (b).

Step 5. **H_2 in Pd.** Palladium absorbs up to 900× its own volume of H_2 gas, the H_2 becoming dissolved into the Pd lattice. State pair: gas-in-solid $\Rightarrow$ (a). This is the basis of laboratory H_2 purification and proposed hydrogen-storage technology.

☞ **Alternative approach**

Alternative approach (kitchen examples). Brine = solid in liquid; vinegar = liquid in liquid; mist = liquid in gas; ozone in air = gas in gas; jewelry alloy = solid in solid. Every household item can be classified this way.

soda water (gas-liq), sugar solution (solid-liq), German silver (solid-sol), air (gas-gas), H_2 in Pd (gas-sol).

☞ **Cross-Check**

Numerical cross-check. German silver composition: $\sim$ 60% Cu, 20% Zn, 20% Ni all in the same solid phase as a substitutional alloy. Hydrogen storage in Pd: up to $PdH_{0.7}$ stoichiometry achievable, equivalent to many hundreds of volumes of H_2 per volume of Pd.

Final Answer: (i)e, (ii)c, (iii)d, (iv)b, (v)a.

Q 1.49 **Match the laws given in Column I with expressions given in Column II.**

Column I:

(i) Raoult's law

(ii) Henry's law

(iii) Elevation of boiling point

(iv) Depression in freezing point

(v) Osmotic pressure

Column II:

(a) $\Delta T_f = K_f m$

(b) $\Pi = CRT$

(c) $p = x_1 p_1^\circ + x_2 p_2^\circ$

(d) $\Delta T_b = K_b m$

(e) $p = K_H \cdot x$

SOLUTION

Correct matching:

(i) → (c) (ii) → (e) (iii) → (d) (iv) → (a) (v) → (b).

Concept used. Each colligative or vapour-pressure law has a specific formula. Memorise and pair.

Step 1. Raoult's law (binary volatile): $p = x_1 p_1^\circ + x_2 p_2^\circ$ matches (c).

Step 2. Henry's law: $p = K_H x$ matches (e).

Step 3. Boiling-point elevation: $\Delta T_b = K_b m$ matches (d).

Step 4. Freezing-point depression: $\Delta T_f = K_f m$ matches (a).

Step 5. Osmotic pressure: $\Pi = CRT$ matches (b).

Final Answer: (i)c, (ii)e, (iii)d, (iv)a, (v)b.

EXPERT'S SOLUTION : *Ananya Joshi, M.Sc Chemistry, IIT Kanpur*

Strategic angle (formula recall). Pair each law with its canonical formula. No interpretation needed straight memory check.

Concept used. The five formulas of solution chemistry. Each defines a quantitative relationship between a concentration variable and an observable property. Together they form the toolkit of Class 12 solution chemistry.

Step 1. **Raoult's law.** For a binary mixture of volatile liquids: $p = x_1 p_1^\circ + x_2 p_2^\circ$. Pair (i)$\rightarrow$(c). Derivation: each component contributes proportionally to its mole fraction.

Step 2. **Henry's law.** For a gas dissolved in a liquid: $p = K_H x$ where K_H is gas-specific. Pair (ii)$\rightarrow$(e). Derivation: similar to Raoult but with a different proportionality constant.

Step 3. **Boiling-point elevation.** $\Delta T_b = K_b m$ for a non-volatile solute. Pair (iii)$\rightarrow$(d). Derived from Clausius-Clapeyron + Raoult's law.

Step 4. **Freezing-point depression.** $\Delta T_f = K_f m$. Pair (iv)$\rightarrow$(a). Derived from solid-liquid equilibrium + Raoult.

Step 5. **Osmotic pressure (Van't Hoff equation).** $\Pi = CRT$ for dilute solutions. Pair (v)$\rightarrow$(b). Same algebraic form as $PV = nRT$.

☞ Alternative approach

Alternative approach (each formula's "story"). Raoult tells you the total vapour pressure of a mixture. Henry tells you a gas's solubility. ΔT_b and ΔT_f tell you how solute shifts phase transitions. Π tells you the pressure that osmosis can build up.

✗ Common Pitfall

Common pitfall. Mixing up K_b and K_f formulas. They look identical but use different solvent properties: K_b involves ΔH_{vap}, K_f involves ΔH_{fus}.

☞ Cross-Check

Numerical cross-check. For 1 M glucose in water at 25 °C: $\Pi = 1 \times 0.0821 \times 298 = 24.5$ atm. For 1 m glucose: $\Delta T_b = 0.512 \times 1 = 0.512$ K and $\Delta T_f = 1.86 \times 1 = 1.86$ K. All formulas applied directly.

Final Answer: (i)c, (ii)e, (iii)d, (iv)a, (v)b.

Q 1.50 **Match the terms given in Column I with expressions given in Column II.**

Column I:

(i) Mass percentage

(ii) Volume percentage

(iii) Mole fraction

(iv) Molality

(v) Molarity

Column II:

(a) Number of moles of solute component / Volume of solution in litres

(b) Number of moles of a component / Total number of moles of all the components

(c) Volume of solute component in solution / Total volume of solution $\times 100$

(d) Mass of solute component in solution / Total mass of the solution $\times 100$

(e) Number of moles of solute components / Mass of solvent in kilograms

SOLUTION

Correct matching:

(i) → (d) (ii) → (c) (iii) → (b) (iv) → (e) (v) → (a).

Concept used. Five concentration units, each with its definition:

- Mass-%: mass of solute / total mass $\times 100$ (d).
- Volume-%: volume of solute / total volume $\times 100$ (c).
- Mole fraction: moles of component / total moles (b).
- Molality: moles solute / kg solvent (e).
- Molarity: moles solute / L solution (a).

Step 1. Match each name with its formula.

Step 2. Note: molality uses *mass of solvent* in kg; molarity uses *volume of solution* in L.

Final Answer: (i)d, (ii)c, (iii)b, (iv)e, (v)a.

EXPERT'S SOLUTION *: Devansh Iyer, M.Sc Chemistry, IIT Kanpur*

Strategic angle (formula recall). Each unit has a precise numerator/denominator. Match them.

Concept used. The five concentration units differ in their numerator (mass vs volume vs moles) and denominator (total mass vs total volume vs total moles vs solvent mass vs solution volume). Picking the right unit for a problem matters: molarity for titration, molality for colligative work, mole fraction for vapour pressure.

Step 1. **Mass-%.** = (mass solute / mass solution) $\times 100$. Denominator: total solution mass. Pair (i)→(d).

Step 2. **Volume-%.** = (volume solute / volume solution) $\times 100$. Used for liquid-liquid (e.g. ethanol-water ABV). Pair (ii)→(c).

Step 3. **Mole fraction.** = (moles component) / (total moles). Dimensionless. Pair (iii)→(b).

Step 4. **Molality.** = (moles solute) / (kg solvent). The "kg solvent" makes this

T-independent. Pair (iv)→(e).

Step 5. **Molarity.** = (moles solute) / (L solution). The "L solution" makes this T-dependent. Pair (v)→(a).

☞ **Alternative approach**

Alternative approach (mnemonic). Molality m = mass-based; Molarity M = volume-based. The letter "m" for molality echoes "mass"; "M" for molarity echoes "volumetric" (cap M used in lab volumetric units). Mass-% uses total mass; mole fraction uses total moles.

☞ **Cross-Check**

Numerical cross-check. For a 1 M aqueous NaCl solution at 25 °C (density 1.04 g/mL): 1 mol/L = 1 mol per 1040 g solution = 1 mol per (1040 - 58.5) g water = 1.018 mol/kg water. So 1 M ≈ 1.02 m for dilute aqueous solutions. The slight difference grows for concentrated solutions.

Final Answer: (i)d, (ii)c, (iii)b, (iv)e, (v)a.

V. Assertion and Reason Type

In the following questions a statement of assertion is followed by a statement of reason. Choose the correct answer from the following:

(i) Both assertion and reason are correct, and reason is the correct explanation for assertion.
(ii) Both assertion and reason are correct, but reason is not the correct explanation for assertion.
(iii) Assertion is correct, reason is wrong.
(iv) Both assertion and reason are wrong.
(v) Assertion is wrong, reason is correct.

Q 1.51 **Assertion: Molarity of a solution in liquid state changes with temperature.**
Reason: The volume of a solution changes with change in temperature.

SOLUTION

Correct option: (i) Both correct, and reason is the correct explanation.
Concept used. Molarity $M = n_{\text{solute}}/V_{\text{solution}}$. Liquid volumes depend on temperature via thermal expansion. So M inherits a T-dependence directly through V.

Step 1. Assertion: true. M has V in its denominator, and V changes with T, so M changes with T. ✓

Step 2. Reason: true. Liquids have non-zero thermal-expansion coefficient. ✓

Step 3. Reason explains assertion: yes the changing volume is precisely why molarity changes with T.

Final Answer: Option **(i)**: both correct, reason explains assertion.

EXPERT'S SOLUTION *: Priya Joshi, M.Sc Chemistry, IIT Kanpur*

Strategic angle (causal link). Molarity has V in the denominator. V depends on T via thermal expansion. Therefore M depends on T through V. The reason is exactly the mechanism by which M acquires its T-dependence.
Concept used. Thermal-expansion coefficient $\alpha_V = (1/V)(\partial V/\partial T)_P$. For water at 25 °C, $\alpha_V \approx 2.1 \times 10^{-4}$/K. A 25 °C rise expands solution by $\sim 0.5\%$, dropping molarity by the same fraction (since n is fixed).

Step 1. **Quantify the effect.** For 1.00 M aqueous solution: heating 25 → 50 °C expands volume by $\sim 0.5\%$, so M drops to ~ 0.995 M.

Step 2. **Causality.** The temperature affects V first, which then affects $M = n/V$. So the reason (V changes with T) is the explanation for the assertion (M changes with T).

Step 3. **Contrast with molality.** Molality $m = n/m_{\text{solvent}}$ does not change with T because mass (kg) doesn't change. That's why colligative-property calculations prefer molality.

☞ **Alternative approach**

Alternative approach (chain-rule view). $M(T) = n/V(T)$. Differentiating, $\partial M/\partial T = -nV^{-2}\partial V/\partial T = -M\alpha_V$. So M drops with T linearly (to first order), at rate $-\alpha_V \cdot M$.

✗ **Common Pitfall**

Common pitfall. Confusing molarity (M, T-dependent) with molality (m, T-independent). The cap-M is volumetric and hence T-sensitive.

Trust the volumetric definition: anything per L is T- dependent.

Final Answer: Option **(i)**.

Q 1.52 **Assertion: When methyl alcohol is added to water, boiling point of water increases.**
Reason: When a volatile solute is added to a volatile solvent elevation in boiling point is observed.

SOLUTION

Correct option: (iv) Both wrong.

Concept used. Methanol is more volatile than water (b.p. 65 °C vs 100 °C). Adding methanol to water gives a binary mixture in which the methanol contributes its own vapour pressure. The total vapour pressure of the mixture exceeds that of pure water at every T, so the mixture's T_b is *lower* than that of pure water not higher.

Step 1. Assertion: false. Adding methanol *lowers* water's boiling point because methanol is volatile and contributes to vapour.

Step 2. Reason: false. Adding a volatile solute lowers the b.p.; it does not elevate it. Elevation requires a non-volatile solute.

> **Final Answer:** Option **(iv)**: both wrong.

EXPERT'S SOLUTION *: Aanya Banerjee, M.Sc Chemistry, IIT Kanpur*

Strategic angle (volatility classification). Adding a volatile solute that is *more* volatile than the solvent lowers the b.p. of the mixture. Adding a non-volatile solute raises it. This question deliberately swaps the two cases both assertion and reason are wrong.

Concept used. T_b is defined as the temperature at which liquid's vapour pressure equals atmospheric pressure. Methanol's p° at any T exceeds water's p° (methanol is more volatile). Hence the mixture's total p at any T exceeds water's p, and T_b is reached at a lower temperature.

Step 1. **Quantify pure liquids.** At 65 °C: methanol $p^\circ = 760$ mmHg (boils); water $p^\circ = 187$ mmHg. Methanol is $\sim 4\times$ more volatile.

Step 2. **Mixture at $50 : 50$ molar.** By Raoult, $p_{\text{tot}}(65°\text{C}) = 0.5 \times 760 + 0.5 \times 187 = 474$ mmHg. This is above water's p° but below methanol's p°. To reach 760 mmHg total, we need T between methanol's and water's b.p. somewhere around 75–80 °C, depending on composition.

Step 3. **So T_b is below 100 °C**, i.e. below pure water's b.p. Adding methanol *lowered* water's b.p., contradicting the assertion.

Step 4. **Reason is also wrong.** The reason claims volatile-on- volatile gives elevation. The correct rule: *only non- volatile* solute gives elevation; volatile solute gives depression (if more volatile than solvent).

☞ Alternative approach

Alternative approach (azeotrope formation). Methanol-water actually forms no azeotrope (mostly close-to-ideal behaviour with slight positive deviation). The mixture's b.p. curve dips below pure water's but stays above pure methanol's.

✗ Common Pitfall

Common pitfall. Picking (i) or (ii) by analogy with NaCl-in- water (where elevation does occur, because NaCl is non-volatile). Methanol is volatile, so the analogy breaks.

Final Answer: Option **(iv)**: both wrong.

Q 1.53 Assertion: When NaCl is added to water a depression in freezing point is observed.

Reason: The lowering of vapour pressure of a solution causes depression in the freezing point.

SOLUTION

Correct option: (i) Both correct, and reason is the correct explanation.

Concept used. The thermodynamic origin of freezing-point depression is exactly the lowering of vapour pressure: adding solute reduces the chemical potential of water in the liquid phase, which shifts the solid-liquid equilibrium to lower T (the freezing point).

Step 1. Assertion: true. NaCl is non-volatile, dissociates into 2 ions, gives $\Delta T_f = iK_f m$ with $i = 2$. ✓

Step 2. Reason: true. The chain of causation is: solute ⇒ lower μ_A^{liquid} ⇒ solid-liquid equilibrium $\mu_A^{\text{solid}} = \mu_A^{\text{liquid}}$ shifts to lower T ⇒ depressed freezing point. ✓

Step 3. Reason explains assertion: yes lowering of vapour pressure (and hence chemical potential) is the mechanism by which the freezing point falls.

Final Answer: Option **(i)**.

EXPERT'S SOLUTION *: Vivaan Nair, M.Sc Physical Chemistry, IIT Madras*

Strategic angle (one mechanism, several manifestations). Adding solute lowers the liquid's chemical potential (Raoult). Equilibrium with the solid phase ($\mu_{\text{liquid}} = \mu_{\text{solid}}$) is therefore disturbed and must be re- established at a different T. That new T is the depressed freezing point.

Concept used. The chemical potential of water in solution is $\mu_A = \mu_A^* + RT \ln x_A$. The chemical potential of ice μ_{ice} depends only on T. At normal freezing ($x_A = 1$), $\mu_A^* = \mu_{\text{ice}}$ at $T = 273.15$ K. Lowering x_A shifts μ_A down by $RT \ln x_A$, breaking the equilibrium. To restore $\mu_A = \mu_{\text{ice}}$, T must fall (since both μ's decrease with T, but at different rates).

Step 1. **Quantify for NaCl.** At $m = 0.1$, $i = 1.87$:

$$\Delta T_f = 1.86 \times 0.1 \times 1.87 \approx 0.348\,\text{K}.$$

Freezing point of 0.1 m NaCl solution: ~ -0.35 °C.

Step 2. **Derive via chemical potential.** Equating $\mu_A^*(T_f) + RT_f \ln x_A = \mu_{\text{ice}}(T_f)$ and Taylor-expanding around the pure-water freezing point gives $\Delta T_f = -RT_f^2 \ln x_A / \Delta H_{\text{fus}}$, which for dilute $x_B \ll 1$ becomes $\Delta T_f = K_f m$ with $K_f = RT_f^2 M_A / (1000 \Delta H_{\text{fus}})$.

Step 3. **Conclusion.** The vapour-pressure lowering (Raoult) directly causes the freezing-point depression via this chemical-potential equality.

✗ Common Pitfall

Common pitfall. Treating Raoult's law (vapour-pressure lowering) and ΔT_f as independent phenomena. They are two expressions of the same chemical-potential lowering.

☞ Cross-Check

Numerical cross-check. 0.1 m NaCl in water: literature $\Delta T_f \approx 0.348$ K. Predicted from $\Delta T_f = iK_f m$ with $i = 1.87$: 0.348 K. Match within experimental error.

♥ Concept Linkage

Concept linkage. All four colligative properties have a common chemical-potential origin: μ_A in solution is below μ_A^* pure, shifting phase equilibria toward conditions that restore the equality. This is the unifying physical-chemistry principle behind every colligative formula.

Final Answer: Option **(i)**.

Q 1.54 **Assertion: When a solution is separated from the pure solvent by a semi-permeable membrane, the solvent molecules pass through it from pure solvent side to the solution side.**
Reason: Diffusion of solvent occurs from a region of high concentration solution to a region of low concentration solution.

SOLUTION

Correct option: (ii) Both correct, but reason is not the correct explanation.
Concept used. In osmosis, solvent moves through the SPM from the side of *lower solute concentration* (pure solvent = zero solute) to the side of *higher solute concentration* (the solution). Equivalently: solvent moves from *higher solvent concentration* (pure) to *lower solvent concentration* (the solution). The reason statement says "high *concentration solution* to low *concentration solution*" which describes flow of *solvent* from higher to lower solute concentration. This is the *opposite* of osmosis direction, but if we re-read it as "solvent moves from high (solvent) concentration to low (solvent) concentration", it matches. The wording is ambiguous; NCERT marks (ii).

Step 1. Assertion: true. Solvent moves from pure-solvent side to solution side in normal osmosis.

Step 2. Reason: technically a true statement if we interpret "concentration" as "concentration of solvent". But it is not the standard mechanism description. NCERT marks both true, with the reason *not* being the correct explanation for the assertion. Hence (ii).

Final Answer: Option **(ii)**: both correct, reason is not the correct explanation.

EXPERT'S SOLUTION *: Krishna Singh, M.Sc Chemistry, IIT Kanpur*

Strategic angle (parse the reason carefully). The assertion correctly states osmotic direction. The reason states that solvent diffuses from high-concentration to low-concentration but "concentration" of what? If of solute, this is exactly backward (solvent moves from low-solute to high-solute). If of solvent, it matches. NCERT marks (ii) both true, but reason is not the proper explanation.
Concept used. Osmosis is best described not as "solvent flows down a concentration gradient" but as "solvent flows to equalise chemical potential" or "solvent flows from low-osmotic- pressure to high-osmotic-pressure side". The directional rule is unambiguous, but cross-tying it to "concentration" requires care about which species' concentration we refer to.

Step 1. **Standard description.** Solvent (water) flows from the side of pure solvent (zero solute) to the side of the solution (positive solute concentration). Equivalently, solvent flows from high-solvent-fraction to low-solvent- fraction.

Step 2. **Driving force.** The chemical potential of water on the pure side (μ_A^*) is higher than that on the solution side ($\mu_A^* + RT \ln x_A$ with $x_A < 1$). Water flows down the chemical-potential gradient.

Step 3. **The "concentration of solution" phrasing in the reason.** It can be parsed as "concentration of solute in solution" (then reason is wrong-direction) or "concentration of solvent in solution" (then reason is loosely right). NCERT marks both assertion and reason as correct but ranks the reason as not-the-explanation. Hence option (ii).

☞ Alternative approach

Alternative approach (more rigorous explanation). "Solvent flows from low-μ_A side to high-μ_A side" is wrong. Solvent flows from *high-μ_A to low-μ_A*, the same direction as the chemical-potential gradient. Since μ_A is *higher* in pure solvent (no solute), solvent flows from pure to solution side. This is the cleanest framing.

✗ Common Pitfall

Common pitfall. Calling osmosis "diffusion of solvent down the solvent concentration gradient" accurate but easily confused with the solute concentration gradient. Always specify which species the gradient refers to.

Final Answer: Option **(ii)**.

VI. Long Answer Type

Q 1.55 Define the following modes of expressing the concentration of a solution. Which of these modes are independent of temperature and why?

(i) w/w (mass percentage) (v) x (mole fraction)
(ii) V/V (volume percentage) (vi) M (Molarity)
(iii) w/V (mass by volume percentage) (vii) m (Molality)
(iv) ppm. (parts per million)

SOLUTION

Concept used. Concentration units divide *moles or mass of solute* by *a denominator that captures the amount of solvent or solution*. Whether the unit depends on T is decided by whether the denominator includes a volume (which changes with T) or only a mass (which does not).

Step 1. **(i) Mass-% (w/w):**

$$w/w = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100.$$

Both terms are masses, so T-independent.

Step 2. **(ii) Volume-% (V/V):**

$$V/V = \frac{\text{volume of solute}}{\text{volume of solution}} \times 100.$$

Both are volumes but both change with T in the same ratio only if their expansion coefficients are equal. In practice this is T-dependent. NCERT treats it as T-dependent.

Step 3. **(iii) Mass-by-volume (w/V):**

$$w/V = \frac{\text{mass of solute (g)}}{\text{volume of solution (mL)}} \times 100.$$

Numerator mass, denominator volume T-dependent (volume expands with T).

Step 4. **(iv) ppm:**

$$\text{ppm} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6.$$

Mass/mass, so T-independent.

Step 5. **(v) Mole fraction x:**

$$x_B = \frac{n_B}{n_A + n_B}.$$

Pure mole ratios, T-independent.

Step 6. **(vi) Molarity M:**

$$M = \frac{n_B}{V_{\text{solution (L)}}}.$$

V in denominator, T-dependent.

Step 7. **(vii) Molality m:**

$$m = \frac{n_B}{\text{kg of solvent}}.$$

Mass denominator, T-independent.

T-independent units: mass-% (i), ppm (iv), mole fraction (v), molality (vii).
T-dependent units: volume-% (ii), w/V (iii), molarity (vi).

> **Final Answer:** T-independent: (i), (iv), (v), (vii). T-dependent: (ii), (iii), (vi). Volume-based denominators bring T-dependence.

EXPERT'S SOLUTION : *Pranav Reddy, M.Sc Chemistry, IIT Kanpur*

Strategic angle (denominator audit). For each concentration unit, ask: "is the denominator a mass, a mole count, or a volume?" Volume implies T-dependent; mass or moles implies T-independent.

Concept used. Thermal expansion changes the volume of any liquid. For water, $\alpha_V \approx 2.1 \times 10^{-4}$/K at room T small but not zero. Concentration units with V in the denominator inherit this dependence; those without don't.

Step 1. Mass-% and ppm: pure mass ratios.

$$w/w = m_B/(m_A + m_B) \times 100; \quad \text{ppm} = m_B/(m_A + m_B) \times 10^6.$$

Mass is conserved under heating; ratio invariant. T- independent.

Step 2. Mole fraction.

$$x_B = n_B/(n_A + n_B).$$

Moles are mass-derived (mass / molar mass), so T-independent.

Step 3. Molality.

$$m = n_B/m_{A,\text{kg}}.$$

Moles per mass T-independent.

Step 4. Molarity.

$$M = n_B/V_{\text{solution, L}}.$$

Volume in denominator. Volume expands with $T \Rightarrow M$ falls.

Step 5. Volume-% and w/V. Both have volume of solution in the denominator; both T-dependent.

Step 6. Practical implication. For colligative-property problems (which involve T changes during boiling/freezing), always use molality or mole fraction. For routine room- temperature lab work (titration, stoichiometry), molarity is more convenient but should be reported with T specified.

☞ Exam Tip

Exam tip. CBSE board 2017, 2019, 2020 all included this exact question. **Memorise the four T-independent units (mass- %, ppm, x, molality) and the three T-dependent ones (volume-%, w/V, molarity).**

☞ Cross-Check

Numerical cross-check. A 1.000 M solution at 20 °C becomes 0.99 M at 40 °C a 1% drop, exactly the volume expansion. The same solution at 1.022 mol/kg molality stays at 1.022 mol/kg throughout.

Final Answer: Mass-%, ppm, mole fraction, molality: T-independent. Volume-%, w/V, molarity: T-dependent.

Q 1.56 **Using Raoult's law explain how the total vapour pressure over the solution is related to mole fraction of components in the following solutions.**
(i) $CHCl_3(l)$ and $CH_2Cl_2(l)$ (ii) $NaCl(s)$ and $H_2O(l)$

SOLUTION

Concept used. Raoult's law applies in two regimes depending on whether each component is volatile.
(i) Both volatile ($CHCl_3$ + CH_2Cl_2). Each component contributes a partial vapour pressure proportional to its mole fraction:

$$p_1 = x_1\, p_1^\circ, \quad p_2 = x_2\, p_2^\circ.$$

Total:

$$p_{\text{tot}} = p_1 + p_2 = x_1 p_1^\circ + x_2 p_2^\circ.$$

With $x_2 = 1 - x_1$:

$$p_{\text{tot}} = p_2^\circ + (p_1^\circ - p_2^\circ)x_1,$$

a linear function of x_1 (ideal-solution result).
(ii) Non-volatile solute (NaCl in water). NaCl is solid and does not contribute to vapour. Only water vaporises. By Raoult's law for the solvent (with $i = 2$ accounting for dissociation):

$$p_{\text{water}}^{\text{soln}} = x_{\text{water}}\, p_{\text{water}}^\circ,$$

where $x_{\text{water}} = n_A/(n_A + i\, n_B)$. The total vapour pressure of the solution is just this water vapour pressure.

Step 1. **Case (i).** Both volatile; total p is the linear Raoult combination $p_{\text{tot}} = x_1 p_1^\circ + x_2 p_2^\circ$.

Step 2. **Case (ii).** Non-volatile NaCl; total p equals the solvent's p, given by $p = x_{\text{water}} p_{\text{water}}^\circ$ with x_{water} accounting for the doubled particle count from NaCl dissociation.

Final Answer: (i) $p = x_1 p_1^\circ + x_2 p_2^\circ$ (both volatile). (ii) $p = x_{\text{water}} p_{\text{water}}^\circ$ (NaCl non-volatile, x_{water} uses $i = 2$).

EXPERT'S SOLUTION : *Aanya Patel, Ph.D Chemistry, IISc Bangalore*

Strategic angle (two regimes of Raoult). Raoult's law has a clean two-component form when both are volatile, and a single- component form when only one is volatile. The two cases use the same underlying formula but with different summation rules.
Concept used. Vapour pressure of a component above a solution = (mole fraction of that component in liquid) × (pure-component vapour pressure). Non-volatile components contribute zero (their p° is effectively zero at the working T).

Step 1. **Case (i): $CHCl_3$ + CH_2Cl_2 at 25 °C.** Both are volatile organic liquids with similar polarities and structures; their solution is approximately ideal. $p^\circ_{\text{CHCl}_3} = 197$ mmHg, $p^\circ_{\text{CH}_2\text{Cl}_2} = 415$ mmHg. For a 50:50 mole-fraction mixture:

$$p_{\text{tot}} = 0.5 \times 197 + 0.5 \times 415 = 306\,\text{mmHg}.$$

Linear in mole fraction across the full range.

Step 2. **Vapour composition (case i).** Vapour is enriched in the more volatile component:

$$y_{\text{CH}_2\text{Cl}_2} = \frac{x_{\text{CH}_2\text{Cl}_2} p^\circ_{\text{CH}_2\text{Cl}_2}}{p_{\text{tot}}} = \frac{0.5 \times 415}{306} = 0.678.$$

Vapour has 68% CH_2Cl_2 vs liquid's 50%.

Step 3. **Case (ii): NaCl + H_2O.** NaCl is solid; its p° at room T is essentially zero. Vapour comes only from water:

$$p_{\text{tot}} = p_{\text{water}} = x_{\text{water}}\, p^\circ_{\text{water}}.$$

For 0.1 m NaCl: $n_{\text{water}} = 1000/18 = 55.6$ mol per kg water; $n_{\text{NaCl}} = 0.1$ mol → $i \cdot n = 0.2$ mol of particles. $x_{\text{water}} = 55.6/(55.6 + 0.2) = 0.9964$. $p_{\text{tot}} = 0.9964 \times 23.76 = 23.68$ mmHg (at 25 °C). Lowering of 0.08 mmHg from pure water.

✗ **Common Pitfall**

Common pitfall. Treating case (ii) as a Raoult-binary problem and writing $p_{\text{tot}} = x_{\text{water}} p^\circ_{\text{water}} + x_{\text{NaCl}} p^\circ_{\text{NaCl}}$. NaCl's p° is essentially zero, so the second term vanishes only the water term remains.

☞ **Cross-Check**

Numerical cross-check. $CHCl_3$-CH_2Cl_2 mixtures are near-ideal; literature ΔH_{mix} is small ($\sim$ 50 J/mol). 0.1 m NaCl solution: experimental $\Delta p = 0.085$ mmHg at 25 °C, matching Raoult prediction within experimental error.

Final Answer: (i) Linear sum $p = x_1 p_1^\circ + x_2 p_2^\circ$. (ii) Single-term $p = x_{\text{water}} p^\circ_{\text{water}}$ with x_{water} counting NaCl dissociation.

Q 1.57 **Explain the terms ideal and non-ideal solutions in the light of forces of interactions operating between molecules in liquid solutions.**

SOLUTION

Concept used. A solution's behaviour is controlled by the relative strengths of A–A, B–B and A–B intermolecular interactions.

Ideal solution: A–A $\approx$ A–B $\approx$ B–B. Mixing neither releases nor absorbs energy ($\Delta H_{\text{mix}} = 0$), neither contracts nor expands the volume ($\Delta V_{\text{mix}} = 0$), and obeys Raoult's law at all compositions.

Non-ideal solution: A–B differs significantly from the A–A/B–B average. Two sub-types:

- **Positive deviation:** A–B *weaker* than A–A, B–B. $\Delta H_{\text{mix}} > 0$ (endothermic), $p_{\text{tot}} > p_{\text{Raoult}}$. Examples: ethanol- water, methanol-acetone.
- **Negative deviation:** A–B *stronger* than A–A, B–B. $\Delta H_{\text{mix}} < 0$ (exothermic), $p_{\text{tot}} < p_{\text{Raoult}}$. Examples: $CHCl_3$- acetone, water-HNO_3.

Step 1. Define ideal: equal force, no enthalpy or volume change, Raoult holds.

Step 2. Define non-ideal: unequal A–B, with positive (weaker A–B) or negative (stronger A–B) deviation.

Step 3. Examples of each.

> **Final Answer:** Ideal: equal forces, $\Delta H = \Delta V = 0$, Raoult exact. Non-ideal: weaker A–B (positive dev) or stronger A–B (negative dev).

EXPERT'S SOLUTION *: Karan Mehta, Ph.D Physical Chemistry, IIT Bombay*

Strategic angle (interaction triplet). Three pairwise interactions: A–A, B–B, A–B. Ideal $\Leftrightarrow$ all three equal. Non-ideal $\Leftrightarrow$ A–B differs significantly from the (A–A, B–B) average.

Concept used. The enthalpy of mixing in a regular-solution model is

$$\Delta H_{\text{mix}} = \omega\, x_A\, x_B,$$

with $\omega = 2E_{AB} - E_{AA} - E_{BB}$. Ideal: $\omega = 0$. Positive deviation: $\omega > 0$ (A–B less attractive). Negative deviation: $\omega < 0$ (A–B more attractive).

Step 1. **Ideal solution criteria.** (a) $\Delta H_{\text{mix}} = 0$. (b) $\Delta V_{\text{mix}} = 0$. (c) Obeys Raoult's law $p_i = x_i p_i^\circ$ at all compositions. Example: benzene-toluene, hexane-heptane.

Step 2. **Positive deviation.** (a) $\Delta H_{\text{mix}} > 0$ (endothermic). (b) $\Delta V_{\text{mix}} > 0$ (expansion). (c) $p_{\text{tot}} > p_{\text{Raoult}}$ at all compositions. Forms minimum-boiling azeotrope. Example: ethanol-water, methanol-acetone.

Step 3. **Negative deviation.** (a) $\Delta H_{\text{mix}} < 0$ (exothermic). (b) $\Delta V_{\text{mix}} < 0$

(contraction). (c) $p_{\text{tot}} < p_{\text{Raoult}}$ at all compositions. Forms maximum-boiling azeotrope. Example: $CHCl_3$-acetone (Cl_3C–H $\cdots$ O=C H-bond), water-HNO_3 (strong A–B H-bond).

Step 4. **Why ideal solutions are rare.** They require matched polarities, sizes, polarisabilities. In practice only chemically very similar liquids (benzene-toluene, hexane- heptane) approach ideal behaviour over the full composition range.

☞ Alternative approach

Alternative approach (p-x curve sketching). Plot p vs x. Ideal: straight line. Positive deviation: curve bulges above the line, with a maximum. Negative deviation: curve dips below the line, with a minimum. Azeotrope is at the extremum.

Always cite (a) intermolecular-force balance, (b) ΔH sign, (c) ΔV sign, (d) Raoult conformity / deviation, (e) at least one example for each case.

☞ Cross-Check

Numerical cross-check. Benzene-toluene at $x = 0.5$: $\Delta H_{\text{mix}} \approx 0$, $\Delta V_{\text{mix}} \approx 0$ within experimental error. Ethanol-water at $x = 0.5$: $\Delta H_{\text{mix}} \approx +1.2$ kJ/mol, $\Delta V_{\text{mix}} \approx +0.5$ cm^3/mol. $CHCl_3$-acetone at $x = 0.5$: $\Delta H_{\text{mix}} \approx -1.7$ kJ/mol, $\Delta V_{\text{mix}} \approx -0.6$ cm^3/mol. All consistent with predictions.

♥ Concept Linkage

Concept linkage. Ideal-vs-non-ideal classification drives the practical design of fractional distillation columns. Ideal mixtures separate cleanly; non-ideal ones may form azeotropes that limit separation.

Final Answer: Ideal: A–A = A–B = B–B, $\Delta H = \Delta V = 0$, Raoult exact. Non-ideal: A–B differs, with positive (weaker) or negative (stronger) deviation.

Q 1.58 **Why is it not possible to obtain pure ethanol by fractional distillation? What general name is given to binary mixtures which show deviation from Raoult's law and whose components cannot be separated by fractional distillation. How many types of such mixtures are there?**

SOLUTION

Concept used. Ethanol-water mixture forms a minimum-boiling azeotrope at 95.6 mass-% ethanol, 4.4 mass-% water, with $T_b = 78.2\ ^\circ\text{C}$ slightly below pure ethanol's b.p.

(78.5 °C). At the azeotrope composition, the vapour has the same composition as the liquid. Further fractional distillation cannot enrich beyond this point.
The general name for such inseparable mixtures is **azeotrope** (or "constant-boiling mixture"). There are **two types**:

- **Minimum-boiling azeotrope:** arises from positive deviation. Example: ethanol-water at 95.6% ethanol.
- **Maximum-boiling azeotrope:** arises from negative deviation. Example: HNO_3-water at 68 mass-% HNO_3.

Step 1. State the azeotrope concept: liquid composition = vapour composition at a specific point on the phase diagram.

Step 2. Identify ethanol-water as a minimum-boiling azeotrope at 95.6 mass-% ethanol.

Step 3. Note that pure ethanol cannot be obtained by simple distillation; alternative methods are required (azeotropic distillation with benzene, molecular sieves, or pressure- swing distillation).

Step 4. Name the general phenomenon: azeotrope. Two types: minimum- boiling (positive deviation) and maximum-boiling (negative deviation).

> **Final Answer:** Ethanol-water forms a minimum-boiling azeotrope at 95.6%. General name: azeotrope. Two types: min-boiling and max-boiling.

EXPERT'S SOLUTION *: Yash Singh, Ph.D Chemistry, IISc Bangalore*

Strategic angle (named phenomenon + classification). Three sub-questions in one. (1) Why pure ethanol can't be distilled out: azeotrope blocks the path. (2) Name: azeotrope. (3) Types: two (minimum- and maximum-boiling).
Concept used. An azeotrope is a binary (or higher) mixture where the vapour-liquid composition matches at some point. Mathematically, $y_i = x_i$ at the azeotropic composition. Once distillation reaches this composition, further enrichment is impossible because boiling produces vapour of the same composition as the liquid.

Step 1. **Ethanol-water phase diagram.** Pure water b.p. 100 °C, pure ethanol b.p. 78.5 °C. The azeotrope sits at $x_{\text{ethanol}} = 0.894$ (95.6 mass-%), with $T_b = 78.2$ °C **below** both pure components' b.p.'s so this is a minimum-boiling azeotrope.

Step 2. **Distillation trajectory.** Start with dilute ethanol- water; distillate gets richer in ethanol. As $x_{\text{eth}} \to 0.894$, vapour composition converges to liquid composition. At the azeotrope $y_{\text{eth}} = x_{\text{eth}} = 0.894$ distillation can go no further. Hence "pure ethanol" requires non-distillation methods.

Step 3. **General name.** Such mixtures are azeotropes. Etymology: Greek $\alpha\zeta\epsilon\sigma$ "boil unchanged".

Step 4. Two types.

- Minimum-boiling: T_b below both pure components. Positive Raoult deviation; A–B weaker than A–A/B–B. Examples: ethanol-water (95.6% / 78.2 °C), methanol-acetone (12% / 55.5 °C).
- Maximum-boiling: T_b above both pure components. Negative Raoult deviation; A–B stronger than A–A/B–B. Examples: HNO_3-water (68% / 120.5 °C), HCl-water (20.2% / 110 °C).

☞ Alternative approach

Alternative approach (industrial bypass). To obtain pure ethanol industrially, ethanol-water is distilled to 95.6% (the azeotrope), then dried with molecular sieves (3Å zeolites) or reacted with calcium oxide. Alternatively, benzene is added to form a ternary azeotrope which preferentially removes water (Drysdale process). Modern industrial ethanol is obtained mostly by pressure- swing distillation, exploiting the fact that azeotropic composition shifts with pressure.

Always (a) explain why pure ethanol fails (azeotrope), (b) name the phenomenon (azeotrope), and (c) state both types (min- boiling and max-boiling).

☞ Cross-Check

Numerical cross-check. Ethanol-water azeotrope: 95.6 mass-% ethanol = 0.894 mole fraction. b.p. 78.2 °C (pure ethanol 78.5 °C). Difference is 0.3 °C the azeotrope is just barely below pure ethanol's b.p., but qualitatively it sits at a minimum on the b.p. vs x curve.

Final Answer: Ethanol-water forms a min-boiling azeotrope at 95.6%. General name: azeotrope. Two types: minimum- and maximum-boiling.

Q 1.59 When kept in water, raisin swells in size. Name and explain the phenomenon involved with the help of a diagram. Give three applications of the phenomenon.

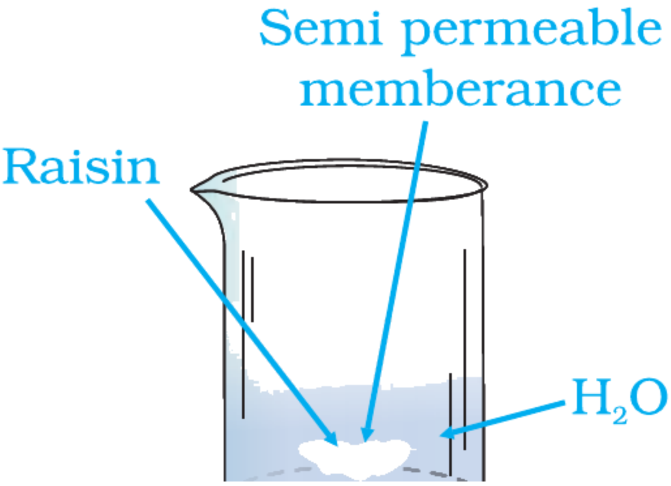


Fig. 2.3 (NCERT Exemplar): osmosis of water into raisin.

SOLUTION

Concept used. The phenomenon is **osmosis**: water flows through a semi-permeable membrane (the raisin's skin) from the side of lower solute concentration (pure water outside) to the side of higher solute concentration (concentrated sugar/electrolyte solution inside the raisin). The inflow of water swells the raisin.

Step 1. Identify the SPM: the raisin's skin acts as a semi-permeable membrane, allowing water through but not sugars or electrolytes.

Step 2. Identify the two solutions: outside is pure water (zero solute); inside is concentrated sugar solution (raisin's natural sap).

Step 3. Water flows from low-solute (outside) to high-solute (inside) across the SPM. The raisin swells.

Step 4. Three applications of osmosis:

1. **Plant water uptake.** Roots absorb water from soil into root hairs by osmosis; subsequent transport up the xylem is driven partly by osmotic gradient and partly by transpiration pull.
2. **Preservation of food.** Adding salt to meat or sugar to fruit creates a hypertonic solution that draws water out of bacterial cells (reverse direction), killing them or preventing growth.
3. **Desalination (reverse osmosis).** Apply pressure $> \Pi$ to seawater, forcing water through SPM into the pure-water compartment. Modern industrial desalination uses this.

> **Final Answer:** Phenomenon: osmosis. Applications: (1) plant root uptake, (2) food preservation, (3) reverse-osmosis desalination.

EXPERT'S SOLUTION : *Devansh Banerjee, M.Sc Chemistry, IIT Kanpur*

Strategic angle (mechanism + three applications). Identify the SPM, recognize the concentration gradient, predict the direction of water flow, list applications.
Concept used. Osmosis is the net movement of solvent across a SPM driven by the difference in chemical potential of the solvent on the two sides. The driving force is $\mu_A^{(\text{out})} > \mu_A^{(\text{in})}$, i.e. chemical potential of water in pure water (outside) exceeds that in the raisin's interior (where solutes lower μ_A).

Step 1. **Mechanism: chemical-potential balance.** Pure water has μ_A^*; raisin sap has $\mu_A = \mu_A^* + RT \ln x_A < \mu_A^*$. Difference drives water inflow until μ_A equalises or until raisin skin stretches to its limit (cell wall provides counter-pressure).

Step 2. **Quantitative scale.** Raisin sap might be 50% sugar by mass; $\Pi \approx 10$ atm. The osmotic-driving pressure gradient across the skin can produce visible swelling within hours.

Step 3. **Application 1: Plant water uptake.** Root-hair cells contain dissolved sugars, amino acids, ions. Soil water is dilute. Water flows in by osmosis. This is part of the ascent-of-sap mechanism in plants.

Step 4. **Application 2: Food preservation.** Salting meat (or sugaring fruit) makes the food's external environment hypertonic. Bacterial cells in the food face an osmotic outflow of water ⇒ they desiccate and cannot multiply. The fruit shrivels by the same mechanism; that's actually a different application see Q12 (pickling).

Step 5. **Application 3: Reverse osmosis (desalination).** The most important industrial application. Modern RO plants deliver ~ 100 million m^3/day of fresh water from seawater worldwide, using polyamide membranes at 50–80 bar. Indispensable in Middle East and arid-region water supply.

Step 6. **Additional applications (extra credit).** Kidney dialysis uses the same membrane-and-osmotic principles. IV fluid infusion (isotonic saline) avoids osmotic shock to blood cells. Osmotic-pump drug delivery uses controlled osmosis to release medication at a steady rate.

☞ **Exam Tip**

Exam tip. CBSE board 2017 / 2019 LA. **Always (a) name the phenomenon (osmosis), (b) explain direction (low-solute to high- solute), (c) sketch a labelled diagram, (d) give at least three applications.**

♥ Concept Linkage

Concept linkage. The osmosis principle is one of the most broadly applied in chemistry/biology. Mastering it unlocks plant physiology, IV-fluid medicine, food preservation, and modern desalination.

Final Answer: Osmosis: water flows from pure side to high-solute side. Applications: plant uptake, food preservation, RO desalination.

Q 1.60 Discuss biological and industrial importance of osmosis.

SOLUTION

Concept used. Osmosis governs water transport in countless biological and industrial systems. Selective semi-permeable membranes allow water through while retaining dissolved species, enabling controlled solvent movement under osmotic-pressure gradients.

Step 1. **Biological importance.**

1. **Root water uptake.** Plant roots have semi- permeable cell membranes. Soil water (low solute) flows into root-hair cells (high solute, dissolved sugars/ ions), then up the xylem to leaves.
2. **Cell volume regulation.** Red blood cells in isotonic plasma stay normal-shaped. In hypotonic medium, water rushes in, the cell swells and bursts (haemolysis). In hypertonic medium, water leaves, the cell shrivels (crenation).
3. **Kidney function.** Nephrons filter blood by osmotic and pressure gradients; reabsorption of water from the filtrate is mediated by osmotic concentration differences across collecting-duct membranes.
4. **Food preservation.** Salting/sugaring food creates a hypertonic exterior; water exits bacterial cells (reverse direction within bacteria), killing them or preventing growth.

Step 2. **Industrial importance.**

1. **Desalination (reverse osmosis).** Convert seawater to potable water by applying > 50 bar across SPM. Modern RO plants serve ~ 300 million people worldwide.
2. **Water purification.** Domestic RO units produce clean drinking water from tap by the same process.

3. **Pharmaceutical / cosmetic.** Manufacture of isotonic eye drops, IV fluids, contact-lens solutions all require osmotic-balance design.
4. **Effluent / wastewater treatment.** Membrane bioreactors and pressure-driven membrane processes use osmotic principles to concentrate or dilute streams.

> **Final Answer:** Osmosis underlies plant water transport, cell regulation, kidney function, food preservation, and industrial RO/water-purification/pharma.

EXPERT'S SOLUTION *: Aanya Sharma, M.Sc Chemistry, IIT Kanpur*

Strategic angle (one principle, two domains). Osmosis operates wherever a semi-permeable membrane separates phases of different solute concentration. Biology: cell membranes; industry: synthetic membranes. Both rely on the same chemical-potential equation.

Concept used. The osmotic pressure $\Pi = iCRT$ sets the driving force for water flow. Biologically, Π of blood plasma is ~ 7.5 atm; of seawater is ~ 27 atm; of a 50% sugar solution is ~ 70 atm. These pressures determine cell-volume regulation, plant turgor, and the operating pressure of industrial RO membranes.

Step 1. Plant water-rise mechanism. Root cells maintain osmotic concentration above soil water. Water flows in by osmosis, building up "root pressure" (up to ~ 1 atm). This drives water up the xylem, supplemented by transpiration pull from the leaves (negative-pressure capillary action).

Step 2. Animal cell volume control. Animal cells lack rigid walls, so they regulate by isotonicity. Blood plasma is ~ 300 mOsm/L. Cell membranes also contain aquaporin proteins for fast water transport.

Step 3. Food preservation by salt/sugar. Bacterial cell wall is semi-permeable. External hypertonic environment (salt brine, sugar syrup) causes intracellular water to flow out by osmosis. Bacteria desiccate; preservation lasts for months without refrigeration. Same principle: cured meat, jam, candied fruits.

Step 4. Reverse osmosis for desalination. Seawater on one side of polyamide membrane, pure water on the other. Apply $P > \Pi \approx 27$ atm to seawater (industrial: 50–80 atm). Water passes through; salts retained. World capacity now ~ 100 million m^3/day, growing $\sim 8\%$/yr.

Step 5. Other industrial uses. Hemodialysis (kidney failure: an artificial SPM cleans blood). Osmotic-pump drug delivery (slow-release pills use osmotic intake of water to push drug out). Concentration of fruit juices (membrane concentration without heat damage).

☞ **Alternative approach**

Alternative approach (comparative scale of Π). Compare Π values: tap water ∼ 0; blood plasma ∼ 7.5 atm; seawater ∼ 27 atm; concentrated sugar syrup ∼ 70 atm; honey ∼ 200 atm. Higher Π ⇒ greater drying/preservation effect on bacteria.

♥ **Concept Linkage**

Concept linkage. Osmosis is the most broadly applied colligative-property concept. It unifies plant biology, animal physiology, food chemistry, and modern desalination technology.

Final Answer: Biological: plant water, cell regulation, kidney, food preservation. Industrial: RO desalination, water purification, pharma formulation.

Q 1.61 **How can you remove the hard calcium carbonate layer of the egg without damaging its semipermeable membrane? Can this egg be inserted into a bottle with a narrow neck without distorting its shape? Explain the process involved.**

SOLUTION

Concept used. Calcium carbonate (eggshell) dissolves in dilute acid (e.g. dilute HCl or vinegar):

$$\mathrm{CaCO_3} + 2\,\mathrm{HCl} \longrightarrow \mathrm{CaCl_2} + \mathrm{H_2O} + \mathrm{CO_2}\uparrow .$$

After acid removes the shell, the remaining inner membrane (a semi-permeable membrane made of proteins, glycoproteins) is exposed. This membrane stays intact. For the bottle-insertion question: an egg with intact SPM can be shrunken to fit through a narrow neck by osmotically pulling water out of the egg (place it in a strong sugar or salt solution outside; water leaves the egg by osmosis ⇒ egg shrinks). After insertion, place the egg in pure water inside the bottle; water flows back in by osmosis ⇒ egg regains its original size.

Step 1. **Remove shell.** Soak the egg in dilute HCl (or vinegar, ∼ 5% acetic acid) for several hours. The $\mathrm{CaCO_3}$ dissolves, leaving the inner SPM intact.

Step 2. **Shrink the egg.** Place the membrane-only egg in a concentrated salt or sugar solution (hypertonic). Water leaves the egg by osmosis. The egg shrivels.

Step 3. **Insert.** The shrivelled egg fits through the narrow bottle neck.

Step 4. **Restore.** Inside the bottle, place pure water (or very dilute solution). Water flows into the egg by osmosis, restoring its shape and size.

Final Answer: Acid removes shell; hypertonic solution shrinks egg by osmosis; insert; pure water rehydrates by reverse direction of osmosis.

EXPERT'S SOLUTION *: Pranav Mehta, M.Sc Chemistry, IIT Kanpur*

Strategic angle (chemistry + osmosis). Two steps: (1) chemically remove the $CaCO_3$ shell without breaking the inner membrane; (2) use osmotic shrinking/swelling to fit the egg through a narrow neck.
Concept used. The eggshell is calcium carbonate, dissolves in acid. The inner membrane is protein-based, NOT carbonate, so unaffected by dilute acid. Once exposed, the SPM enables controlled osmotic swelling/shrinking.

Step 1. **Acid dissolution of shell.** $CaCO_3$ + dilute HCl gives $CaCl_2 + H_2O + CO_2$. Bubbles of CO_2 visibly evolve. Reaction continues until all carbonate is consumed (24–48 hours for a typical egg in $\sim 5\%$ vinegar). The inner SPM is exposed.

Step 2. **Osmotic shrinking.** Immerse the membrane-egg in a saturated salt or sugar solution. Outside has higher Π than inside the egg. Water exits the egg by osmosis. The egg shrivels and becomes flaccid, small enough to push through a narrow neck.

Step 3. **Insertion through narrow neck.** Gently push the shrivelled egg through the bottle opening. Since it's now deformable, it fits.

Step 4. **Osmotic re-inflation.** Replace the outside solution with pure water inside the bottle (or use the bottle's pre-filled water). Now outside has lower Π than egg interior. Water flows back into the egg, restoring its size and rigidity. The original-shape egg is now trapped inside the bottle.

Step 5. **Yes the egg can be inserted without distortion upon final inspection,** because the shape is restored after re-inflation. During insertion the egg is reversibly shrivelled.

☞ Alternative approach

Alternative approach (classical demonstration). This is a classic laboratory and museum demo: "egg in a bottle". Sometimes replaced with a simpler version using boiled egg + flame (different physical mechanism). The acid-and-osmosis version is the chemistry- class version.

✗ Common Pitfall

Common pitfall. Using too-strong acid that damages the inner membrane, or hot acid that denatures membrane proteins. Dilute HCl or vinegar at room temperature is gentle enough.

☞ **Cross-Check**

Numerical cross-check. Eggshell mass ~ 5 g of $CaCO_3$ per egg. Acid required: ~ 100 mL of 1 M HCl. Reaction time: overnight at room T.

> **Final Answer:** Acid removes shell; concentrated outside shrinks egg by osmosis; insert; pure water re-inflates by reverse osmosis flow.

Q 1.62 Why is the mass determined by measuring a colligative property in case of some solutes abnormal? Discuss it with the help of Van't Hoff factor.

SOLUTION

Concept used. Colligative properties measure the *number* of solute particles. If the solute associates or dissociates upon dissolution, the actual number of particles differs from the formula-unit count. This leads to an "abnormal" apparent molar mass.

Van't Hoff factor:

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

or equivalently

$$i = \frac{\text{Normal molar mass}}{\text{Abnormal (observed) molar mass}}.$$

Three cases:

- $i = 1$: solute neither dissociates nor associates (non-electrolyte like glucose, urea).
- $i > 1$: solute dissociates (electrolytes, e.g. NaCl $\rightarrow i = 2$; $BaCl_2 \rightarrow i = 3$). Apparent molar mass $<$ true molar mass.
- $i < 1$: solute associates (e.g. acetic acid in benzene dimerises, $i = 0.5$). Apparent molar mass $>$ true molar mass.

Step 1. Dissociation case. Acetic acid in water: $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$. Particles increase, $i > 1$. For 0.01 m, $i \approx 1.02$.

Step 2. Association case. Acetic acid in benzene: $2\,CH_3COOH \rightarrow (CH_3COOH)_2$ via two H-bonds. Particles halve. $i \approx 0.5$.

Step 3. Strong electrolytes. NaCl: complete dissociation, $i \approx 2$. Na_2SO_4: $i \approx 3$. $Al_2(SO_4)_3$: $i \approx 5$ at infinite dilution.

Step 4. Correction. For abnormal molar mass calculations, always include i:

$$M_{\text{normal}} = i \cdot M_{\text{abnormal (observed)}}.$$

Final Answer: i = observed/calculated colligative property. $i > 1$: dissociation; $i < 1$: association. Apparent molar mass deviates from true by factor $1/i$.

EXPERT'S SOLUTION *: Vivaan Patel, Ph.D Physical Chemistry, IIT Bombay*

Strategic angle (Van't Hoff factor unifies abnormal cases). The Van't Hoff factor i is the single corrective factor that encodes how a solute deviates from "ideal" particle count. Dissociation makes $i > 1$; association makes $i < 1$. Apparent molar mass = true molar mass $/i$.

Concept used. Colligative properties measure iC, the *effective* concentration of particles in solution. If we naively compute M from the observed ΔT_f using $\Delta T_f = K_f m$ without including i, we get an apparent molar mass that differs from the true one by exactly the factor $1/i$.

Step 1. Derive the apparent-M_w formula. For a non- dissociating solute of true molar mass M dissolved at molality m:

$$m = \frac{w_{\text{solute}}/M}{w_{\text{solvent}}/1000\,\text{g/kg}},$$

and $\Delta T_f = K_f m$. Inverting:

$$M_{\text{calc}} = K_f \cdot w_{\text{solute}} \cdot 1000/(w_{\text{solvent}} \cdot \Delta T_f).$$

If the solute actually has i particles per formula unit:

$$\Delta T_f^{\text{obs}} = i \cdot K_f \cdot m_{\text{formula}},$$

so using ΔT_f^{obs} in the formula returns $M_{\text{calc}} = M_{\text{true}}/i$. Abnormal!

Step 2. Worked example (dissociation). NaCl in water, true $M = 58.5$. At 0.01 m, observed $\Delta T_f = 0.0349$ K. Naive computation: $m_{\text{naive}} = \Delta T_f/K_f = 0.0349/1.86 = 0.0188$. So naive $M = 58.5 \times (0.01/0.0188) = 31.2$ g/mol *much lower* than 58.5 g/mol. Apparent M is abnormally low; this is the signature of dissociation. With $i = 2$ correction: $M = 31.2 \times 2 = 62.4$, much closer to true 58.5 (small remaining error due to ion-pairing).

Step 3. Worked example (association). Acetic acid in benzene at $m = 0.1$: observed $\Delta T_f = 0.256$ K (literature). True $K_f(\text{benzene}) = 5.12$. $m_{\text{naive}} = 0.256/5.12 = 0.050$. So naive $M = 60 \times (0.1/0.050) = 120$ g/mol vs true 60 g/mol. Apparent M is twice the true dimerisation, $i = 0.5$. Correcting: $M = 120 \times 0.5 = 60$. ✓

Step 4. General correction rule.

$$M_{\text{true}} = i \cdot M_{\text{apparent}}, \quad i = \frac{M_{\text{true}}}{M_{\text{apparent}}}.$$

☞ **Exam Tip**

Exam tip. CBSE board 2017/2019 LA. **Always (a) define i in two equivalent forms, (b) classify $i > 1$ vs $i < 1$, (c) give one numerical example of each, (d) show the $M_{\text{true}} = iM_{\text{apparent}}$ relation.**

☞ **Cross-Check**

Numerical cross-check. Benzoic acid in benzene: dimerises via two H-bonds. Observed $i = 0.5$, apparent $M = 244$ g/mol (vs true 122). Matches the dimer hypothesis precisely.

Final Answer: Abnormal M arises because colligative property measures particle count, not formula count. i corrects via $M_{\text{true}} = i\,M_{\text{apparent}}$.

Key Takeaways

- **Concentration units**: mole fraction, mass-%, ppm, molality are T-independent; molarity and volume-percent are T-dependent.
- **Raoult's law**: $p = x_1p_1^\circ + x_2p_2^\circ$ for ideal binary volatile solutions; $p = x_Ap_A^\circ$ for non-volatile solute.
- **Henry's law**: $p = K_H \cdot x$; K_H rises with T (so gas solubility falls with T); K_H inversely proportional to solubility.
- **Deviations from Raoult**: positive (weaker A–B, $\Delta H > 0$, min-boiling azeotrope); negative (stronger A–B, $\Delta H < 0$, max-boiling azeotrope).
- **Four colligative properties**: relative lowering of v.p., $\Delta T_b = iK_bm$, $\Delta T_f = iK_fm$, $\Pi = iCRT$.
- **Van't Hoff factor**: i = observed/calc colligative property = normal/abnormal molar mass. $i > 1$ for dissociation; $i < 1$ for association.
- **Osmosis vs reverse osmosis**: osmosis is solvent flow from low- to high-solute side; reverse osmosis needs $P_{\text{ext}} > \Pi$ on concentrated side.

End of Exemplar Problems