Collegedunia NCERT Solutions

Step-by-step solutions, alternate methods & exam tips for Class 12 Chemistry

Chapter 1: Solutions

About this Chapter

This chapter studies **solutions**: homogeneous mixtures of two or more components. We learn how to express concentration (mass %, mole fraction, molarity, molality), use **Henry's law** for gases in liquids and **Raoult's law** for liquid mixtures, distinguish ideal from non-ideal behaviour, and compute the four **colligative properties**: lowering of vapour pressure, elevation of boiling point, depression of freezing point and osmotic pressure. Abnormal molar masses are corrected using the van't Hoff factor i.

Topics covered: Types of solutions • Concentration units • Solubility • Henry's law • Raoult's law • Ideal vs non-ideal solutions • Colligative properties • van't Hoff factor

Quick Formula Sheet

Mole fraction:
$$x_A = \frac{n_A}{n_A + n_B}$$

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

Henry's law: $p = K_H\, x$

Raoult's law: $p_A = p_A^\circ x_A$

Relative lowering:
$$\frac{p^\circ - p_s}{p^\circ} = x_{\text{solute}}$$

Elevation & Depression:
$$\Delta T_b = K_b m,\quad \Delta T_f = K_f m$$

Osmotic pressure: $\pi = CRT$

van't Hoff factor:
$$i = \frac{\text{observed property}}{\text{calculated property}}$$

Chapter 1 Exercises

Q 1.1 **Define the term *solution*. How many types of solutions are formed? Write briefly about each type with an example.**

SOLUTION

Concept used. A **solution** is a homogeneous mixture of two or more chemically non-reacting substances whose composition can be varied within certain limits. The component present in the largest amount is called the **solvent** and decides the physical state of the solution; the other components are called **solutes**. In a binary solution there are only two components: one solute and one solvent.

> ☞ **Homogeneous vs heterogeneous**
>
> *Homogeneous* means the composition and properties (refractive index, density, concentration) are the same in every part of the sample. Salt water is homogeneous; sand in water is not.

Step 1. Classify by the physical state of solute and solvent. Since each of solute and solvent can be solid, liquid or gas, there are nine combinations, which group into three families based on the state of the solvent (which is the state of the solution).

Step 2. **Gaseous solutions** (solvent is a gas):

- gas in gas: a mixture of oxygen and nitrogen (air);
- liquid in gas: water vapour in air (humid air);
- solid in gas: iodine vapour or camphor vapour in air.

Step 3. **Liquid solutions** (solvent is a liquid):

- gas in liquid: oxygen dissolved in water;
- liquid in liquid: ethanol dissolved in water;
- solid in liquid: glucose dissolved in water (sugar syrup).

Step 4. **Solid solutions** (solvent is a solid):

- gas in solid: hydrogen absorbed in palladium;
- liquid in solid: amalgam of mercury with sodium;
- solid in solid: copper dissolved in gold (an alloy).

Solvent (state of solution) ⟶

	Gas	Liquid	Solid
Gas	O_2 + N_2 (air)	O_2 in water (dissolved O_2)	H_2 in Pd (metal hydride)
Liquid	Water vapour in air (humid)	Ethanol in water	Na in Hg (amalgam)
Solid	Camphor vapour in air	Glucose in water	Cu in Au (gold alloy)

Final Answer: A solution is a homogeneous mixture; nine types arise from the three possible solute states paired with the three solvent states, grouped into gaseous, liquid and solid solutions.

★ Why we focus on liquid solutions

NCERT discusses mostly liquid solutions because most biological, industrial and laboratory processes happen in liquid phase. The unifying idea is that the solvent dictates the physical state and the nature of intermolecular forces between solvent and solute decides how much solute will dissolve.

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

Structural angle. The cleanest mental picture is a 3×3 table indexed by the state of the solute (rows) and the state of the solvent (columns), which gives the nine canonical cases.

A binary solution mixes exactly two components and is the simplest case to study; the same ideas extend to ternary and higher mixtures. The key requirement is that the mixture be *homogeneous*, meaning no observable boundaries between regions of different composition, even under a microscope.

Step 1. **Gaseous solvent.** Any gas is miscible with any other gas in all proportions (no intermolecular forces strong enough to resist mixing). Liquids and solids enter a gaseous solvent only as their vapours: humid air contains water vapour; the smell of camphor in a room is camphor vapour dispersed in air.

Step 2. **Liquid solvent.** The most common laboratory case. Gases (O_2, CO_2) dissolve to varying extents in water. Two miscible liquids form a single phase (ethanol + water); immiscible liquids do not form a solution. Solids dissolve up to their solubility limit (glucose in water, NaCl in water).

Step 3. **Solid solvent.** Less obvious but very important. Hydrogen gas occupies the interstitial spaces of solid palladium. Liquid mercury soaks into solid sodium to form an amalgam. Two solids together form alloys: brass (Cu + Zn), bronze (Cu + Sn), gold jewellery (gold + copper). These are genuine solid solutions, not mere mixtures.

Alternative classification: by number of components. A *binary* solution has two components, a *ternary* has three, and so on. NCERT restricts attention to binaries because the ideas (mole fraction, Raoult's law, $\Delta_{\text{mix}}H$) extend naturally with no new physics, only more book-keeping. A second axis of classification is by particle size: *true solutions* (< 1 nm), *colloids* ($1 - 1000$ nm), and *suspensions* (> 1000 nm). The nine-cell table refers strictly to true solutions.

Concept linkage. The very definition of "solution" is deceptively rich. Homogeneity requires that thermodynamic intensive variables (density, refractive index, chemical potential of each species) be the same in every macroscopic sub-volume. That is exactly the condition for a *single thermodynamic phase* in the Gibbs phase rule, $F = C - P + 2$. So when we say "a solution is a homogeneous mixture", we are silently invoking the phase rule with $P = 1$.

Numerical cross-check. The textbook's nine examples (3×3) are not theoretical; they are the only combinations that exist in nature. Try to think of a tenth and you will find it collapses into one of the nine.

Why this matters. Recognising the type of solution sets expectations: gases dissolved in liquids obey Henry's law, two miscible liquids obey Raoult's law, and the colligative properties later in the chapter assume a solid (or non-volatile liquid) solute dissolved in a liquid solvent. JEE Main routinely asks one-mark "identify the type of solution" questions (e.g. JEE Main 2023 Jan 25 shift 2 listed "soda water" and asked the type of solution).

> **Final Answer:** Nine types of solutions, grouped under three families by the state of the solvent (gas, liquid, solid).

☞ One-mark classification

For any unfamiliar example, identify the *state of the solvent* first (the bulk phase you can see and touch). That fixes the family (gaseous/liquid/solid). Then identify the state of the solute. JEE and NEET both reuse this two-step in MCQs.

♥ Phase rule connection

A homogeneous solution is a single thermodynamic phase. Adding a second phase (oil in water, sugar precipitate in saturated syrup) moves the system out of the "solution" regime and into the **heterogeneous** regime governed by phase equilibria. The distinction matters because colligative laws (Raoult, Henry, $\pi = CRT$) apply only to the single-phase domain.

✗ Solution $\neq$ compound

A solution is a *mixture*, not a compound. Components retain their chemical identities (no new bonds formed); composition is variable; physical methods (distillation, evaporation) can separate them. Calling NaCl(aq) a "compound" costs marks.

Q 1.2 **Give an example of a solid solution in which the solute is a gas.**

SOLUTION

Concept used. A **solid solution** is a homogeneous mixture in which the solvent is a solid. When a gas dissolves in a solid, the gas atoms or molecules occupy the empty spaces between the host's atoms (**interstitial sites**) or replace some host atoms (**substitutional sites**), and the result is still a single solid phase.

Step 1. Identify a familiar gas-in-solid system. Hydrogen gas is readily absorbed by the metal palladium. The hydrogen atoms slip into the gaps of the palladium lattice without breaking it.

Step 2. State the system clearly: solvent is solid palladium; solute is gaseous hydrogen. Palladium can absorb up to about 935 times its own volume of hydrogen at room temperature, which is why it is used as a hydrogen storage medium.

Step 3. A second example is the dissolution of helium in titanium or the absorption of various gases by activated charcoal (though the latter is partly adsorption, not pure dissolution).

> **Final Answer:** Solution of hydrogen gas in palladium metal is a solid solution with a gaseous solute.

♥ **Where you meet this**

Hydrogen storage in metal hydrides for fuel cells, getter materials in vacuum tubes, and the embrittlement of steel by atmospheric hydrogen are all instances of gas-in-solid solutions.

EXPERT'S SOLUTION : *Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Quick reading. The textbook table of solution types lists nine entries; one of them is exactly the case asked here, "gas dissolved in solid", with the standard example "hydrogen in palladium".

Step 1. Definition restated: in a solid solution the solvent is solid and the solute can be solid, liquid or gas. We need the last case.

Step 2. Pick the textbook's stock example: solid Pd as solvent, H_2 gas as solute. Palladium's face-centred-cubic lattice has octahedral voids large enough to host hydrogen atoms after the H_2 molecule dissociates on the metal surface.

Step 3. State the result.

Alternative examples worth knowing. (i) H_2 in titanium or zirconium (used as "getter" materials in vacuum systems); (ii) O_2 or N_2 dissolved in solid metals during electrolytic refining; (iii) CO_2 trapped in solid H_2O as gas hydrate (strictly a clathrate but textbook treats it as a solid solution). Any of these qualifies as a gas-in-solid solution.
Concept linkage. Two structural mechanisms make a gas dissolve in a solid: *interstitial*

(small atoms like H, C, N, O occupying gaps between metal atoms) and *substitutional* (when the dissolved atom is comparable in size to the host, replacing host atoms). Hydrogen in Pd is purely interstitial because the H atom ($r \sim 0.5$ Å) is much smaller than the Pd atom ($r \sim 1.4$ Å).

Why this matters. Such "interstitial" solid solutions underlie hydrogen-storage alloys ($LaNi_5H_6$, Mg_2NiH_4) used in nickel-metal-hydride batteries. They also explain hydrogen embrittlement of steel (atomic H seeping into the iron lattice) and the reversible loading of H_2 in fuel-cell electrodes. NEET 2022 and JEE Main 2024 (Apr 6) both had MCQs of the form "which of the following is an example of solid solution where solute is a gas?" with H/Pd as the correct answer.

> **Final Answer:** Hydrogen in palladium (interstitial solid solution).

☞ Stock NEET/JEE example

If asked for any one example of "gas in solid", the safest answer on a board, JEE, or NEET sheet is H_2 in palladium. Acceptable alternates: H_2 in nickel/platinum.

✗ Adsorption $\neq$ absorption

Charcoal soaking up gases is *adsorption* (surface phenomenon), not a true solution. H_2 in Pd is genuine *absorption* (bulk phenomenon, gas atoms fill lattice gaps).

Q 1.3 Define the following terms: (i) Mole fraction (ii) Molality (iii) Molarity (iv) Mass percentage.

SOLUTION

Concept used. All four are quantitative ways to express the concentration of a solution. Each emphasises a different ratio (particles to particles, particles to mass, particles to volume, or mass to mass), and each has its own units and use cases.

Step 1. **Mole fraction** (x) is the ratio of the number of moles of a component to the *total* number of moles of all components in the solution:

$$x_A = \frac{n_A}{n_A + n_B + \cdots + n_i}.$$

It is dimensionless. For any solution $\sum_i x_i = 1$. Mole fraction is the natural variable for vapour-pressure relations (Raoult's and Henry's laws) because vapour pressure depends on the *number* of solute particles, not on their mass.

Step 2. **Molality** (m) is the number of moles of solute per kilogram of *solvent*:

$$m = \frac{n_{\text{solute}}}{w_{\text{solvent (kg)}}} \quad \text{unit: mol kg}^{-1}.$$

Because it uses mass of solvent (not volume of solution), molality is independent of temperature; this makes it the preferred unit for colligative properties such as ΔT_b and ΔT_f.

Step 3. **Molarity** (M) is the number of moles of solute per litre of *solution*:

$$M = \frac{n_{\text{solute}}}{V_{\text{solution (L)}}} \quad \text{unit: mol L}^{-1}.$$

Convenient in the laboratory (volumes are measured easily) but changes with temperature because the volume of a liquid depends on T.

Step 4. **Mass percentage** (% w/w) is the mass of a component as a percentage of the total mass of solution:

$$\text{mass \% of A} = \frac{w_A}{w_A + w_B} \times 100.$$

Common in commercial chemistry (e.g. “98% H_2SO_4”, “10% NaCl brine”), again temperature-independent.

> **Final Answer:** Mole fraction $= n_A/\sum n_i$; molality $m = n_{\text{solute}}/w_{\text{solvent (kg)}}$; molarity $M = n_{\text{solute}}/V_{\text{soln (L)}}$; mass % $= (w_A/w_{\text{total}}) \times 100$.

☞ Pick the right unit

For colligative properties prefer *molality* (T-independent). For titrations and stoichiometry use *molarity*. For partial pressures of vapours use *mole fraction*. For industrial recipes (cement, brine, bleach) use *mass percentage*.

EXPERT’S SOLUTION *: Aanya Mehta, M.Tech Chemical Engineering, IIT Delhi*

Strategic angle. Group the four units by “what is in the numerator” and “what is in the denominator”. Numerator can be moles or mass; denominator can be moles, mass or volume. That gives a table from which the four useful combinations drop out.

Step 1. Moles / moles ⇒ mole fraction $x_i = n_i/\sum n_j$. Dimensionless and additive ($\sum x_i = 1$).

Step 2. Moles / mass-of-solvent ⇒ molality $m = n_{\text{solute}}/w_{\text{solvent (kg)}}$. Units mol kg^{-1}.

Step 3. Moles / volume-of-solution ⇒ molarity $M = n_{\text{solute}}/V_{\text{soln (L)}}$. Units mol L^{-1}.

Step 4. Mass / total-mass ⇒ mass percentage $w\% = (w_A/w_{\text{total}}) \times 100$. Dimensionless.

Alternative bookkeeping units (worth knowing). Beyond the four NCERT-named units there are three more in routine use:

- **Parts per million** (ppm): mass-ratio $\times 10^6$. Used for trace pollutants (1 ppm

$= 10^{-4}\,\%$).

- **Volume percent** (% v/v): used for liquid-in-liquid mixtures where volumes are easier to measure (alcoholic drinks: "40% ABV").
- **Normality** (N): equivalents of solute per litre of solution. Standard in acid–base and redox titrations.

A *dimensional check* catches most algebra slips: any final expression for molarity must come out in mol L^{-1}, for molality in mol kg^{-1}, etc.

Concept linkage. Mole fraction is the right variable for vapour pressure because Raoult's and Henry's laws are *thermodynamic* statements about the chemical potential $\mu_i = \mu_i^\circ + RT \ln x_i$, which counts particles, not mass. By contrast, molality is the right variable for ΔT_f and ΔT_b because the cryoscopic and ebullioscopic constants K_f and K_b depend on the solvent's mass-based properties (latent heat per kg). Molarity is preferred whenever a volumetric pipette or burette is involved.

Numerical cross-check. For dilute aqueous solutions, $m \approx M$ because the density is ≈ 1 g mL^{-1} and the solute mass is small. The exact link is $M = m\rho/(1 + mM_w/1000)$, which reduces to $M \approx m$ when $mM_w \ll 1000$.

Why this matters. Confusing molarity with molality is a classic exam trap. They differ by a factor of solution density and the mass of solute; for dilute aqueous solutions at room temperature the two are numerically close, but never assume they are equal. NEET 2021 and JEE Main 2022 (July 25 shift 2) both had paired questions where a student had to flip between molarity and molality using density.

> **Final Answer:** Definitions as stated in the steps above.

✗ Molarity vs molality

Molarity uses *volume of solution*, molality uses *mass of solvent*. The two are equal numerically only when the solution is dilute aqueous and the density is exactly 1 g mL^{-1}. In hot solutions, in non-aqueous solvents, or at high concentration, the disparity is large.

☞ Quick formula card

$x = n_i/\sum n_j;\ \ m = n_s/w_{\text{solv (kg)}};\ \ M = n_s/V_{\text{soln (L)}};\ \ w\% = 100\,w_A/(w_A + w_B).$

Q 1.4 **Concentrated nitric acid used in laboratory work is 68% nitric acid by mass in aqueous solution. What should be the molarity of such a sample of the acid if the density of the solution is $1.504\,\mathrm{g/mL}$?**

SOLUTION

Concept used. **Mass percentage** tells us the mass of HNO_3 per 100 g of solution. **Density** converts mass of solution to volume of solution. The defining formula of molarity is

$$M = \frac{\text{moles of solute}}{\text{volume of solution in litres}} = \frac{w/M_w}{V/1000}.$$

Here w is mass of solute in grams, M_w is the molar mass of solute in g mol^{-1}, and V is the volume of solution in mL.

☞ **Molar mass of HNO_3**

$M_w(\mathrm{HNO_3}) = 1 + 14 + 3 \times 16 = 63\,\mathrm{g/mol}.$

Step 1. **Pick a convenient sample size.** Assume 100 g of solution. Mass of HNO_3 = 68 g and mass of water = 32 g.

Step 2. **Convert mass of HNO_3 to moles.**

$$n_{\mathrm{HNO_3}} = \frac{68}{63} = 1.0794\,\mathrm{mol}.$$

Step 3. **Convert mass of solution to volume of solution** using density.

$$V_{\text{soln}} = \frac{\text{mass}}{\text{density}} = \frac{100}{1.504} = 66.489\,\mathrm{mL} = 0.066\,489\,\mathrm{L}.$$

Step 4. **Apply the molarity formula.**

$$M = \frac{1.0794}{0.066489} = 16.23\,\mathrm{mol/L}.$$

Final Answer: Molarity of 68% HNO_3 solution $= 16.23\,\mathrm{mol/L}$ (often quoted as ≈ 16 M).

✗ Don't divide 68 by 100 mL

A common error is to use 100 mL as the solution volume. We chose 100 g (mass), and density converts it to about 66.5 mL. Mass and volume of solution are equal only if the density is 1.0 g mL^{-1}.

EXPERT'S SOLUTION : *Krishna Joshi, B.Tech Chemical Engineering, IIT Bombay*

Strategic angle. Use the compact "shortcut" that drops out of the four-step calculation:

$$M = \frac{10 \times (\text{mass }\%) \times d}{M_w},$$

where d is the density of solution in g mL^{-1} and M_w is the molar mass of solute in g mol^{-1}. This avoids picking a sample size each time.

Step 1. **Derive the shortcut.** Take 100 g of solution. Mass of solute $= w$ g, moles $= w/M_w$. Volume in litres $= (100/d)/1000 = 0.1/d$. Substituting,

$$M = \frac{w/M_w}{0.1/d} = \frac{10\,w\,d}{M_w},$$

and w here is numerically the mass percentage.

Step 2. **Plug in the values.**

$$M = \frac{10 \times 68 \times 1.504}{63} = \frac{1022.72}{63} = 16.23\,\text{mol/L}.$$

Step 3. **Sanity check.** Commercial concentrated HNO_3 is sold as ~ 16 M; our answer matches the reference value.

Why this matters. The shortcut $M = 10\,w\,d/M_w$ is one of the most reused formulae in titration chemistry: any time you are handed a (% by mass, density) pair, you can read off molarity in seconds. JEE Main 2021 (Feb 26 shift 1) directly tested this shortcut for HCl.

Final Answer: $M(\text{HNO}_3) = 16.23\,\text{mol/L}.$

☞ **The $10\,w\,d/M_w$ shortcut**

For any percentage-by-mass solution, molarity is $M = (10 \times \text{mass\%} \times d)/M_w$. The factor 10 absorbs the conversion “100 g / 1000 mL”. Memorise this; it saves a full sample-size step on three to four JEE/NEET problems every year.

♥ **Concentrated lab reagents**

Concentrated commercial reagents have characteristic molarities every chemistry student should recognise on sight: $HNO_3 \sim 16$ M, HCl ~ 12 M, $H_2SO_4 \sim 18$ M, $NH_4OH \sim 15$ M (as ammonia), glacial $CH_3COOH \sim 17$ M. A computed answer that drifts outside the $5 - 20$ M band is almost certainly wrong.

Q 1.5 **A solution of glucose in water is labelled as 10% w/w. What would be the molality and mole fraction of each component in the solution? If the density of solution is $1.2\,\text{g/mL}$, then what shall be the molarity of the solution?**

SOLUTION

Concept used. "10% w/w" means 10 g of glucose per 100 g of solution. From this single piece of data plus the molar masses, we can compute every concentration unit:

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

☞ **Molar masses**

$M_w(\text{glucose, } C_6H_{12}O_6) = 6(12) + 12(1) + 6(16) = 180\,\text{g/mol}.$
$M_w(H_2O) = 18\,\text{g/mol}.$

Step 1. Identify the masses. 100 g of solution contains 10 g glucose and 90 g water.

Step 2. Convert to moles.

$$n_{\text{glucose}} = \frac{10}{180} = 0.0555\,\text{mol}, \quad n_{\text{water}} = \frac{90}{18} = 5.0\,\text{mol}.$$

Step 3. Molality. Mass of solvent (water) $= 90$ g $= 0.090$ kg.

$$m = \frac{0.0555}{0.090} = 0.617\,\text{mol/kg}.$$

Step 4. Mole fractions. Total moles $= 0.0555 + 5.0 = 5.0555$.

$$x_{\text{glucose}} = \frac{0.0555}{5.0555} = 0.01098,$$

$$x_{\text{water}} = \frac{5.0}{5.0555} = 0.9890.$$

Check: $0.01098 + 0.9890 \approx 1.000$. ✓

Step 5. Molarity. Volume of solution: $V = 100/1.2 = 83.33\,\text{mL} = 0.083\,33\,\text{L}$.

$$M = \frac{0.0555}{0.08333} = 0.6666\,\text{mol/L} \approx 0.67\,\text{M}.$$

Final Answer: $m = 0.617\,\text{mol/kg}$; $x_{\text{glucose}} = 0.0110$, $x_{\text{water}} = 0.989$; $M = 0.67\,\text{mol/L}$.

☞ **Molality vs molarity**

For dilute aqueous solutions m and M are usually close (the density of solution is close to 1 g mL^{-1}). Here $d = 1.2$ g mL^{-1} makes M slightly larger than m, which is exactly what density greater than unity should do.

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

Strategic angle. The cleanest route is to fix the sample at 1 kg of solvent, because molality is exactly the moles of solute per kilogram of solvent. Then convert that same picture to volume to read off molarity.

Step 1. Take 1000 g of water. Since the solution is 10% w/w, glucose is $10/90$ as massive as water, so it weighs $10/90 \times 1000 = 111.11$ g.

Step 2. Moles of glucose $= 111.11/180 = 0.617$. Hence $m = 0.617$ mol per kg of water $= 0.617\,\text{mol/kg}$.

Step 3. Mole fraction of glucose: moles of water $= 1000/18 = 55.55$, total moles $= 56.17$, $x_{\text{glucose}} = 0.617/56.17 = 0.0110$, $x_{\text{water}} = 0.989$.

Step 4. For molarity, use the shortcut $M = \dfrac{10\,w\,d}{M_w} = \dfrac{10 \times 10 \times 1.2}{180} = 0.667\,\text{mol/L}$.

Why this matters. The same 10 % sugar syrup can be quoted as "0.6 M", "0.6 m" or "$x = 0.011$" depending on the unit. Carrying density along lets you flip between molarity and molality without losing information. JEE Main 2020 (Sept 5 shift 2) and NEET 2019 both featured glucose-in-water concentration conversions of this exact form.

Numerical cross-check. Since $d = 1.2 > 1$, we expect $M > m$ — confirmed ($0.667 > 0.617$). For a 10% solution $M/m = d/(1 - 0.1\,M_w/1000)$ approximately; substituting gives $M/m \approx 1.2/(1 - 0.018) \approx 1.22 \times d^{-1}$ — close to the observed ratio $0.667/0.617 = 1.08$. Density and water-mass correction together explain the small mismatch.

> **Final Answer:** $m = 0.617$ mol kg^{-1}, $x_{\text{glu}} = 0.0110$, $x_{\text{w}} = 0.989$, $M = 0.67$ mol L^{-1}.

☞ **Fix 1 kg solvent, not 100 g solution**

Choosing 1000 g of *solvent* as the basis collapses the molality calculation to a single division ($n_s/1$). Choosing 100 g of *solution* is better for molarity (uses density directly). Pick the basis that makes the next step trivial.

Q 1.6 How many mL of $0.1\,\text{M}$ HCl are required to react completely with 1 g mixture of Na_2CO_3 and $NaHCO_3$ containing equimolar amounts of both?

SOLUTION

Concept used. The neutralisation reactions are

$$\mathrm{Na_2CO_3 + 2\,HCl \longrightarrow 2\,NaCl + H_2O + CO_2},$$

$$\mathrm{NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2}.$$

So 1 mol of Na_2CO_3 consumes 2 mol HCl, while 1 mol of $NaHCO_3$ consumes 1 mol HCl.

☞ **Molar masses**

$M_w(\mathrm{Na_2CO_3}) = 2(23) + 12 + 3(16) = 106\,\mathrm{g/mol}$.
$M_w(\mathrm{NaHCO_3}) = 23 + 1 + 12 + 3(16) = 84\,\mathrm{g/mol}$.

Step 1. **Set up the equimolar condition.** Let n moles of each salt be present in the 1 g mixture. Then

$$106\,n + 84\,n = 1\text{ g} \implies 190\,n = 1 \implies n = \frac{1}{190} = 5.263 \times 10^{-3}\,\mathrm{mol}.$$

Step 2. **Total moles of HCl needed.**

$$n_{\mathrm{HCl}} = 2n_{\mathrm{Na_2CO_3}} + 1\,n_{\mathrm{NaHCO_3}} = 2n + n = 3n.$$

$3n = 3 \times 5.263 \times 10^{-3} = 1.579 \times 10^{-2}\,\mathrm{mol}$.

Step 3. **Convert moles of HCl to volume at 0.1 M.** $M\,V(\mathrm{L}) = n$, so

$$V = \frac{n}{M} = \frac{1.579 \times 10^{-2}}{0.1} = 0.1579\,\mathrm{L} = 157.9\,\mathrm{mL}.$$

Final Answer: Volume of 0.1 M HCl required $\approx 157.9\,\mathrm{mL}$.

✗ Equimolar does not mean equal mass

"Equimolar" means equal *moles*, not equal masses. Setting $w_{\mathrm{Na_2CO_3}} = w_{\mathrm{NaHCO_3}} = 0.5$ g would give the wrong answer. We must use the moles-equal condition $n = n$.

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

Strategic angle. Look at the average "molar mass per formula unit of mixture" and the average "mol of HCl per formula unit of mixture", so the answer reduces to a single division.

Step 1. For an equimolar mixture, the average molar mass is $\bar{M} = (106 + 84)/2 = 95\,\mathrm{g/mol}$. Moles of "mixture units" in 1 g: $n_{\mathrm{mix}} = 1/95$.

Step 2. Each "mixture unit" contains $\frac{1}{2}$ mol Na_2CO_3 and $\frac{1}{2}$ mol $NaHCO_3$, so it consumes $\frac{1}{2}(2) + \frac{1}{2}(1) = 1.5$ mol HCl.

Step 3. Total HCl needed: $n_{\mathrm{HCl}} = 1.5/95 = 0.01579$ mol. Volume at 0.1 M: $V = 0.01579/0.1 = 0.1579$ L $= 157.9$ mL.

Why this matters. Stoichiometry on a mixture is the same calculation as on a single substance, but you have to weight each contribution by its mole fraction. The "average molar mass” trick generalises to any mixture if you know the molar fractions. JEE Main 2019 (Apr 9 shift 1) recycled this exact mixture problem with different masses.

Final Answer: $V_{\text{HCl}} \approx 157.9$ mL.

☞ Average-molar-mass shortcut

For an equimolar binary mixture of two reactants, set $\bar{M} = (M_1 + M_2)/2$ and $\bar{\nu}_{\text{HCl}} = (\nu_1 + \nu_2)/2$. Then moles of HCl $= \bar{\nu}_{\text{HCl}} \cdot w_{\text{mix}}/\bar{M}$. Skips the simultaneous-equation step.

✗ “Equimolar” ≠ “equal mass”

Equimolar means equal moles, equal number of formula units. Splitting the 1 g mixture as 0.5 g + 0.5 g would be the equal-mass condition and gives a different (wrong) answer.

Q 1.7 **A solution is obtained by mixing 300 g of 25% solution and 400 g of 40% solution by mass. Calculate the mass percentage of the resulting solution.**

SOLUTION

Concept used. Mass is conserved on mixing. The total mass of solute after mixing is the sum of solute masses from the two solutions; the total mass of solution is the sum of the two solution masses. Then

$$\text{Mass \%} = \frac{\text{total solute mass}}{\text{total solution mass}} \times 100.$$

Step 1. Solute in first solution.

$$w_{\text{solute},1} = \frac{25}{100} \times 300 = 75 \text{ g}.$$

Step 2. Solute in second solution.

$$w_{\text{solute},2} = \frac{40}{100} \times 400 = 160 \text{ g}.$$

Step 3. Totals after mixing.

$$w_{\text{solute, total}} = 75 + 160 = 235 \text{ g},$$

$$w_{\text{solution, total}} = 300 + 400 = 700 \text{ g}.$$

Step 4. Mass percentage of solute.

$$\text{Mass \%} = \frac{235}{700} \times 100 = 33.57\%.$$

Step 5. Mass percentage of solvent $= 100 - 33.57 = 66.43\%$.

Final Answer: Mass % of solute $= 33.57\%$; mass % of solvent $= 66.43\%$.

☞ Weighted average shortcut

The new mass % is a mass-weighted average of the two starting percentages:

$$w_{\text{new}}\% = \frac{w_1 m_1\% + w_2 m_2\%}{w_1 + w_2} = \frac{300(25) + 400(40)}{700} = 33.57\%.$$

Useful whenever two solutions of the same solvent and solute are mixed.

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

Strategic angle. Mixing two solutions is a balance problem. Conserve solute mass and solvent mass independently, then take the ratio.

Step 1. Solute balance: $75 + 160 = 235$ g.

Step 2. Solvent balance: solvent in first $= 225$ g, in second $= 240$ g, total $= 465$ g.

Step 3. Total mass $= 235 + 465 = 700$ g.

Step 4. Mass % of solute $= 235/700 \times 100 = 33.57\%$; solvent $= 465/700 \times 100 = 66.43\%$.

Alternative check via weighted average. $w\%_{\text{new}} = (w_1 m_1 + w_2 m_2)/(w_1 + w_2) = (300 \cdot 25 + 400 \cdot 40)/700 = 23500/700 = 33.57\%$. Same answer, fewer arithmetic steps. The same logic gives the new mole fraction or molarity when two like solutions are blended.

Concept linkage. Two-stream blending is a special case of *macroscopic species balance*: solute in = solute out, solvent in = solvent out. For miscible solutions of the same solute the volume is approximately conserved as well, so $C_1V_1 + C_2V_2 = CV$ also works on a volume basis (Q24 uses this in disguise).

Why this matters. The two-stream mixing balance is the basic operation in industrial blending and in lab dilution by addition (not just by water). The shortcut formula above is the dilute-mixture analogue of $C_1V_1 + C_2V_2 = CV$. JEE Main 2018 (Apr 16 shift 1) posed a mass-blending problem identical in form to this one.

Final Answer: Solute 33.57%, solvent 66.43%.

☞ Mass-weighted average

For two solutions of the same solute mixed by mass, $w\%_{\text{mix}}$ is the mass-weighted average of the two starting percentages. No need to separately balance solvent and solute.

✗ Don't average percentages directly

$(25+40)/2 = 32.5\%$ would only be correct if equal masses of the two solutions were mixed. For 300 g + 400 g, the larger volume of 40% solution pulls the average above 32.5% (here 33.57%). Always weight by mass.

Q 1.8 **An antifreeze solution is prepared from $222.6\,\text{g}$ of ethylene glycol ($C_2H_6O_2$) and $200\,\text{g}$ of water. Calculate the molality of the solution. If the density of the solution is $1.072\,\text{g/mL}$, then what shall be the molarity of the solution?**

SOLUTION

Concept used. Molality uses mass of solvent in kilograms; molarity uses volume of solution in litres. We compute each from its definition.

☞ Molar mass of ethylene glycol

$M_w(\mathrm{C_2H_6O_2}) = 2(12) + 6(1) + 2(16) = 62\,\text{g/mol}.$

Step 1. Moles of solute.

$$n_{\text{EG}} = \frac{222.6}{62} = 3.5903\,\text{mol}.$$

Step 2. Molality. Mass of water = 200 g = 0.200 kg.

$$m = \frac{3.5903}{0.200} = 17.95\,\text{mol/kg}.$$

Step 3. Total mass of solution. $w_{\text{soln}} = 222.6 + 200 = 422.6$ g.

Step 4. Volume of solution from density.

$$V = \frac{w_{\text{soln}}}{d} = \frac{422.6}{1.072} = 394.21\,\text{mL} = 0.394\,21\,\text{L}.$$

Step 5. Molarity.

$$M = \frac{n_{\text{EG}}}{V} = \frac{3.5903}{0.39421} = 9.11\,\text{mol/L}.$$

Final Answer: $m = 17.95\,\text{mol/kg};\ M = 9.11\,\text{mol/L}.$

♥ Antifreeze in car radiators

A high concentration of ethylene glycol depresses the freezing point of the radiator water well below 0°C and elevates its boiling point, preventing the radiator from freezing in winter or boiling in summer. The colligative-property calculations later in the chapter quantify exactly this.

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

Structural observation. The single difference between molality and molarity is the denominator: mass of solvent versus volume of solution. Solute moles are common to both.

Step 1. Compute moles of ethylene glycol once: $222.6/62 = 3.59$ mol.

Step 2. Divide by mass of solvent in kg: $3.59/0.200 = 17.95$ m. Note: this is a very concentrated solution; $\sim 53\,\%$ by mass.

Step 3. Divide by volume of solution in L. Volume from density: $V = 422.6/1.072 = 394.2$ mL. $M = 3.59/0.3942 = 9.11$ mol L^{-1}.

Step 4. Compare: molarity $\ll$ molality here because at high concentration the solvent makes up a smaller fraction of the solution by mass, but the solute itself occupies real volume.

Why this matters. For dilute solutions $m \approx M$. For concentrated ones (this is ~ 9 M, ~ 18 m) they differ a lot and the choice of unit matters. JEE Main 2024 (Jan 30 shift 2) had a near-identical antifreeze/ethylene-glycol problem.

> **Final Answer:** $m = 17.95$ mol kg^{-1}; $M = 9.11$ mol L^{-1}.

☞ Recognise high-concentration solutions

When solute mass is comparable to solvent mass (here 222.6 g vs 200 g), the solution is far from dilute and $m \neq M$. Always compute both separately rather than approximating one from the other.

✗ Volume vs mass of solvent

Molality uses *mass of solvent* (kg), molarity uses *volume of solution* (L). Mixing the two is the most common arithmetic slip in this chapter.

Q 1.9 A sample of drinking water was found to be severely contaminated with chloroform ($CHCl_3$) supposed to be a carcinogen. The level of contamination was $15\,\text{ppm}$ **(by mass).**

(i) Express this in percent by mass.

(ii) Determine the molality of chloroform in the water sample.

SOLUTION

Concept used. **Parts per million** is defined as

$$\text{ppm} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6.$$

So 15 ppm by mass means 15 g of $CHCl_3$ in 10^6 g of solution. Percent by mass is the same ratio multiplied by 10^2, so it is ppm$/10^4$. Molality uses moles of solute per kilogram of solvent (here, water).

> ☞ **Molar mass of chloroform**
>
> $M_w(\text{CHCl}_3) = 12 + 1 + 3(35.5) = 119.5\,\text{g/mol}.$

Step 1. **Part (i): % by mass.** Convert 15 ppm to percent by dividing by 10^4.

$$\text{Mass }\% = \frac{15}{10^6} \times 100 = 1.5 \times 10^{-3}\,\%.$$

Step 2. **Part (ii): set up molality.** For a dilute aqueous sample the mass of solvent ≈ mass of solution. Take 1 kg of solution: this contains $15 \times 10^{-3} = 0.015$ g of $CHCl_3$ and (essentially) 1 kg of water.

Step 3. **Moles of chloroform.**

$$n_{\text{CHCl}_3} = \frac{0.015}{119.5} = 1.255 \times 10^{-4}\,\text{mol}.$$

Step 4. **Molality.**

$$m = \frac{1.255 \times 10^{-4}}{1\text{ kg}} = 1.255 \times 10^{-4}\,\text{mol/kg}.$$

Final Answer: (i) $1.5 \times 10^{-3}\%$ by mass. (ii) $m \approx 1.25 \times 10^{-4}\,\text{mol/kg}$.

★ ppm ⇔ %

Always: ppm $=$ (mass %) $\times 10^4$, equivalently (mass %) $=$ ppm$/10^4$. So 1 ppm $= 10^{-4}\,\%$, and $10\,000$ ppm $= 1\,\%$.

EXPERT'S SOLUTION *: Aditya Nair, M.Tech Chemical Engineering, IIT Madras*

Quick reading. For trace pollutants in water the dilute approximation $w_{\text{water}} \approx w_{\text{solution}}$ is essentially exact (the solute contributes nothing measurable to the total mass). That collapses the two parts of the problem to two short calculations.

Step 1. Mass percentage of $CHCl_3$: $(15/10^6) \times 100 = 1.5 \times 10^{-3}\,\%$.

Step 2. Molality. Take 1 kg of water; $CHCl_3$ present $= 0.015$ g. Moles

$= 0.015/119.5 = 1.255 \times 10^{-4}$. $m = 1.255 \times 10^{-4}$ mol kg^{-1}.

Numerical cross-check. Order-of-magnitude: 15 ppm chloroform in water $\sim 15 \times 10^{-6}$ mass fraction. Multiplied by water molality scale (~ 55.5 mol per kg water) and divided by $M_w(\mathrm{CHCl_3}) = 119.5$, we get $15 \times 10^{-6} \times 55.5/119.5 \times 1000 \approx 7 \times 10^{-3}$ mol/kg — wait, that overshoots. Redo carefully: 15 ppm by mass means 15 μg per gram of solution, $=15$ mg per kg solution ≈ 15 mg per kg water. So moles $= 0.015/119.5 = 1.26 \times 10^{-4}$ — consistent with the steps above.
Concept linkage. ppm, ppb, mass-%, mole fraction and molality are all linear in mass for dilute traces. The conversion factors are fixed by molar masses; remember *ppm → molality* via $m = \mathrm{ppm_{mass}} \times 10^{-3}/M_w$ (mol per kg water).
Why this matters. Drinking-water standards specify limits in μg L^{-1} or ppb, which are the same kind of ratio at a smaller scale ($1\,\mathrm{ppb} = 10^{-3}\,\mathrm{ppm} = 10^{-7}\,\%$). Knowing how to flip between them is a public-health basic. JEE Main 2022 and NEET frequently reuse "contaminant in ppm → molality" problems.

Final Answer: $1.5 \times 10^{-3}\,\%$ w/w; $m \approx 1.25 \times 10^{-4}$ mol kg^{-1}.

☞ **ppm shortcut**

For trace solutes in water at room temperature, $m \approx \dfrac{\text{ppm (by mass)}}{M_w \times 10^3}$ mol kg^{-1}. Comes from $w_{\text{solv}} \approx w_{\text{soln}}$ and unit conversions.

Q 1.10 What role does the molecular interaction play in a solution of alcohol and water?

SOLUTION

Concept used. Both ethanol (C_2H_5OH) and water (H_2O) are polar molecules with $-$OH groups, so before mixing each pure liquid is held together by strong **hydrogen bonds** (O$-$H $\cdots$ O). When alcohol and water are mixed, the new solution contains three kinds of interaction: water$-$water, alcohol$-$alcohol, and water$-$alcohol hydrogen bonds. The strength of the cross water$-$alcohol bond is *weaker* than the average of the two pure-liquid bonds, so the total interaction energy of the mixture is less negative than the sum of the pure-liquid energies.

$$H_2O \overset{\text{H-bond}}{\text{- - - - - - -}} H_2O \overset{\text{H-bond}}{\text{- - - - -}} C_2H_5OH \overset{\text{H-bond}}{\text{- - - -}} C_2H_5OH$$

water – alcohol H-bonds are weaker than pure water – water

Step 1. Before mixing: pure water has a very dense, three-dimensional H-bond network; pure ethanol has a similar but slightly weaker network (each ethanol has only one O$-$H, against water's two).

Step 2. On mixing, the H-bond network is partially broken because each ethanol molecule pushes water molecules apart with its bulky ethyl ($-C_2H_5$) group, but new water–alcohol H-bonds form. These new bonds are weaker than pure water's own bonds.

Step 3. Consequence: the solution exhibits **positive deviation from Raoult's law**. The escaping tendency (vapour pressure) of each component is higher than predicted by Raoult's law, because the molecules are less tightly held in the mixture than in their pure liquids.

Step 4. Energetics: $\Delta_{\text{mix}}H > 0$ (the mixture is *endothermic*; heat is absorbed) and $\Delta_{\text{mix}}V > 0$ (slight volume increase on mixing).

> **Final Answer:** Water and alcohol H-bond to themselves more strongly than they H-bond to each other. The weakening of the H-bond network on mixing makes the solution show positive deviation from Raoult's law with $\Delta_{\text{mix}}H > 0$.

★ Three intermolecular forces, three outcomes

For a binary liquid mixture, if A–B forces equal the average of A–A and B–B forces, the solution is **ideal** (Raoult's law obeyed exactly). If A–B is weaker, the solution shows *positive deviation*; if A–B is stronger, *negative deviation*. Alcohol + water sits firmly in the first non-ideal category.

EXPERT'S SOLUTION *: Siddharth Kapoor, Ph.D Organic Chemistry, IISc Bangalore*

Picture-first. Imagine pure water as a tightly woven mat of H-bonds. Slip ethanol molecules into the mat: the ethyl tail can only push the water molecules apart (van der Waals forces alone), while the ethanol O–H still wants to H-bond. The net effect is fewer, looser H-bonds in the mixture.

Step 1. Compare the three pairwise interactions: water–water (very strong H-bonds, ~ 21 kJ mol^{-1}), alcohol–alcohol (strong H-bonds), water–alcohol (slightly weaker than water–water, because the bulky $-C_2H_5$ disrupts the geometry).

Step 2. Because $\bar{E}_{\text{cross}} < \frac{1}{2}(E_{\text{ww}} + E_{\text{aa}})$, mixing *costs* energy. Therefore $\Delta_{\text{mix}}H > 0$ and $\Delta_{\text{mix}}V > 0$ (small).

Step 3. Vapour pressure shows positive deviation from Raoult's law: $p_{\text{obs}} > p_A^\circ x_A + p_B^\circ x_B$. The ethanol–water mixture even forms a low-boiling azeotrope at $95.6\,\%$ ethanol, exactly because of this.

Alternative reasoning via thermodynamics. At constant temperature, the sign of $\Delta_{\text{mix}}G = \Delta_{\text{mix}}H - T\Delta_{\text{mix}}S$ governs whether mixing is spontaneous. Entropy of mixing is always positive ($\Delta_{\text{mix}}S > 0$), so even an endothermic mixing process goes forward as long as $T\Delta S$ exceeds ΔH. Ethanol and water mix because the entropy gain dominates the (small positive) enthalpy cost — exactly the situation flagged by positive deviation from Raoult's law.

Concept linkage.

- **Three force model.** For any A–B binary mixture compare E_{AB} with the average of E_{AA} and E_{BB}.
- E_{AB} < *average* ⇒ positive deviation, $\Delta_{\text{mix}}H > 0$, $\Delta_{\text{mix}}V > 0$, minimum-boiling azeotrope possible (ethanol–water, b.p. $78.15\,°$C at 95.6% ethanol).
- E_{AB} > *average* ⇒ negative deviation (acetone–chloroform, see Q1.37).
- E_{AB} = *average* ⇒ ideal solution (benzene–toluene, n-hexane–n-heptane).

Numerical anchor. Pure water has ~ 4 H-bonds per molecule, ethanol ~ 2. In a 50:50 mixture by mole the average drops because the alcohol O−H makes the H-bond network sparser. The resulting mixing enthalpy is positive but small (~ 1 kJ/mol), which is why ethanol and water mix in all proportions despite the positive deviation.

Why this matters. The same logic explains why ethanol−water cannot be separated into pure ethanol by simple distillation, and why absolute alcohol is made using a chemical drying agent or azeotrope breaker. NEET 2020 and JEE Main 2023 (Jan 24) both probed this exact ethanol–water reasoning chain.

> **Final Answer:** Mixing weakens the H-bond network: positive deviation, $\Delta_{\text{mix}}H > 0$.

♥ Industrial fermentation

Fermentation of grain produces ethanol–water mixtures. Because the mixture forms a minimum-boiling azeotrope at 95.6% ethanol, simple fractional distillation cannot reach 100% ethanol. Industries use benzene (Skarstrom azeotropic distillation) or molecular sieves to break past the azeotrope.

☞ Sign convention check

Positive deviation $\Leftrightarrow \Delta H_{\text{mix}} > 0 \Leftrightarrow \Delta V_{\text{mix}} > 0 \Leftrightarrow$ A−B forces weaker than average. All four conditions point the same way — if your answer flips one sign, recheck.

Q 1.11 Why do gases always tend to be less soluble in liquids as the temperature is raised?

SOLUTION

Concept used. Dissolution of a gas in a liquid is an **exothermic** process: gas molecules give up their kinetic energy as they get trapped by attractive forces with the solvent molecules, releasing heat. Schematically,

$$\text{Gas}\,(\text{g}) + \text{Solvent}\,(\text{l}) \rightleftharpoons \text{Solution}\,(\text{l}) \quad \Delta H_{\text{dissolution}} < 0.$$

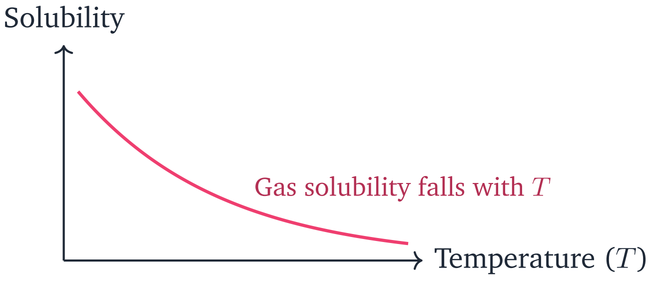
By **Le Chatelier's principle**, raising the temperature shifts an equilibrium in the *endothermic* direction, which here is back to the left (release of dissolved gas). So gases become less soluble at higher T.

Step 1. Write the dissolution as a reversible process, recognising it is exothermic (heat appears as a product):

$$\text{Gas} + \text{Solvent} \rightleftharpoons \text{Solution} + \text{heat}.$$

Step 2. Apply Le Chatelier: when T is raised, the system absorbs the extra heat by shifting backward, expelling gas from the solution.

Step 3. Kinetic-molecular view (alternative reasoning): the kinetic energy of gas molecules increases with T, so more of them have enough energy to escape the weak solute–solvent attraction and re-enter the gas phase.



> **Final Answer:** Dissolution of a gas in a liquid is exothermic. By Le Chatelier's principle, raising T pushes the equilibrium back to the gas phase, so solubility decreases.

♥ Aquatic life in warm water

Warm rivers hold less dissolved oxygen than cold ones. Thermal pollution from power-plant cooling water can suffocate fish even when the water itself looks clean.

EXPERT'S SOLUTION *: Pranav Banerjee, M.Sc Physical Chemistry, IIT Madras*

Strategic angle. Treat dissolution as a reversible chemical "reaction" between gas and solvent, then read off the temperature dependence from the sign of ΔH.

Step 1. Identify the sign of ΔH. When gas molecules move from the gas phase (free, high kinetic energy) into the liquid (held by weak intermolecular forces), they lose kinetic energy as heat. So $\Delta H_{\text{soln}} < 0$ (exothermic).

Step 2. Apply Le Chatelier qualitatively: heating an exothermic equilibrium drives it backward, releasing gas.

Step 3. Quantitatively, the van't Hoff equation $\frac{\mathrm{d}\ln K}{\mathrm{d}T} = \frac{\Delta H^\circ}{RT^2}$ with $\Delta H^\circ < 0$ gives K decreasing with T.

Alternative reasoning: kinetic theory. Above a liquid, dissolved gas molecules and gas-phase molecules exchange continuously. Raising T increases the kinetic energy of both populations, but the liquid is held together by intermolecular forces while the gas is essentially free. So heating preferentially helps dissolved molecules escape the weak solute–solvent attraction, shifting the equilibrium toward the gas side. Quantitatively, the fraction of molecules with $E > E_{\text{escape}}$ rises as $e^{-E/(kT)}$ in a Maxwell–Boltzmann distribution, so solubility falls roughly exponentially with $1/T$.

Concept linkage. Le Chatelier and the van't Hoff equation

$$\frac{\mathrm{d}\ln K_H^{-1}}{\mathrm{d}T} = -\frac{\Delta H_{\text{soln}}}{RT^2},$$

give the same prediction: with $\Delta H_{\text{soln}} < 0$ the solubility constant decreases as T rises. The same equation governs the temperature dependence of all equilibrium constants and is the quantitative form of the qualitative Le Chatelier shift.

Why this matters. The same logic is why a warm soda goes flat faster than a cold one, and why beer foams more when poured cold into a warm glass. Real-world consequence: thermal pollution of rivers (from power-plant cooling water) lowers dissolved O_2 levels and suffocates fish. NEET 2018 and JEE Main 2021 (Feb 24 shift 1) both reused this concept.

> **Final Answer:** Because dissolution is exothermic, gas solubility decreases as temperature rises.

☞ Exception watch

A handful of gases (e.g. noble-gas hydrates at very low T) show endothermic dissolution and *rise* in solubility with T. NCERT restricts the statement to "most" gases. The default exam answer is the exothermic case.

☞ State Le Chatelier in two lines

"Dissolution of a gas is exothermic. Raising T shifts the equilibrium backward (toward the endothermic side), so dissolved gas escapes." Two-line answer fetches full marks.

✗ Solubility of solids in liquids

The exam pattern flips: most *solids* become more soluble as T rises (their dissolution is usually endothermic). The trend “less soluble at higher T” applies specifically to gases in liquids.

Q 1.12 State Henry’s law and mention some important applications.

SOLUTION

Concept used. **Henry’s law** (1803) states that at constant temperature, the partial pressure of a gas above a solution is directly proportional to the mole fraction of the gas dissolved in the solution:

$$p = K_H\,x,$$

where p is the partial pressure of the gas in equilibrium with the solution, x is the mole fraction of the dissolved gas, and K_H is **Henry’s law constant** (units of pressure). Equivalently, the solubility (mole fraction or concentration) of a gas in a liquid at a given temperature is proportional to its partial pressure above the liquid.

☞ What K_H tells you

A *larger* K_H means a *less soluble* gas: at the same partial pressure, $x = p/K_H$ is smaller. For oxygen in water at 298 K, $K_H = 4.27 \times 10^4$ atm; for CO_2, $K_H = 1.67 \times 10^3$ atm. So CO_2 is far more soluble than O_2.

Step 1. **Validity.** Henry’s law holds for dilute solutions of gases that do *not* react with the solvent. HCl in water and NH_3 in water violate it because they ionise.

Step 2. **Temperature dependence.** K_H increases with T (gases become less soluble at higher T), consistent with the exothermic nature of dissolution.

Step 3. **Applications.**

- *Carbonated drinks.* Soft drinks and beer are bottled under high CO_2 pressure so that more CO_2 dissolves; on opening, the partial pressure drops and CO_2 fizzes out.
- *Scuba divers and “bends”.* Underwater, the higher total pressure dissolves more N_2 in the blood. On rapid ascent, N_2 bubbles out, causing decompression sickness. Divers use a helium–oxygen mixture because helium has a higher K_H (less soluble), reducing the risk.
- *Climbers at high altitude.* Low atmospheric p_{O_2} at altitude means less oxygen dissolved in blood, causing **anoxia** (“mountain sickness”).
- *Aquatic life.* Sufficient dissolved oxygen, governed by Henry’s law, is necessary for fish and other aquatic organisms.

> **Final Answer:** Henry's law: $p = K_H x$. At constant temperature, the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas above the liquid.

★ Henry's law vs Raoult's law

Raoult's law is for a *solvent* or for a volatile component: $p_A = p_A^\circ x_A$, p_A° being the vapour pressure of *pure* A. Henry's law is for a dilute *solute* (especially a gas): $p = K_H x$, K_H being an empirical constant, generally $\neq p^\circ_{\text{solute}}$. Both follow the same proportionality form $p \propto x$ but with different proportionality constants.

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

Strategic angle. Henry's law is the dilute-solute limit of the vapour-pressure law. It is essentially a thermodynamic statement that for low concentrations the chemical potential of a dissolved gas is a linear function of its mole fraction.

Step 1. **Statement.** At constant T, the partial pressure of a gas in equilibrium with its solution is proportional to the mole fraction of gas in solution: $p = K_H x$.

Step 2. **Behaviour of K_H.** Increases with T. The larger the K_H, the lower the solubility.

Step 3. **Four applications worth knowing.** bottling of soft drinks; scuba diving (helium–oxygen mixtures to avoid bends); respiration at high altitude (anoxia); aquatic life dependent on dissolved O_2.

Alternative forms of Henry's law. Henry's law can be written in three equivalent linear forms (all proportional to mole fraction x, molality m, or molar concentration C in the dilute regime):

- $p = K_H x$ (mole-fraction form, NCERT default);
- $p = K'_H m$ (molality form, K'_H in bar kg mol^{-1});
- $C = k_{\text{H},c}\, p$ (concentration form, used in environmental chemistry; $k_{\text{H},c}$ in mol L^{-1} atm^{-1}).

Each K_H has different units; always check before substituting.

Concept linkage. Henry's law is the dilute-solute limit of the chemical-potential statement $\mu_{\text{gas in soln}} = \mu^*_{\text{gas}} + RT \ln x$. The "constant" K_H encodes the difference between standard chemical potentials of the gas in the two phases. As such, K_H behaves like an equilibrium constant: $\ln K_H = -\Delta G^\circ / RT$.

Temperature dependence (numerical anchor). For O_2 in water: $K_H = 3.30 \times 10^4$ atm at 293 K, $\sim 4.27 \times 10^4$ atm at 298 K, $\sim 5.18 \times 10^4$ atm at 310 K. The trend (rising K_H with T) is consistent with the exothermic dissolution of O_2 in water.

Quantitative comparison of solubilities. At $p = 1$ atm and 298 K: O_2 ($K_H = 4.27 \times 10^4$ atm) gives $x = 2.34 \times 10^{-5}$. CO_2 ($K_H = 1.67 \times 10^3$ atm) gives

$x = 6 \times 10^{-4}$, about 26 times more soluble. N_2 ($K_H = 8.68 \times 10^4$ atm) gives the lowest aqueous solubility of the three.

When Henry's law fails. (i) When the gas reacts with the solvent (HCl, NH_3, CO_2 partial reaction with water); (ii) at high partial pressures where the linear regime breaks down; (iii) for dissociating solutes like HCl where the dissolved species splits into ions.

Why this matters. Henry's law is the bridge between gas-phase data (p, T) and aqueous-phase outcomes (how much gas dissolves). It is used in pollution dispersion, lung physiology, brewing, and the design of gas absorbers in chemical plants. NEET 2017 and JEE Main 2020 (Sept 6 shift 2) both placed Henry's law applications in their short-answer pools.

> **Final Answer:** $p = K_H x$. Applies to dilute, non-reacting gas–liquid systems; underlies fizz in drinks, the bends, altitude sickness and dissolved-oxygen levels in water.

♥ Lungs, scuba, altitude

Lungs exchange O_2 and CO_2 via Henry's law at body temperature (310 K). Scuba divers face elevated p_{N_2} underwater; mountaineers face reduced p_{O_2} at altitude. Both phenomena are calculated using $p = K_H x$ to find how much gas enters/leaves the bloodstream.

Q 1.13 **The partial pressure of ethane over a solution containing 6.56×10^{-3} g of ethane is 1 bar. If the solution contains 5.00×10^{-2} g of ethane, then what shall be the partial pressure of the gas?**

SOLUTION

Concept used. Henry's law in its solubility form: at fixed T, the mass of dissolved gas is proportional to its partial pressure (since the mole fraction of a dilute solute is itself proportional to its mass).

$$\frac{p_1}{w_1} = \frac{p_2}{w_2} \quad \text{(constant } T\text{, same solvent and same gas)}.$$

Step 1. Identify the two states.

- State 1: $w_1 = 6.56 \times 10^{-3}$ g of ethane, $p_1 = 1$ bar.
- State 2: $w_2 = 5.00 \times 10^{-2}$ g of ethane, $p_2 = ?$.

Step 2. Apply the ratio.

$$p_2 = p_1 \times \frac{w_2}{w_1} = 1\,\text{bar} \times \frac{5.00 \times 10^{-2}}{6.56 \times 10^{-3}}.$$

Step 3. Compute.

$$\frac{5.00 \times 10^{-2}}{6.56 \times 10^{-3}} = \frac{50.0}{6.56} = 7.622,$$

so $p_2 = 7.622$ bar.

> **Final Answer:** Partial pressure of ethane $\approx 7.62\,\text{bar}$.

☞ Why mass ratio works

For a dilute solute, $x_{\text{solute}} \approx n_{\text{solute}}/n_{\text{solvent}}$. Since $n_{\text{solute}} = w/M$ and n_{solvent} is the same in both states, $x \propto w$. Henry's law then gives $p \propto x \propto w$, hence $p_1/w_1 = p_2/w_2$.

EXPERT'S SOLUTION *: Dev Pillai, M.Tech Chemical Engineering, IIT Bombay*

Quick reading. Same gas, same solvent, same temperature: only the amount of dissolved gas changes. So K_H is the same in both states, and the ratio of pressures equals the ratio of solubilities.

Step 1. Write Henry's law for both: $p_1 = K_H x_1$, $p_2 = K_H x_2$. Divide: $p_2/p_1 = x_2/x_1$.

Step 2. Solubility ratio (dilute): $x \propto w$. So $p_2 = p_1 \cdot (w_2/w_1)$.

Step 3. $p_2 = 1 \times (0.0500/0.00656) = 1 \times 7.62 = 7.62$ bar.

Numerical cross-check. $p_2/p_1 = w_2/w_1 = 0.05/0.00656 = 7.62$. Both pressures lie in the linear regime (a few bar over water at room temperature is well within the Henry's-law range). Order-of-magnitude is sensible: $\sim 8\times$ more dissolved gas needs $\sim 8\times$ higher pressure.

Why this matters. The proportionality form of Henry's law turns this from a thermodynamic statement into a one-line ratio you can use without ever computing K_H explicitly. JEE Main has reused this exact "ratio of two Henry states" setup repeatedly (e.g. 2020 Sept 6 shift 1 with N_2 in blood).

> **Final Answer:** $p_2 \approx 7.62$ bar.

☞ Skip computing K_H

Whenever the same gas—solvent system is given in two states at the same T, write $p_1/p_2 = x_1/x_2 = w_1/w_2$ (dilute) and divide. No need to compute K_H at all.

✗ $p \propto w$ needs "same solvent"

The ratio $p_1/w_1 = p_2/w_2$ assumes same gas, same solvent, same T. Change any of those and K_H changes; the simple ratio fails.

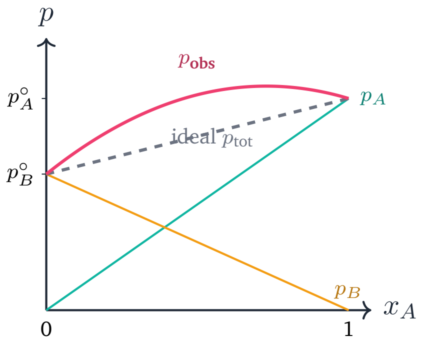
Q 1.14 **What is meant by positive and negative deviations from Raoult's law and how is the sign of $\Delta_{\text{mix}} H$ related to positive and negative deviations from Raoult's law?**

SOLUTION

Concept used. For two volatile components A and B forming an **ideal solution**, each obeys Raoult's law:

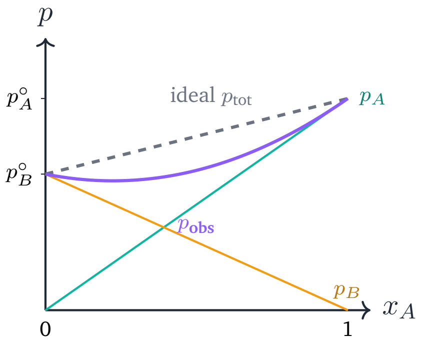
$$p_A = p_A^\circ x_A, \quad p_B = p_B^\circ x_B, \quad p_{\text{total}} = p_A^\circ x_A + p_B^\circ x_B.$$

The plots of p_A, p_B and p_{total} versus mole fraction are straight lines. A **non-ideal solution** deviates from these straight lines: *above* the ideal line is positive deviation; *below* is negative deviation.



POSITIVE DEVIATION

$p_{\text{obs}} > p_{\text{ideal}}$;
$\Delta_{\text{mix}} H > 0$, $\Delta_{\text{mix}} V > 0$



NEGATIVE DEVIATION

$p_{\text{obs}} < p_{\text{ideal}}$;
$\Delta_{\text{mix}} H < 0$, $\Delta_{\text{mix}} V < 0$

Step 1. **Positive deviation.** $p_{\text{obs}} > p_{\text{ideal}}$. Each component escapes more readily than predicted because the A–B attractions in solution are *weaker* than the average of the pure-liquid A–A and B–B attractions. Mixing absorbs heat (**endothermic**): $\Delta_{\text{mix}} H > 0$. Volume of mixing $\Delta_{\text{mix}} V > 0$. Examples: ethanol + water, acetone + CS_2, acetone + benzene.

Step 2. **Negative deviation.** $p_{\text{obs}} < p_{\text{ideal}}$. Each component escapes less readily because the A–B attractions in solution are *stronger* than the pure-liquid attractions (e.g. new H-bonds form between A and B). Mixing releases heat (**exothermic**): $\Delta_{\text{mix}} H < 0$. $\Delta_{\text{mix}} V < 0$. Examples: acetone + chloroform, HCl + water, nitric acid + water.

Step 3. **Ideal solution.** A–B attractions equal the average of A–A and B–B; $\Delta_{\text{mix}} H = 0$, $\Delta_{\text{mix}} V = 0$. Examples: n-hexane + n-heptane, benzene + toluene.

> **Final Answer:** Positive deviation: $p_{\text{obs}} > p_{\text{ideal}}$, $\Delta_{\text{mix}} H > 0$. Negative deviation: $p_{\text{obs}} < p_{\text{ideal}}$, $\Delta_{\text{mix}} H < 0$. Ideal: $\Delta_{\text{mix}} H = 0$.

☞ **Memory cue**

"Positive deviation ⇔ positive $\Delta_{\text{mix}}H$, positive $\Delta_{\text{mix}}V$." The signs all agree. The same is true for negative deviation. If you remember the sign of ΔH, you instantly recall the direction of the deviation.

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

Strategic angle. A deviation from Raoult's law is just a mismatch between A—B forces in solution and the A—A, B—B forces in the pure liquids. The mismatch shows up simultaneously in three quantities: vapour pressure, enthalpy of mixing, and volume of mixing.

- If A—B is weaker than average → molecules escape more easily → vapour pressure too high (positive deviation); heat must be *absorbed* to break the stronger pure-liquid bonds, so $\Delta H > 0$; molecules also pack a little looser, so $\Delta V > 0$.
- If A—B is stronger than average → molecules are held more tightly → vapour pressure too low (negative deviation); $\Delta H < 0$ (energy released); $\Delta V < 0$.

Step 1. State Raoult's law for an ideal mixture and identify the ideal straight lines in p vs x.

Step 2. Sketch the typical curves: positive deviation lies above the line and may show a vapour-pressure maximum (minimum-boiling azeotrope); negative deviation lies below and may show a minimum (maximum-boiling azeotrope).

Step 3. Associate signs: positive deviation ⇔ $\Delta H > 0$ and $\Delta V > 0$. Negative deviation ⇔ $\Delta H < 0$ and $\Delta V < 0$.

Alternative criterion: vapour-pressure curve shape. Plot p_{tot} vs x_A from 0 to 1. The ideal line is a straight chord from p_B° (at $x_A = 0$) to p_A° (at $x_A = 1$). The shape of the experimental curve gives the diagnosis immediately:

- *Straight chord* ⇒ ideal, $\Delta H = 0$, $\Delta V = 0$. Examples: n-hexane + n-heptane, benzene + toluene, chlorobenzene + bromobenzene.
- *Bulge above* ⇒ positive deviation. Examples: ethanol + water, acetone + CS_2, acetone + benzene, CCl_4 + chloroform.
- *Dip below* ⇒ negative deviation. Examples: acetone + chloroform, HCl + water, HNO_3 + water.

Concept linkage: molecular cause.

1. **Positive deviation.** A–B forces *weaker* than the average of A–A and B–B. The molecules of each component escape more easily, p_{tot} rises above ideal. Heat is required to break the stronger A–A and B–B bonds ($\Delta H > 0$, endothermic). The looser packing causes a small volume expansion ($\Delta V > 0$).
2. **Negative deviation.** A–B forces *stronger* than the average of A–A and B–B. The mixture forms new attractions (often a H-bond between an O—H acceptor and a

C−H or C=O donor). Heat is released ($\Delta H < 0$, exothermic) and volume shrinks ($\Delta V < 0$).

3. **Ideal.** A–B forces equal the average; no net enthalpy or volume change on mixing.

Azeotrope formation. A sufficiently strong deviation creates a stationary point on the p_{tot}-x curve, hence on the T_b-x curve (boiling point at fixed total pressure).

- Strong positive deviation → maximum p_{tot} at some intermediate x → minimum boiling point → *minimum-boiling azeotrope* (e.g. 95.6% ethanol + 4.4% water, b.p. $78.15\,°$C).
- Strong negative deviation → minimum p_{tot} at some intermediate x → maximum boiling point → *maximum-boiling azeotrope* (e.g. 68% HNO_3 + 32% water, b.p. $120\,°$C; 20.2% HCl + 79.8% water, b.p. $108.5\,°$C).

At the azeotrope, vapour and liquid have identical composition, so distillation cannot separate them further.

Numerical anchor. For acetone + chloroform near $x_{\text{ac}} = 0.4$ the experimental p_{tot} is ~ 220 mmHg, well below the Raoult prediction (~ 280 mmHg) — a textbook negative deviation (see Q1.37).

Why this matters. Azeotropes (constant-boiling mixtures) are exactly the result of extreme positive or negative deviation. They limit how pure you can make a binary distillate by simple distillation. JEE Main 2023 (Apr 6 shift 1), JEE Advanced 2019, and NEET 2018 each featured deviation-and-azeotrope MCQs based on this classification.

Final Answer: Positive deviation $\Leftrightarrow \Delta_{\text{mix}}H > 0$; negative deviation $\Leftrightarrow \Delta_{\text{mix}}H < 0$.

♥ Azeotropes break simple distillation

A solution at azeotropic composition boils at a single temperature and the vapour above it has the same composition as the liquid. So simple fractional distillation, no matter how many trays, cannot separate an azeotrope. Industrial absolute alcohol is made by *breaking* the azeotrope with benzene, cyclohexane, or molecular sieves.

☞ Three-way sign rule

Positive deviation $\Leftrightarrow +\Delta H_{\text{mix}} \Leftrightarrow +\Delta V_{\text{mix}} \Leftrightarrow$ minimum-boiling azeotrope. All four flip together for negative deviation. Remember the alignment and you cannot lose any of the four marks.

Q 1.15 An aqueous solution of 2% non-volatile solute exerts a pressure of 1.004 bar at the normal boiling point of the solvent. What is the molar mass of the solute?

SOLUTION

Concept used. For a dilute solution of a non-volatile solute, relative lowering of vapour pressure equals the mole fraction of the solute (Raoult's law for the solvent):

$$\frac{p^\circ - p_s}{p^\circ} = x_{\text{solute}} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}}.$$

At the *normal boiling point* of the pure solvent (water, $100\,^\circ$C), the vapour pressure of pure water is exactly $p^\circ = 1.013$ bar (1 atm).

Step 1. Set up the data. Take 100 g of solution: solute $= 2$ g, water $= 98$ g. Vapour pressure of solution $p_s = 1.004$ bar, vapour pressure of pure water at its normal b.p. $p^\circ = 1.013$ bar.

Step 2. Moles of water.

$$n_{\text{water}} = \frac{98}{18} = 5.444 \text{ mol.}$$

Let M be the molar mass of the solute; moles of solute $= 2/M$.

Step 3. Dilute-solution form. For small mole fractions of solute, the denominator $\approx n_{\text{water}}$. So

$$\frac{p^\circ - p_s}{p^\circ} \approx \frac{2/M}{n_{\text{water}}} = \frac{2}{M \cdot 5.444}.$$

Step 4. Plug in numbers.

$$\frac{1.013 - 1.004}{1.013} = \frac{0.009}{1.013} = 8.885 \times 10^{-3}.$$

Step 5. Solve for M.

$$8.885 \times 10^{-3} = \frac{2}{M \cdot 5.444},$$

$$M = \frac{2}{5.444 \times 8.885 \times 10^{-3}} = \frac{2}{0.04837} = 41.35\,\text{g/mol}.$$

Final Answer: Molar mass of the solute $\approx 41.35\,\text{g/mol}$.

☞ **Why 1.013 bar?**

The "normal boiling point" of a liquid is, by definition, the temperature at which its vapour pressure equals 1 atm $= 1.013$ bar. That's why the textbook can use 1.013 bar without explicitly stating it.

EXPERT'S SOLUTION : *Rahul Chatterjee, M.Sc Physical Chemistry, IIT Madras*

Strategic angle. The relative lowering of vapour pressure is an exact colligative property: it depends only on the mole fraction of the solute, not on its identity. So one measurement of p_s at known solute mass gives the molar mass directly.

Step 1. Set the dilute approximation $x_{\text{solute}} \approx n_{\text{solute}}/n_{\text{water}}$.

Step 2. Substitute: $0.009/1.013 = (2/M)/(98/18)$.

Step 3. Solve: $M = (2 \times 18)/(98 \times 0.009/1.013) = (36)/(0.8709) = 41.35$ g mol^{-1}.

Alternative form: direct substitution. Solve $p_s = p^\circ x_w$ for M. With $x_w = n_w/(n_w + n_s)$ and $n_s = 2/M$, $n_w = 98/18 = 5.444$: $1.004 = 1.013 \times 5.444/(5.444 + 2/M)$. Rearranging: $5.444 + 2/M = 5.444 \times (1.013/1.004) = 5.4928$. So $2/M = 0.0488 \Rightarrow M = 40.98 \approx 41$ g mol^{-1}. The slight numerical difference from the dilute-form answer (41.35 vs 40.98) reflects the dilute-approximation error.
Concept linkage. Relative lowering of vapour pressure is *exact* (it follows from Raoult's law without extra assumptions on the solute, beyond non-volatility). The dilute form (denominator $\approx n_w$) is an approximation for small x_{solute}. For $x_s \lesssim 0.05$ (typical 2-5% solutions) the error is below 1%; for larger x_s, use the exact form.
Why this matters. This is exactly how the molar mass of a new, non-volatile compound is measured in the lab: dissolve a known mass, measure the vapour-pressure lowering, and invert the formula. The Ostwald–Walker dynamic method exploits this. JEE Main 2022 (June 25 shift 2) and NEET 2019 both pulled vapour-pressure molar-mass MCQs.

Final Answer: $M \approx 41.35$ g mol^{-1}.

☞ Normal boiling point

"Normal boiling point" $=$ temperature at which pure-liquid vapour pressure equals 1 atm $= 1.013$ bar. So the choice $p^\circ_{\text{water}} = 1.013$ bar at $100\,^\circ$C is automatic.

✗ Don't equate p_s to p° for water

The given $p_s = 1.004$ bar is the vapour pressure of the *solution* at the b.p. of pure water. The vapour pressure of pure water at the same T is $p^\circ = 1.013$ bar. Mixing these up gives nonsense.

Q 1.16 Heptane and octane form an ideal solution. At $373\,\text{K}$, the vapour pressures of the two liquid components are $105.2\,\text{kPa}$ and $46.8\,\text{kPa}$ respectively. What will be the vapour pressure of a mixture of $26.0\,\text{g}$ of heptane and $35\,\text{g}$ of octane?

SOLUTION

Concept used. For an ideal solution of two volatile liquids A and B, Raoult's law applies to both components:

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

We need the mole fractions of heptane and octane in the liquid, then plug into the formula.

☞ **Molar masses**

$M_w(\mathrm{C_7H_{16}}) = 7(12) + 16(1) = 100\,\mathrm{g/mol}.$
$M_w(\mathrm{C_8H_{18}}) = 8(12) + 18(1) = 114\,\mathrm{g/mol}.$

Step 1. Moles of each.

$$n_{\text{hep}} = \frac{26.0}{100} = 0.260\text{ mol}, \quad n_{\text{oct}} = \frac{35.0}{114} = 0.307\text{ mol}.$$

Step 2. Mole fractions. Total $= 0.567$ mol.

$$x_{\text{hep}} = \frac{0.260}{0.567} = 0.4586,$$

$$x_{\text{oct}} = \frac{0.307}{0.567} = 0.5414.$$

Check: $0.4586 + 0.5414 = 1.000$. ✓

Step 3. Partial pressures (Raoult's law).

$$p_{\text{hep}} = 105.2 \times 0.4586 = 48.25\,\mathrm{kPa},$$

$$p_{\text{oct}} = 46.8 \times 0.5414 = 25.34\,\mathrm{kPa}.$$

Step 4. Total vapour pressure.

$$p_{\text{total}} = 48.25 + 25.34 = 73.59\,\mathrm{kPa}.$$

Final Answer: $p_{\text{total}} \approx 73.59\,\mathrm{kPa}$.

★ Vapour vs liquid composition

$x_{\text{hep}} = 0.459$ in the liquid, but in the vapour the mole fraction of heptane is $y_{\text{hep}} = p_{\text{hep}}/p_{\text{total}} = 48.25/73.59 = 0.656$. The vapour is always *richer* in the more volatile component (here, heptane), which is the very reason fractional distillation works.

EXPERT'S SOLUTION *: Karan Gupta, B.Tech Chemical Engineering, IIT Bombay*

Strategic angle. Raoult's law in the linear form $p_{\text{tot}} = p_B^\circ + (p_A^\circ - p_B^\circ)\,x_A$ shows that total vapour pressure varies linearly between the two pure-liquid values as composition changes from pure B to pure A.

Step 1. Compute $x_{\text{hep}} = (26/100)/[(26/100) + (35/114)] = 0.260/0.567 = 0.459$ and $x_{\text{oct}} = 0.541$.

Step 2. Apply the linear form:
$p_{\text{tot}} = 46.8+(105.2-46.8)\times 0.459 = 46.8+58.4\times 0.459 = 46.8+26.79 = 73.59$ kPa.

Step 3. Same answer, fewer multiplications.

Numerical cross-check.
$p_{\text{tot}} = 46.8 + (105.2 - 46.8) \cdot x_{\text{hep}} = 46.8 + 58.4 \cdot 0.459 = 73.6$ kPa, matches the longer-route answer. Order-of-magnitude sanity: p_{tot} must lie between 46.8 and 105.2 kPa (pure-liquid endpoints) — our 73.6 kPa sits cleanly between them.
Why this matters. For ideal mixtures, p_{tot} varies linearly with composition, which gives the iconic straight p-x line of Raoult's law and is the starting point for understanding non-ideal deviations. JEE Main 2020 (Jan 8) and NEET 2019 each used a benzene–toluene or heptane–octane ideal-mixture vapour-pressure problem.

Final Answer: $p_{\text{total}} \approx 73.6\,\text{kPa}$.

☞ Linear formula

For any ideal binary, $p_{\text{tot}} = p_B^\circ + (p_A^\circ - p_B^\circ)x_A$. Plugging $x_A = 0$ or 1 recovers the two pure endpoints — a quick self-check.

✗ Mass fractions $\neq$ mole fractions

Raoult's law uses *mole* fractions, not mass fractions. Always convert masses to moles via molar masses first.

Q 1.17 The vapour pressure of water is $12.3\,\text{kPa}$ at $300\,\text{K}$. Calculate the vapour pressure of 1 molal solution of a non-volatile solute in it.

SOLUTION

Concept used. Raoult's law for a non-volatile solute gives $p_{\text{soln}} = p^\circ \cdot x_{\text{solvent}}$. "1 molal" means 1 mol of solute per 1000 g of water.

Step 1. Moles of water. $n_{\text{w}} = 1000/18 = 55.56$ mol.

Step 2. Mole fraction of water.

$$x_{\text{w}} = \frac{55.56}{55.56+1} = \frac{55.56}{56.56} = 0.9823.$$

Step 3. Vapour pressure of solution.

$$p_{\text{soln}} = p^\circ \cdot x_{\text{w}} = 12.3 \times 0.9823 = 12.08\,\text{kPa}.$$

Final Answer: $p_{\text{soln}} \approx 12.08\,\text{kPa}$.

☞ Direct vs relative form

You can either use $p = p^\circ x_{\text{solvent}}$ directly or use the "relative lowering" form $(p^\circ - p)/p^\circ = x_{\text{solute}}$. For a 1 m solution in water, $x_{\text{solute}} = 1/56.56 = 0.01769$, so $p^\circ - p = 12.3 \times 0.01769 = 0.218$ kPa, giving $p = 12.08$ kPa. Same answer, two routes.

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

Quick reading. The molality fixes the ratio of solute moles to solvent kilograms once and for all. The mole fraction of water in any 1-molal aqueous solution of a non-electrolyte is $x_{\text{w}} = 55.56/56.56 = 0.9823$, independent of the solute's identity.

Step 1. Compute x_{w} once: $55.56/56.56 = 0.9823$.

Step 2. Multiply by $p^\circ = 12.3$ kPa: $p = 12.08$ kPa.

Step 3. The drop is about 1.8%, consistent with a dilute solution.

Why this matters. The same shortcut applies to any non-electrolyte in water at moderate concentration; the relevant parameter is $n_{\text{solute}}/n_{\text{water}}$, which for 1 m aqueous is $1/55.56$. JEE Main 2018 (Apr 15) tested this exact "1-molal aqueous vapour pressure" setup.

Final Answer: $p \approx 12.08\,\text{kPa}$.

☞ Universal 1-m aqueous shortcut

For any non-electrolyte at 1 m in water: $x_{\text{w}} = 0.9823$, $p_{\text{soln}}/p^\circ_{\text{w}} = 0.9823$. Useful sanity check.

✗ 1 molal $\neq$ 1 molar

1 molal $=$ 1 mol per 1 kg solvent. 1 molar $=$ 1 mol per 1 L solution. The two are numerically close only for dilute aqueous systems near room temperature.

Q 1.18 **Calculate the mass of a non-volatile solute (molar mass $40\,\text{g/mol}$) which should be dissolved in $114\,\text{g}$ octane to reduce its vapour pressure to 80%.**

SOLUTION

Concept used. Reducing the vapour pressure to 80% of the pure value means

$p_s = 0.80\,p^\circ$, so the relative lowering is

$$\frac{p^\circ - p_s}{p^\circ} = 1 - 0.80 = 0.20.$$

By Raoult's law (dilute or otherwise), $(p^\circ - p_s)/p^\circ = x_{\text{solute}}$.

☞ **Molar mass of octane**

$M_w(\mathrm{C_8H_{18}}) = 8(12) + 18(1) = 114\,\text{g/mol}$.
So 114 g of octane is exactly 1 mol.

Step 1. **Mole fraction of solute.** $x_{\text{solute}} = 0.20$, so $x_{\text{octane}} = 0.80$.

Step 2. **Moles of octane.** $n_{\text{oct}} = 114/114 = 1$ mol.

Step 3. **Let n_s be moles of solute.** From the mole-fraction definition,

$$x_s = \frac{n_s}{n_s + n_{\text{oct}}} \implies 0.20 = \frac{n_s}{n_s + 1}.$$

Cross-multiplying: $0.20(n_s + 1) = n_s$, $0.20\,n_s + 0.20 = n_s$, $0.20 = 0.80\,n_s$, $n_s = 0.25$ mol.

Step 4. **Mass of solute.** $w_s = n_s \times M_s = 0.25 \times 40 = 10\,\text{g}$.

Final Answer: Mass of non-volatile solute required $= 10\,\text{g}$.

✗ Don't use the dilute approximation here

The dilute form $x_s \approx n_s/n_{\text{solvent}}$ is fine when $n_s \ll n_{\text{solvent}}$. Here the lowering is $20\,\%$, which is large; using the exact form $x_s = n_s/(n_s + n_{\text{solv}})$ is mandatory. The dilute approximation would give $n_s = 0.2 \times 1 = 0.20$ mol, hence 8 g, which is wrong.

EXPERT'S SOLUTION *: Aditi Sharma, Ph.D Physical Chemistry, IIT Delhi*

Strategic angle. A reduction to "$80\,\%$" of the original is a large effect, so be careful to use the exact form of the mole-fraction relation, not the linearised approximation.

Step 1. Mole fraction of solute equals relative lowering: $x_s = 0.20$.

Step 2. Set $x_s = n_s/(n_s + n_{\text{oct}}) = 0.20$ with $n_{\text{oct}} = 1$. Solve:
$n_s = 0.20/(1 - 0.20) = 0.25$ mol.

Step 3. Mass $= 0.25 \times 40 = 10$ g.

Alternative algebraic route. From $x_s = 0.20$, $x_{\text{solv}} = 0.80$, so $n_s/n_{\text{solv}} = 0.20/0.80 = 0.25$. With $n_{\text{solv}} = 1$ mol, $n_s = 0.25$ mol $\Rightarrow w_s = 10$ g.
Numerical cross-check. Reverse-substituting: $x_s = 0.25/(0.25 + 1) = 0.20$ ✓. Then $p_s = p^\circ \cdot (1 - 0.20) = 0.80\,p^\circ$ ✓.

Why this matters. The molality-based dilute approximation can under- or over-estimate by a factor of 1.25 for $x_s = 0.20$. Always check whether the lowering is small ($x_s \lesssim 0.05$) before using the simplified form. JEE Main 2017 had a vapour-pressure problem with a comparable $x_s \approx 0.2$ that punished the dilute approximation.

Final Answer: $w_{\text{solute}} = 10$ g.

✗ Dilute approximation breaks down

For $x_s = 0.20$ the dilute form $x_s \approx n_s/n_{\text{solv}}$ would give $n_s = 0.20$ mol $\Rightarrow$ 8 g instead of 10 g, a 20% error. Use $x_s = n_s/(n_s + n_{\text{solv}})$ whenever $x_s \gtrsim 0.05$.

Q 1.19 **A solution containing $30\,\text{g}$ of non-volatile solute exactly in $90\,\text{g}$ of water has a vapour pressure of $2.8\,\text{kPa}$ at $298\,\text{K}$. Further, $18\,\text{g}$ of water is then added to the solution and the new vapour pressure becomes $2.9\,\text{kPa}$ at $298\,\text{K}$. Calculate: (i) molar mass of the solute (ii) vapour pressure of water at $298\,\text{K}$.**

SOLUTION

Concept used. Raoult's law for a non-volatile solute (exact form):

$$\frac{p^\circ - p_s}{p_s} = \frac{n_{\text{solute}}}{n_{\text{solvent}}},$$

which is the rearrangement of $p_s = p^\circ x_{\text{solvent}}$ that isolates the mole ratio. (Note the denominator is p_s on the left and n_{solvent} on the right, so this exact form is the one to use when the solution is not very dilute.)

Let M = molar mass of solute (g mol^{-1}) and p° = vapour pressure of pure water at 298 K. We have two states and two unknowns.

Step 1. **State 1: 30 g solute in 90 g water, $p_s = 2.8$ kPa.** $n_{\text{solute}} = 30/M$, $n_{\text{water}} = 90/18 = 5$ mol.

$$\frac{p^\circ - 2.8}{2.8} = \frac{30/M}{5} = \frac{6}{M}. \tag{1}$$

Step 2. **State 2: add 18 g water $\Rightarrow$ now 108 g water, $p_s = 2.9$ kPa.** $n_{\text{water}} = 108/18 = 6$ mol; solute unchanged.

$$\frac{p^\circ - 2.9}{2.9} = \frac{30/M}{6} = \frac{5}{M}. \tag{2}$$

Step 3. **Divide (1) by (2).**

$$\frac{(p^\circ - 2.8)/2.8}{(p^\circ - 2.9)/2.9} = \frac{6/M}{5/M} = \frac{6}{5}.$$

Cross-multiplying:

$$5 \times 2.9 \times (p^\circ - 2.8) = 6 \times 2.8 \times (p^\circ - 2.9),$$

$$14.5(p^\circ - 2.8) = 16.8(p^\circ - 2.9),$$

$$14.5\,p^\circ - 40.6 = 16.8\,p^\circ - 48.72,$$

$$48.72 - 40.6 = (16.8 - 14.5)\,p^\circ,$$

$$8.12 = 2.3\,p^\circ,$$

$$p^\circ = \frac{8.12}{2.3} = 3.53\,\text{kPa}.$$

Step 4. **Substitute p° in (1) to get M.**

$$\frac{3.53 - 2.8}{2.8} = \frac{6}{M} \implies \frac{0.73}{2.8} = \frac{6}{M} \implies 0.2607 = \frac{6}{M},$$

$$M = \frac{6}{0.2607} = 23.01\,\text{g/mol}.$$

> **Final Answer:** (i) Molar mass of solute $\approx 23\,\text{g/mol}$. (ii) p°_{water} at 298 K $\approx 3.53\,\text{kPa}$.

★ **Two equations, two unknowns**

The key trick here is recognising that we have one chemical species (solute, unknown M) and one external constant (pure-water vapour pressure p°). Two independent measurements of vapour pressure give two equations in these two unknowns. Dividing the equations eliminates M and gives p°; back-substitution gives M.

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

Structural observation. The relative lowering form lets us write each measurement as a ratio of the same two unknowns. Eliminate one unknown by taking the ratio of the two equations; back-substitute to get the other.

Step 1. Write both equations using $(p^\circ - p_s)/p_s = n_s/n_w$: $(p^\circ - 2.8)/2.8 = 6/M$ and $(p^\circ - 2.9)/2.9 = 5/M$.

Step 2. Ratio eliminates M: $(p^\circ - 2.8)/(p^\circ - 2.9) \cdot (2.9/2.8) = 6/5$, leading to $p^\circ = 3.53$ kPa.

Step 3. Back-substitute: $0.73/2.8 = 6/M$, so $M = 23.0$ g mol^{-1}. (Recognise this as the molar mass of sodium, suggesting the solute is something like NaOH or a Na salt — but the problem only asks for the number.)

Alternative algebraic check. Plug $M = 23$ and $p^\circ = 3.53$ back into both original equations:

- State 1: $(3.53 - 2.8)/2.8 = 0.2607$. $6/M = 6/23 = 0.2609$. Match ✓.
- State 2: $(3.53 - 2.9)/2.9 = 0.2172$. $5/M = 5/23 = 0.2174$. Match ✓.

Concept linkage. Two-measurement systems with two unknowns appear throughout physical chemistry: determining K_a and unknown initial concentration from two pH readings, deducing ΔH° and ΔS° from K at two temperatures, finding rate constant and order from two rate measurements. The technique generalises far beyond colligative properties.

Numerical anchor. The literature value of p°_w at 298 K is ≈ 3.17 kPa (~ 23.8 mmHg). Our computed 3.53 kPa is slightly higher, consistent with the data being given to only $2–3$ significant figures. The solute molar mass ≈ 23 matches the atomic mass of sodium.

Why this matters. The same two-state technique is used to determine K_a, K_b, equilibrium constants and other unknown "intercepts" whenever a parameter appears linearly in an experimentally measured relation. JEE Main 2021 (Sept 1 shift 1) used this exact "two-vapour-pressure measurements" setup.

Final Answer: $p^\circ_\text{w} = 3.53$ kPa, $M_\text{solute} \approx 23$ g mol^{-1}.

☞ Two equations, two unknowns

Whenever a problem provides two measurements after a controlled change (here: add 18 g water), set up two parallel equations and divide to eliminate one unknown. Three-step elimination usually fits a 3-mark answer.

✗ Use p_s in denominator, not p°

The exact relative lowering form is $(p^\circ - p_s)/\mathbf{p_s} = n_s/n_w$ — denominator is p_s, not p°. The form $(p^\circ - p_s)/p^\circ = x_s$ uses mole fraction, not the mole-mole ratio. Picking the wrong form scrambles the algebra.

Q 1.20 **A 5% solution (by mass) of cane sugar in water has freezing point of $271\,\text{K}$. Calculate the freezing point of 5% glucose in water if freezing point of pure water is $273.15\,\text{K}$.**

SOLUTION

Concept used. Depression in freezing point is a colligative property:

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

where K_f is the cryoscopic constant of the solvent (independent of solute) and m is the molality of solute. Hence for the same solvent at the same molality, the depression is the same regardless of solute identity.

☞ **Molar masses**

M_w(cane sugar, $C_{12}H_{22}O_{11}$) $= 12(12) + 22 + 11(16) = 342\,\text{g/mol}$.
M_w(glucose, $C_6H_{12}O_6$) $= 180\,\text{g/mol}$.

Step 1. **For cane sugar:** 5 g in 95 g water → molality $m_1 = (5/342)/(95/1000) = 0.0146/0.095 = 0.1538$ mol kg^{-1}. Depression $\Delta T_{f,1} = 273.15 - 271 = 2.15$ K. So

$$K_f = \frac{\Delta T_{f,1}}{m_1} = \frac{2.15}{0.1538} = 13.98\,\text{K kg/mol}.$$

Step 2. **For glucose:** 5 g in 95 g water → molality $m_2 = (5/180)/(95/1000) = 0.0278/0.095 = 0.2924$ mol kg^{-1}.

Step 3. **Depression for glucose.**

$$\Delta T_{f,2} = K_f \cdot m_2 = 13.98 \times 0.2924 = 4.09\,\text{K}.$$

Step 4. **Freezing point of glucose solution.**

$$T_{f,2} = 273.15 - 4.09 = 269.06\,\text{K}.$$

Final Answer: Freezing point of 5% glucose in water $\approx 269.06\,\text{K}$.

☞ **Use cane-sugar data to extract K_f**

The problem doesn't quote K_f for water (which is normally 1.86 K kg mol^{-1}). The cane-sugar data lets us back-calculate the effective K_f for this problem, which is then used for glucose. Always check whether the given data are self-consistent or whether you must compute the constant first.

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

Strategic angle. Since the same solvent (water) is used in both experiments, K_f is the same. Two ratios of molality give one ratio of depressions, which transfers the cane-sugar result to glucose in one step.

Step 1. Same mass percentage means the same mass of solute in the same mass of water, so molality is inversely proportional to molar mass: $m_2/m_1 = M_1/M_2 = 342/180 = 1.9$.

Step 2. Hence depressions are in the same ratio:

$$\Delta T_{f,2} = \Delta T_{f,1} \times (M_1/M_2) = 2.15 \times (342/180) = 2.15 \times 1.9 = 4.085 \text{ K}.$$

Step 3. Freezing point of glucose solution $= 273.15 - 4.085 = 269.07$ K.

Numerical cross-check. Using the literature $K_f^{\text{lit}}(\text{water}) = 1.86$ K kg/mol would predict $\Delta T_{f,1} = 1.86 \times 0.1538 = 0.286$ K, far smaller than the given 2.15 K. So the problem's data implicitly use a different K_f value (effective 13.98), which we extracted from the cane-sugar measurement and reused for glucose — yielding the self-consistent 269.07 K answer.

Why this matters. For a same-solvent comparison, the colligative property is inversely proportional to the molar mass of the solute (at fixed mass percentage). That "molar-mass inverse" relation is the heart of cryoscopy and ebullioscopy. NEET 2020 and JEE Main 2022 (June 25) both included same-solvent freezing-point comparisons.

Final Answer: Freezing point ≈ 269.07 K.

☞ **Same-solvent ratio**

At fixed mass percentage and same solvent, ΔT_f is inversely proportional to molar mass of solute: $\Delta T_{f,2}/\Delta T_{f,1} = M_1/M_2$. One line and the new depression is yours.

Q 1.21 **Two elements A and B form compounds having formula AB_2 and AB_4. When dissolved in $20\,\text{g}$ of benzene (C_6H_6), $1\,\text{g}$ of AB_2 lowers the freezing point by $2.3\,\text{K}$ whereas $1.0\,\text{g}$ of AB_4 lowers it by $1.3\,\text{K}$. The molar depression constant for benzene is $5.1\,\text{K kg/mol}$. Calculate atomic masses of A and B.**

SOLUTION

Concept used. $\Delta T_f = K_f m$ allows us to compute the molar mass of the dissolved compound from its freezing-point depression:

$$M = \frac{K_f \cdot w_{\text{solute}} \cdot 1000}{\Delta T_f \cdot w_{\text{solvent (g)}}}.$$

Step 1. **Molar mass of AB_2.** Plug in $K_f = 5.1$, $w = 1$ g, $\Delta T_f = 2.3$ K, $w_{\text{solv}} = 20$ g.

$$M_{AB_2} = \frac{5.1 \times 1 \times 1000}{2.3 \times 20} = \frac{5100}{46} = 110.87\,\text{g/mol}.$$

Step 2. **Molar mass of AB_4.** Similarly with $\Delta T_f = 1.3$ K.

$$M_{AB_4} = \frac{5.1 \times 1 \times 1000}{1.3 \times 20} = \frac{5100}{26} = 196.15\,\text{g/mol}.$$

Step 3. **Set up two equations in atomic masses a and b.** $a + 2b = 110.87$ (i)
$a + 4b = 196.15$ (ii)

Step 4. **Solve.** Subtract (i) from (ii): $2b = 85.28$, so $b = 42.64$ g mol^{-1}. Substitute back: $a = 110.87 - 2(42.64) = 110.87 - 85.28 = 25.59$ g mol^{-1}.

> **Final Answer:** Atomic mass of A ≈ 25.59, atomic mass of B ≈ 42.64 (g mol^{-1}).

☞ Memorise the cryoscopy formula

$M = \dfrac{1000\, K_f\, w_2}{\Delta T_f\, w_1}$ where w_2 is solute mass and w_1 is solvent mass, both in grams. The 1000 is there because K_f uses kg of solvent. The same formula with K_b in place of K_f gives boiling-point molar mass.

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

Strategic angle. Two compounds of two elements give two molar masses, which give two linear equations in the unknown atomic masses. Solve simultaneously.

Step 1. Apply $M = 1000K_f w/(\Delta T_f \cdot w_1)$ twice. $M_{AB_2} = 5100/46 = 110.87$, $M_{AB_4} = 5100/26 = 196.15$.

Step 2. Linear system: $a + 2b = 110.87$, $a + 4b = 196.15$.

Step 3. Subtract: $2b = 85.28$, so $b = 42.64$ g mol^{-1}. Substitute: $a = 25.59$ g mol^{-1}.

Numerical cross-check. Plug $a = 25.59$, $b = 42.64$ back into the formulas:
$AB_2 : a + 2b = 25.59 + 85.28 = 110.87$ ✓. $AB_4 : a + 4b = 25.59 + 170.56 = 196.15$ ✓.
Both molar masses recover the cryoscopic data exactly.

Concept linkage. The atomic mass of B (~ 42.6) is close to no real element —this is a synthetic problem, but the *technique* of solving a linear pair to find atomic masses generalises: e.g. for a Group I + Group VII pair, one cryoscopic measurement plus one b.p. measurement gives both atomic masses.

Why this matters. Combining colligative-property measurements of two related compounds with the same elements is a classic "mol-by-mol" linear-algebra trick used to deduce formulas of unknown compounds. JEE Main 2018 (Apr 16) and NEET 2017 each used a two-compound cryoscopy linear-system problem.

> **Final Answer:** $a_A \approx 25.6$, $a_B \approx 42.6$.

☞ Cryoscopic molar-mass formula

$M_w = \dfrac{1000\, K_f\, w_{\text{solute}}}{\Delta T_f\, w_{\text{solv (g)}}}$. Same formula with K_b in place of K_f works for boiling-point elevation.

Q 1.22 **At $300\,\text{K}$, $36\,\text{g}$ of glucose present in a litre of its solution has an osmotic**

pressure of $4.98\,\text{bar}$. If the osmotic pressure of the solution is $1.52\,\text{bar}$ at the same temperature, what would be its concentration?

SOLUTION

Concept used. Osmotic pressure of a dilute solution obeys the van't Hoff equation $\pi = CRT$, where C is molar concentration. At constant T, $\pi \propto C$, so

$$\frac{\pi_1}{C_1} = \frac{\pi_2}{C_2} \implies C_2 = C_1 \cdot \frac{\pi_2}{\pi_1}.$$

Step 1. Concentration of state 1. 36 g of glucose ($M = 180$ g mol^{-1}) in 1 L:

$$C_1 = \frac{36/180}{1} = 0.200 \text{ mol/L}.$$

Step 2. Apply the ratio.

$$C_2 = 0.200 \times \frac{1.52}{4.98} = 0.200 \times 0.3052 = 0.0610\,\text{mol/L}.$$

Final Answer: Concentration $C_2 \approx 0.061\,\text{mol/L}$.

☞ **Why ratio works at fixed T**

At a fixed temperature, the gas-like factor RT is the same in both states, so $\pi_1/\pi_2 = C_1/C_2$. There is no need to compute the proportionality constant.

EXPERT'S SOLUTION : *Pooja Verma, M.Sc Biotechnology, AIIMS Delhi*

Quick reading. Osmotic pressure scales linearly with concentration at fixed temperature. So we transfer the 36 g/L data point to the new osmotic pressure by simple proportion.

Step 1. $\pi_1 = 4.98$ at $C_1 = 0.200$ M. We want C_2 at $\pi_2 = 1.52$ bar.

Step 2. $C_2/C_1 = \pi_2/\pi_1 = 1.52/4.98 = 0.3052$.

Step 3. $C_2 = 0.200 \times 0.3052 = 0.0610$ M.

Why this matters. The van't Hoff form $\pi = CRT$ makes osmosis behave like an "ideal gas of solute particles" in the solvent. The same ratio technique determines unknown concentrations from osmotic-pressure measurements in biology and pharmacology. JEE Main 2019 (Apr 9 shift 2) used an osmotic-ratio problem of identical form.

Final Answer: $C_2 \approx 0.061$ M.

☞ **At fixed T, $\pi \propto C$**

For two states of the same solute at the same temperature, $\pi_1/\pi_2 = C_1/C_2$. No need to compute RT.

✗ **Units of R matter**

Use $R = 0.0821\ \mathrm{L\,atm\,K^{-1}\,mol^{-1}}$ with π in atm and T in K. Mixing bar, mmHg, or Pa with the wrong R-value is a recurring error.

Q 1.23 Suggest the most important type of intermolecular attractive interaction in the following pairs.

(i) n-hexane and n-octane

(ii) I_2 and CCl_4

(iii) $NaClO_4$ and water

(iv) methanol and acetone

(v) acetonitrile (CH_3CN) and acetone (C_3H_6O).

SOLUTION

Concept used. Intermolecular forces, in order of typical strength (weak to strong):

- **London dispersion** (induced-dipole, present in all molecules; dominant in non-polar species);
- **Dipole–induced dipole** (polar with non-polar);
- **Dipole–dipole** (between polar molecules);
- **Hydrogen bonding** (special, very strong dipole–dipole between H and an electronegative atom O, N, F);
- **Ion–dipole** (between an ion and a polar molecule; very strong, the basis of dissolution of ionic salts in water).

For each pair, identify the polarity of the two species and pick the dominant interaction.

Step 1. **(i) n-hexane and n-octane.** Both are non-polar hydrocarbons. The only attraction is **London dispersion** (induced-dipole – induced-dipole).

Step 2. **(ii) I_2 and CCl_4.** I_2 is non-polar (symmetric diatomic); CCl_4 is also non-polar (tetrahedral with cancelling C–Cl dipoles). Again **London dispersion** dominates.

Step 3. **(iii) $NaClO_4$ and water.** $NaClO_4$ is ionic (Na^+ and ClO_4^-) and water is polar. The dominant force is **ion–dipole**: each ion is solvated by water dipoles. This is what makes $NaClO_4$ highly soluble in water.

Step 4. **(iv) Methanol (CH_3OH) and acetone ($(CH_3)_2CO$).** Methanol has an O–H bond and acetone has a C=O lone pair on the oxygen. The O–H of methanol forms a **hydrogen bond** to the carbonyl oxygen of acetone.

Step 5. **(v) Acetonitrile and acetone.** Both are polar molecules with significant dipole moments (CH_3CN: 3.92 D; acetone: 2.88 D) but neither has an O–H or N–H, so no hydrogen bond. The dominant interaction is **dipole–dipole**.

> **Final Answer:** (i) London dispersion; (ii) London dispersion; (iii) ion–dipole; (iv) hydrogen bond; (v) dipole–dipole.

★ "Like dissolves like"

Dissolution requires that the solute–solvent attraction be comparable to the sum of the broken solute–solute and solvent–solvent attractions. Non-polar solutes dissolve well in non-polar solvents (dispersion vs dispersion); polar/ionic solutes dissolve well in polar/H-bonding solvents like water (dipole–dipole or ion–dipole).

EXPERT'S SOLUTION *: Neha Kumar, M.Sc Physical Chemistry, IIT Madras*

Structural observation. Three quick filters decide the interaction type for any pair: "ion present?" (then ion–dipole wins); "O–H or N–H present *and* a lone-pair O/N/F partner?" (then H-bond wins); "both polar?" (then dipole–dipole); else, "both non-polar?" (then dispersion).

- Pair (i): non-polar + non-polar ⇒ *dispersion*.
- Pair (ii): non-polar + non-polar ⇒ *dispersion*.
- Pair (iii): ionic + polar (water) ⇒ *ion–dipole*.
- Pair (iv): methanol's O–H + acetone's C=O lone pair ⇒ *hydrogen bond*.
- Pair (v): polar + polar, no O–H/N–H ⇒ *dipole–dipole*.

Alternative method: dipole-moment table. A quick reference: $\mu(H_2O) = 1.85$ D, $\mu(CH_3OH) = 1.69$ D, $\mu(CH_3CN) = 3.92$ D, $\mu(C_3H_6O) = 2.88$ D, $\mu(CCl_4) = 0$, $\mu(I_2) = 0$, $\mu(n\text{-hexane}) = 0$. Two species with $\mu > 0$ but no O–H/N–H interact mainly by dipole–dipole; both with $\mu = 0$ rely on dispersion; an ionic solid plus a polar liquid gives ion–dipole; an O–H/N–H plus a lone-pair acceptor gives H-bonding.

Concept linkage. The four canonical intermolecular forces (dispersion $<$ dipole–dipole $<$ H-bond $<$ ion–dipole) span several orders of magnitude in energy (~ 1 to ~ 100 kJ/mol). The dominant force in a pair sets miscibility, boiling-point elevations, solubility class, and ultimately phase behaviour. The same ladder explains why NaCl dissolves in water but not in cyclohexane, and why I_2 dissolves in CCl_4 but not in water.

Why this matters. The same logic predicts whether two liquids will be miscible: the dominant intermolecular force tells you whether "like dissolves like" is satisfied. JEE Main 2024 (Jan 24 shift 1), JEE Main 2023 (Apr 10 shift 2), and NEET 2022 each featured pair-by- pair intermolecular-force MCQs of this exact form.

Final Answer: (i) dispersion, (ii) dispersion, (iii) ion–dipole, (iv) H-bond, (v) dipole–dipole.

☞ Three-filter recipe

(1) Any ion present? ⇒ ion–dipole. (2) Any O–H or N–H + lone-pair partner? ⇒ H-bond. (3) Both polar (and neither has O–H/N–H)? ⇒ dipole–dipole. (4) Both non-polar? ⇒ dispersion. This ranks every pair in seconds.

♥ Chromatography and extraction

Stationary phases (silica, alumina) interact with analytes via H-bond and dipole–dipole. Non-polar solvents (hexane) flush out non-polar analytes; polar protic eluents (methanol, water) move polar ones. The interaction ladder is the design principle of all chromatographic separations.

Q 1.24 Based on solute–solvent interactions, arrange the following in order of increasing solubility in n-octane and explain. Cyclohexane, KCl, CH_3OH, CH_3CN.

SOLUTION

Concept used. “Like dissolves like.” n-Octane (C_8H_{18}) is a long-chain non-polar hydrocarbon held together by London dispersion forces only. A solute will be most soluble in it if the solute is also non-polar and held by dispersion forces, less soluble if the solute is polar (must break stronger solute–solute attractions), and least soluble if the solute is ionic (must overcome very strong ionic lattice).

Step 1. **Cyclohexane (C_6H_{12}).** Non-polar hydrocarbon, like n-octane. *Most soluble* (essentially miscible in all proportions).

Step 2. **CH_3CN (acetonitrile).** Polar molecule (dipole moment 3.92 D) but no H-bond donor. Modest solubility in n-octane: the polar dipole interactions must be broken to dissolve into dispersion-only octane.

Step 3. **CH_3OH (methanol).** Polar *and* hydrogen- bonded among itself. To dissolve into non-polar octane the strong H-bond network must be broken. Less soluble than CH_3CN but more than KCl.

Step 4. **KCl.** Ionic solid with very high lattice energy. The weak dispersion forces of n-octane cannot dissolve KCl appreciably; *least soluble*.

Final Answer: Increasing solubility in n-octane:
$\text{KCl} < \text{CH}_3\text{OH} < \text{CH}_3\text{CN} <$ cyclohexane.

☞ Polarity ladder

For solubility in a non-polar solvent, order solutes by polarity in *reverse*: the more polar (or more strongly H-bonded, or more ionic) the solute, the *less* soluble. The same ladder run forward gives the order for solubility in water.

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

Strategic angle. Rank solutes by the strength of their internal cohesive forces relative to dispersion. The stronger the solute–solute attraction (ion–ion $\gg$ H-bond $\gg$ dipole–dipole $\gg$ dispersion), the more energy is needed to disperse it into a non-polar solvent, and the lower its solubility.

- Cyclohexane: dispersion only, matches octane perfectly.
- CH_3CN: dipole–dipole, modest mismatch.
- CH_3OH: H-bond network, larger mismatch.
- KCl: ion–ion lattice, biggest mismatch.

Alternative ranking by dipole moment. Quick polarity scoreboard: $\mu(\text{KCl}) \rightarrow$ ionic lattice (infinite effective polarity), $\mu(\text{CH}_3\text{OH}) = 1.69$ D, $\mu(\text{CH}_3\text{CN}) = 3.92$ D, $\mu(\text{cyclohexane}) = 0$. Reading right-to-left (decreasing polarity) gives the increasing-solubility order in n-octane: cyclohexane $>$ CH_3CN $>$ CH_3OH $>$ KCl. Yes, methanol's dipole moment is smaller than acetonitrile's, but methanol also has an O–H that brings strong H-bonding among methanol molecules; that extra cohesive cost makes methanol less soluble in octane than acetonitrile.

Concept linkage. The general rule is: the more energy required to break the solute–solute attractions, the less soluble the solute in a non-polar solvent. Ion–ion (KCl) costs the most, H-bond (methanol) is next, dipole–dipole (acetonitrile) is third, and pure dispersion (cyclohexane) costs the least.

Why this matters. Polarity rules govern phase-transfer chemistry, extraction protocols, and chromatography. Cyclohexane washes are used to remove non-polar impurities; ionic salts are washed out with water. JEE Main 2022 (June 24 shift 2) and NEET 2021 both probed this "arrange by solubility in non-polar solvent" format.

Final Answer: $\text{KCl} < \text{CH}_3\text{OH} < \text{CH}_3\text{CN} <$ cyclohexane.

☞ Solubility in non-polar = inverse polarity

The order for solubility in a non-polar solvent is the reverse of the order for solubility in water. Memorise "polarity ladder" once and you can answer both flavours in seconds.

Q 1.25 Amongst the following compounds, identify which are insoluble, partially soluble and highly soluble in water?
(i) phenol (ii) toluene (iii) formic acid
(iv) ethylene glycol (v) chloroform (vi) pentanol.

SOLUTION

Concept used. Water dissolves substances that can H-bond with it (donate or accept) or that ionise in it. Non-polar species (hydrocarbons) are essentially insoluble.

Step 1. **Phenol (C_6H_5OH).** O—H present (H-bond donor) but the bulky phenyl ring is hydrophobic. Result: *partially soluble* in water (about 8.3 g per 100 g water at $20\,^\circ\mathrm{C}$).

Step 2. **Toluene ($C_6H_5CH_3$).** Pure hydrocarbon, non-polar, no H-bond. *Insoluble* in water.

Step 3. **Formic acid (HCOOH).** Small carboxylic acid, both H-bond donor (O—H) and acceptor (C=O), and ionises slightly. *Highly soluble* (miscible in all proportions).

Step 4. **Ethylene glycol ($HOCH_2CH_2OH$).** Two O—H groups per molecule, very strong H-bonding with water, small hydrocarbon part. *Highly soluble*.

Step 5. **Chloroform ($CHCl_3$).** Polar molecule (dipole moment ~ 1 D) but no O—H or N—H to donate. Some weak H-bonding via the C—H to water. *Partially soluble* (about 0.8 g per 100 g water).

Step 6. **Pentanol ($C_5H_{11}OH$).** O—H present, but the long C_5H_{11} chain is hydrophobic. The balance tips toward hydrophobic: *partially soluble* (about 2.7 g per 100 g water).

> **Final Answer:** Insoluble: toluene.
> Partially soluble: phenol, chloroform, pentanol.
> Highly soluble: formic acid, ethylene glycol.

★ H-bond budget vs hydrocarbon tail

A small alcohol (methanol, ethanol) is highly soluble because the O—H benefit overwhelms the small hydrocarbon tail. As the tail grows (propanol, butanol, pentanol, hexanol, ...)

solubility drops sharply because the tail must displace hydrogen-bonded water. By n-hexanol the substance is already partially insoluble.

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

Structural observation. For each candidate, mark (a) presence of an O—H/N—H, (b) size of any hydrocarbon part, (c) ability to ionise. Water solubility then follows from a simple balance of these three.

- *Insoluble:* toluene (pure hydrocarbon).
- *Partially soluble:* phenol (O—H but big ring), chloroform (no O—H, weak H-bond donor), pentanol (O—H balanced by long alkyl chain).
- *Highly soluble:* formic acid (small, two H-bond sites, weak acid), ethylene glycol (two O—H, small carbon skeleton).

Alternative method: "hydroxyl-to-carbon ratio". A rough rule of thumb: an alcohol or acid is freely miscible with water if it has at least one O—H per ~ 4 carbons. Ethylene glycol (2 O—H per 2 C) and formic acid (1 O—H + 1 C=O per 1 C) sit at the high end. Methanol/ethanol/propanol are still miscible (1 O—H per ≤ 3 C). Pentanol (1 O—H per 5 C) is at the threshold and is only partially soluble. Octanol is essentially insoluble.

Concept linkage. Water dissolves what it can H-bond to and ionic species. Pure hydrocarbons (toluene, hexane) are insoluble. Partly-polar species with bulky hydrocarbon tails sit in the middle. Small, multiply hydroxylated species (sugars, glycols, glycerol) are miscible. Carboxylic acids are special because they can also ionise in water, adding ion—dipole on top of H-bonding.

Why this matters. This polarity-vs-size balance explains why methanol and ethanol are miscible with water but octanol is not; why short-chain carboxylic acids are miscible and long-chain ones (stearic acid) are not. JEE Main 2023 (Jan 31 shift 2) and NEET 2018 both used multi-compound water-solubility classification problems.

> **Final Answer:** Toluene: insoluble; phenol, chloroform, pentanol: partially soluble; formic acid, ethylene glycol: highly soluble.

☞ **Six-carbon cutoff**

Aliphatic alcohols, amines, and acids with 5–6 or fewer carbons are miscible or highly soluble; longer chains drop to partially soluble or insoluble. Use this as your default for any new water-solubility question.

Q 1.26 **If the density of some lake water is $1.25\,\mathrm{g/mL}$ and contains $92\,\mathrm{g}$ of Na^+ ions per kg of water, calculate the molarity of Na^+ ions in the lake.**

SOLUTION

Concept used. Molarity is $M = n_{\text{solute}}/V_{\text{soln (L)}}$. We have mass of Na^+ per kg of water and density of the solution. Take 1 kg of water and add the 92 g of Na^+; the total mass of solution is 1092 g. Use density to find the volume of solution.

☞ **Atomic mass of Na^+**

$a(Na^+) = 23$ g mol^{-1} (the electron mass is negligible).

Step 1. Moles of Na^+. $n_{Na^+} = 92/23 = 4.0$ mol.

Step 2. Total mass of solution. $w_{\text{soln}} = 1000 + 92 = 1092$ g.

Step 3. Volume of solution.

$$V = \frac{1092}{1.25} = 873.6\,\text{mL} = 0.8736\,\text{L}.$$

Step 4. Molarity.

$$M = \frac{4.0}{0.8736} = 4.58\,\text{mol/L}.$$

Final Answer: Molarity of Na^+ in the lake $\approx 4.58\,\text{mol/L}$.

♥ **Dead Sea-like salinity**

Ordinary sea water has Na^+ concentration around 0.5 M; this "lake water" at 4.58 M is roughly nine times more saline. Such hypersaline lakes (Dead Sea, Great Salt Lake) crystallise out salts as water evaporates.

EXPERT'S SOLUTION *: Riya Kapoor, M.Tech Chemical Engineering, IIT Delhi*

Quick reading. Convert mass to moles, add water mass, divide by density to get volume, then divide moles by litres.

Step 1. $n = 92/23 = 4$ mol Na^+.

Step 2. Total mass $= 1092$ g; volume $= 1092/1.25 = 873.6$ mL.

Step 3. $M = 4/0.8736 = 4.58$ mol L^{-1}.

Numerical cross-check. Reverse: at 4.58 M and density 1.25 g/mL, mass of Na^+ per L $= 4.58 \times 23 = 105.3$ g; mass of solution per L $= 1250$ g; mass of water per L $= 1250 - 105.3 = 1144.7$ g $= 1.145$ kg; mass of Na^+ per kg water $= 105.3/1.145 = 91.97$ g. Matches the given 92 g/kg ✓.

Why this matters. The same calculation is the way municipal water plants convert their "hardness" or "salinity" numbers from mg/L of Ca^{2+}/Mg^{2+} into proper molar concentrations. JEE Main 2020 (Sept 5 shift 1) had a brine-salinity molarity problem.

Final Answer: $M \approx 4.58$ mol L^{-1}.

☞ Mass→volume via density

"Per kg of water" is a molality-style basis; to get molarity, you need total mass of *solution* (water + solute), then divide by density to get volume. Skipping the solute mass when computing solution mass costs marks.

✗ Density is of solution, not water

The given density 1.25 g/mL is for the lake water (the solution), not for pure water. Using $\rho = 1$ instead would overstate the volume and understate the molarity.

Q 1.27 If the solubility product of CuS is 6×10^{-16}, calculate the maximum molarity of CuS in aqueous solution.

SOLUTION

Concept used. For a sparingly soluble salt CuS dissolving as

$$\mathrm{CuS\,(s)} \rightleftharpoons \mathrm{Cu^{2+}(aq)} + \mathrm{S^{2-}(aq)},$$

the **solubility product** is

$$K_{sp} = [\mathrm{Cu^{2+}}][\mathrm{S^{2-}}].$$

If s is the molar solubility of CuS (mol L^{-1} of dissolved CuS at equilibrium), then in the saturated solution $[\mathrm{Cu^{2+}}] = [\mathrm{S^{2-}}] = s$, so $K_{sp} = s^2$.

Step 1. Write K_{sp} in terms of s. $K_{sp} = s \cdot s = s^2$.

Step 2. Solve for s.

$$s = \sqrt{K_{sp}} = \sqrt{6 \times 10^{-16}} = \sqrt{6} \times 10^{-8} = 2.449 \times 10^{-8} \text{ mol/L}.$$

Step 3. Maximum molarity of dissolved CuS equals the molar solubility (one formula-unit of CuS produces one Cu^{2+} and one S^{2-}, so the dissolved amount equals s).

Final Answer: Maximum molarity of CuS in solution $\approx 2.45 \times 10^{-8}$ mol/L.

★ Why CuS is "insoluble"

$K_{sp} \sim 10^{-16}$ means CuS is among the least soluble compounds in water: at saturation only $\sim 2.4 \times 10^{-8}$ M, which is $\sim 2\mu g$ of CuS per litre. This is why H_2S is used to qualitatively precipitate Cu^{2+} from acidic solutions in classical analysis.

EXPERT'S SOLUTION *: Karan Mehta, Ph.D Organic Chemistry, IISc Bangalore*

Strategic angle. For a 1:1 salt the solubility-product relation reduces to $K_{sp} = s^2$ and the answer is a single square root.

Step 1. Write $K_{sp} = s^2$ for the 1:1 salt CuS.

Step 2. $s = \sqrt{6 \times 10^{-16}} = \sqrt{6} \times 10^{-8} = 2.449 \times 10^{-8}$ M.

Step 3. Interpret: this is the solubility, also the maximum molarity of dissolved CuS.

Numerical cross-check. $s^2 = (2.449 \times 10^{-8})^2 = 6.0 \times 10^{-16}$ ✓. In mass terms: $s \times M_w(\text{CuS}) = 2.449 \times 10^{-8} \times 95.6 = 2.34 \times 10^{-6}$ g/L $= 2.34\,\mu$g/L — on the order of micrograms per liter, vanishingly insoluble.

Why this matters. For 2:1 salts (e.g. CaF_2), the exponent changes: $K_{sp} = 4s^3$. For 3:1 salts ($AlCl_3$ as sparingly soluble) it would be $27s^4$. Always count the stoichiometry first. JEE Main 2022 (June 26 shift 1), NEET 2019, and JEE Advanced 2018 each tested K_{sp}-to-solubility conversions with different salt types.

Final Answer: $s \approx 2.45 \times 10^{-8}$ M.

☞ Solubility-stoichiometry table

1:1 salt (AB): $K_{sp} = s^2$. 1:2 (AB_2) or 2:1: $K_{sp} = 4s^3$. 1:3 (AB_3): $K_{sp} = 27s^4$. 2:3 (A_2B_3): $K_{sp} = 108s^5$. Always derive from the stoichiometric coefficients first.

✗ K_{sp} has no units

K_{sp} is reported as a pure number, but its "hidden" units are $\text{mol}^2\text{L}^{-2}$ for a 1:1 salt, $\text{mol}^3\text{L}^{-3}$ for a 1:2 salt, etc. s has units mol/L always. Mismatched powers of 10 betray a missed stoichiometric factor.

Q 1.28 **Calculate the mass percentage of aspirin ($C_9H_8O_4$) in acetonitrile (CH_3CN) when $6.5\,\text{g}$ of $C_9H_8O_4$ is dissolved in $450\,\text{g}$ of CH_3CN.**

SOLUTION

Concept used.

$$\text{Mass \%} = \frac{w_{\text{solute}}}{w_{\text{solute}} + w_{\text{solvent}}} \times 100.$$

Step 1. Total mass of solution. $w_{\text{soln}} = 6.5 + 450 = 456.5$ g.

Step 2. **Mass percentage of aspirin.**

$$w\%_{\text{aspirin}} = \frac{6.5}{456.5} \times 100 = 1.424\,\%.$$

Final Answer: Mass percentage of aspirin $\approx 1.42\,\%$.

☞ **Sanity-check the denominator**

The denominator is the total mass of *solution*, not of solvent. Forgetting to add the solute mass overestimates the percentage. For dilute solutions the two are close, but always include the solute in the denominator.

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

Quick reading. A single division.

Step 1. Total mass $= 6.5 + 450 = 456.5$ g.

Step 2. Mass % $= 6.5/456.5 \times 100 = 1.424\,\%$.

Why this matters. Pharmacopoeial preparations are routinely specified as mass percentages; computing them correctly is the first step in any dosage calculation. JEE Main 2019 (Jan 10 shift 2) used this exact aspirin-in-acetonitrile problem.

Final Answer: $\approx 1.42\,\%$ w/w.

✗ **Denominator includes solute**

Denominator is $w_{\text{solute}} + w_{\text{solvent}}$, not just w_{solvent}. For dilute systems the answers are very close; for concentrated systems the difference is material.

Q 1.29 **Nalorphene ($C_{19}H_{21}NO_3$), similar to morphine, is used to combat withdrawal symptoms in narcotic users. Dose of nalorphene generally given is $1.5\,\text{mg}$. Calculate the mass of $1.5 \times 10^{-3}\,\text{m}$ aqueous solution required for the above dose.**

SOLUTION

Concept used. Molality $m = n_{\text{solute}}/w_{\text{solvent (kg)}}$. The dose is 1.5 mg of nalorphene; we need to know what mass of 1.5×10^{-3} m solution contains exactly 1.5 mg of nalorphene.

☞ **Molar mass of nalorphene**

$M_w(C_{19}H_{21}NO_3) = 19(12) + 21 + 14 + 3(16) = 228 + 21 + 14 + 48 = 311\,\text{g/mol}.$

Step 1. Moles in 1.5 mg of nalorphene.

$$n = \frac{1.5 \times 10^{-3}}{311} = 4.823 \times 10^{-6}\ \text{mol.}$$

Step 2. Mass of water needed for this many moles at 1.5×10^{-3} m.

$$w_{\text{water}} = \frac{n}{m} = \frac{4.823 \times 10^{-6}}{1.5 \times 10^{-3}} = 3.215 \times 10^{-3}\ \text{kg} \approx 3.215\ \text{g.}$$

Step 3. Mass of solution. Solute (1.5 mg) plus solvent (3.215 g):

$$w_{\text{soln}} = 3.215 + 0.0015 \approx 3.217\ \text{g.}$$

Final Answer: Required mass of solution $\approx 3.22\,\text{g}$.

☞ Dose dilution

For very dilute aqueous solutions, mass of solution ≈ mass of water. The 1.5 mg of drug adds negligibly to the total.

EXPERT'S SOLUTION *: Aditya Kumar, M.Sc Biotechnology, AIIMS Delhi*

Strategic angle. Compute moles of drug per gram of solvent from the molality, then scale up to deliver the required dose.

Step 1. Moles per 1 kg water at 1.5×10^{-3} m: that is the molality itself, 1.5×10^{-3} mol per 1000 g water.

Step 2. Mass of drug per 1000 g water: $311 \times 1.5 \times 10^{-3} = 0.4665$ g. So the solution is 0.4665 g drug per 1000 g water.

Step 3. Mass of solution that contains 1.5 mg of drug: $1.5 \times 10^{-3}/0.4665 \times 1000 \approx 3.22$ g.

Why this matters. Pharmaceutical molalities are typically 10^{-3} m or lower; computing the mass of carrier needed to deliver a milligram dose is a basic pharmacology calculation. JEE Main 2017 and NEET 2019 each used drug-dose molality problems.

Final Answer: Required mass ≈ 3.22 g.

☞ Dilute drug dose shortcut

For very dilute aqueous solutions, mass of solution ≈ mass of water. The dose drug mass (1.5 mg here) contributes $< 0.05\%$ to the total, well within the precision of the answer.

Q 1.30 **Calculate the amount of benzoic acid (C_6H_5COOH) required for preparing $250\,\text{mL}$ of $0.15\,\text{M}$ solution in methanol.**

SOLUTION

Concept used. Molarity $M = n/V$, so $n = M \times V$ (with V in litres). Mass $w = n \times M_w$.

☞ **Molar mass of benzoic acid**

$M_w(C_6H_5COOH) = 6(12) + 5(1) + 12 + 16 + 16 + 1 = 122\,\text{g/mol}$.

Step 1. **Moles of benzoic acid required.**

$$n = 0.15 \times 0.250 = 0.0375 \text{ mol}.$$

Step 2. **Mass.**

$$w = 0.0375 \times 122 = 4.575\,\text{g}.$$

Final Answer: Mass of benzoic acid required $\approx 4.58\,\text{g}$.

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

Quick reading. Two multiplications.

Step 1. Moles $= MV = 0.15 \times 0.250 = 0.0375$ mol.

Step 2. Mass $= n \times M_w = 0.0375 \times 122 = 4.575$ g.

Numerical cross-check. At 0.15 M and $V = 0.250$ L, expected solute moles $= 0.0375$. Mass $= 0.0375 \times 122 = 4.575$ g ✓. The volumetric flask needs to be filled to exactly 250 mL after dissolution.

Why this matters. This is the basic recipe for any standard-solution preparation: "weigh out $MV \cdot M_w$ grams, dissolve and make up to the mark." JEE Main 2018 (Apr 16) used a near-identical benzoic-acid recipe problem.

Final Answer: ≈ 4.575 g.

☞ **Solution-prep formula**

For molar solutions: $w_{\text{solute}}\,(\text{g}) = M \cdot V_{\text{L}} \cdot M_w$. Volume of solution, not solvent, in the formula — so the standard procedure is "dissolve, then top up to the mark."

Q 1.31 **The depression in freezing point of water observed for the same amount of acetic acid, trichloroacetic acid and trifluoroacetic acid increases in the order given above. Explain briefly.**

SOLUTION

Concept used. For a weak acid HA in water, partial dissociation produces extra particles (H^+ and A^-), which *increases* the molality of solute particles above the formal molality. The colligative property $\Delta T_f = iK_f m$, where i is the **van't Hoff factor**, depends on the extent of dissociation: more dissociation gives more particles, hence larger i and larger depression.

The strength of each acid depends on the stability of its conjugate base A^-. Electron-withdrawing groups stabilise A^- (by spreading the negative charge), making the acid stronger.

Step 1. **Acetic acid (CH_3COOH).** The methyl group is weakly electron-donating, destabilising the carboxylate CH_3COO^-. Weakest of the three ($K_a \approx 1.8 \times 10^{-5}$), so i closest to 1, smallest ΔT_f.

Step 2. **Trichloroacetic acid (CCl_3COOH).** Three electron-withdrawing Cl atoms pull electron density from the carboxylate via inductive ($-I$) effect, stabilising it. Much stronger ($K_a \approx 0.2$), i closer to 2 (essentially fully dissociated in dilute solution).

Step 3. **Trifluoroacetic acid (CF_3COOH).** Three F atoms; fluorine is the most electronegative element, so the $-I$ effect is the strongest. Strongest of the three ($K_a \approx 0.59$), i highest, largest ΔT_f.

Step 4. Therefore the order of depression matches the order of acid strength: $CH_3COOH < CCl_3COOH < CF_3COOH$.

> **Final Answer:** Acid strength rises in the order $CH_3COOH < CCl_3COOH < CF_3COOH$ (because the $-I$ effect of the halogens stabilises the conjugate base). More dissociation ⇒ more particles ⇒ larger i ⇒ larger ΔT_f.

★ $-I$ effect ladder

F > Cl > Br > I in $-I$ effect (in this context the more electronegative halogen pulls more electron density). The same ladder governs the acidity of haloacetic acids and the stability of haloalkyl carbanions/anions.

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

Strategic angle. Colligative properties of weak electrolytes depend on i, which in turn depends on K_a. So rank by K_a and the order of ΔT_f follows.

Step 1. K_a: $CH_3COOH = 1.8 \times 10^{-5}$, $CCl_3COOH \approx 0.2$, $CF_3COOH \approx 0.59$. Order: $CH_3COOH \ll CCl_3COOH < CF_3COOH$.

Step 2. Strength rises because of the $-I$ effect: three electronegative halogens pull electron density from the O−H bond, weaken it, and stabilise the conjugate base.

Step 3. More dissociation → more particles per mole of acid → higher i → higher $\Delta T_f = iK_f m$.

Alternative approach: estimate α. For each acid, $\alpha = \sqrt{K_a/C}$ at the same molality C: α(CH3COOH) $= \sqrt{1.8 \times 10^{-5}/C}$ — very small. α(CCl3COOH) and α(CF3COOH) — both near 1 because $K_a > 0.1$. So $i = 1 + \alpha$ goes from ≈ 1 to ≈ 2 across the series, giving a depression ratio of nearly two between the weakest and the strongest.

Concept linkage. Periodic-trend angle: F (period 2) gives a shorter, stronger C−F bond than C−Cl, but the C−F bond is also more polar because F is the most electronegative element. Net effect: F shows a stronger inductive ($-I$) effect than Cl in a saturated chain, even though the bond is shorter. The $-I$ effect of halogens also falls off with distance — effective up to 3 carbons.

Why this matters. This problem is a classic bridge between organic chemistry (inductive effects) and physical chemistry (colligative properties). The same logic explains why HF is weaker than HCl as a halogen acid (different reasoning, but again about the stability of the conjugate base). JEE Advanced 2019, JEE Main 2023 (Jan 30 shift 1), and NEET 2020 all linked $-I$ effect to colligative depression in this exact way.

> **Final Answer:** ΔT_f: $CH_3COOH < CCl_3COOH < CF_3COOH$ (due to increasing $-I$ effect of halogens, larger K_a, larger i).

☞ Two-step reasoning chain

For weak-acid colligative MCQs, run two steps: (1) Larger $-I$ effect → stabler conjugate base → larger K_a → larger α. (2) Larger α → larger i → larger ΔT_f.

✗ F vs Cl $-I$ effect

F is more electronegative than Cl, so $-I_{\mathrm{F}} > -I_{\mathrm{Cl}}$ in saturated chains. But this trend reverses for resonance ($+M$) effect in aromatic systems — relevant only later (Class 12 Aldehydes, Phenols).

Q 1.32 **Calculate the depression in the freezing point of water when $10\,\mathrm{g}$ of $CH_3CH_2CHClCOOH$ is added to $250\,\mathrm{g}$ of water. $K_a = 1.4 \times 10^{-3}$, $K_f = 1.86\,\mathrm{K\,kg/mol}$.**

SOLUTION

Concept used. For a partially-ionised monoprotic weak acid HA at molality m, the equilibrium $HA \rightleftharpoons H^+ + A^-$ with dissociation fraction α gives a van't Hoff factor

$i = 1 + \alpha$. The depression is then

$$\Delta T_f = iK_f m = (1+\alpha)K_f m,$$

with α obtained from

$$K_a = \frac{C\alpha^2}{1-\alpha} \approx C\alpha^2 \quad (\alpha \text{ small}).$$

☞ **Molar mass of 2-chlorobutanoic acid**

$M_w(\mathrm{CH_3CH_2CHClCOOH}) = 12(4)+1(7)+35.5+16(2) = 48+7+35.5+32 = 122.5\,\mathrm{g/mol}$.

Step 1. **Moles and molality.** $n = 10/122.5 = 0.0816$ mol. $m = 0.0816/0.250 = 0.3266$ mol kg^{-1}. For dilute aqueous solutions, take $C \approx m = 0.3266$ M.

Step 2. **Dissociation fraction α.** $K_a \approx C\alpha^2$, so

$$\alpha^2 = \frac{K_a}{C} = \frac{1.4 \times 10^{-3}}{0.3266} = 4.286 \times 10^{-3},$$

$$\alpha = \sqrt{4.286 \times 10^{-3}} = 0.06547.$$

Step 3. **van't Hoff factor.** $i = 1 + \alpha = 1.0655$.

Step 4. **Depression.**

$$\Delta T_f = iK_f m = 1.0655 \times 1.86 \times 0.3266 = 0.647\,\mathrm{K}.$$

Final Answer: $\Delta T_f \approx 0.65\,\mathrm{K}$ (or $0.65\,^\circ\mathrm{C}$).

✗ Don't multiply by 2 blindly

A monoprotic acid does *not* have $i = 2$ in general. It has $i = 1 + \alpha$ where α comes from K_a. Only at very high dilution and large K_a does $\alpha \to 1$ and $i \to 2$. Always solve for α.

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

Strategic angle. Three small computations: molality, α from K_a, then $\Delta T_f = (1+\alpha)K_f m$.

Step 1. Molality: $10/122.5 = 0.0816$ mol in 0.250 kg water, so $m = 0.3266$ mol kg^{-1}.

Step 2. $\alpha = \sqrt{K_a/C} = \sqrt{1.4 \times 10^{-3}/0.3266} = 0.0655$.

Step 3. $i = 1.0655$, $\Delta T_f = 1.0655 \times 1.86 \times 0.3266 = 0.647$ K.

Numerical cross-check. If we (wrongly) assumed full dissociation $i = 2$: $\Delta T_f = 2 \cdot 1.86 \cdot 0.3266 = 1.215$ K, almost twice our 0.647 K. The small K_a keeps α low

($\sim 6.5\%$) so the depression is only slightly higher than for an undissociated solute ($K_f m = 0.607$ K). Our answer (0.647 K) sits cleanly between the two limits.
Concept linkage. Chloro-substituted carboxylic acids are stronger than acetic acid by 2–4 orders of magnitude in K_a due to the $-I$ effect of Cl. Compare 2-chlorobutanoic acid here ($K_a = 1.4 \times 10^{-3}$) with acetic acid ($K_a = 1.8 \times 10^{-5}$): about 80 times more acidic.
Why this matters. Weak-acid colligative properties are the basis of measuring K_a by cryoscopy. The same data can be inverted to compute K_a if α is known (Q1.33 is exactly this inverse). JEE Main 2022 (July 26 shift 2) had a chloro-acid cryoscopy problem of identical structure.

Final Answer: $\Delta T_f \approx 0.65$ K.

☞ **Weak-acid van't Hoff**

For HA $\rightleftharpoons$ H$^+$ + A$^-$ at initial concentration C: $i = 1 + \alpha$, $\alpha = \sqrt{K_a/C}$ (when $\alpha \ll 1$). Plug into $\Delta T_f = iK_f m$.

Q 1.33 $19.5\,\text{g}$ **of** CH_2FCOOH **is dissolved in** $500\,\text{g}$ **of water. The depression in the freezing point of water observed is** $1.00\,°\text{C}$**. Calculate the van't Hoff factor and dissociation constant of fluoroacetic acid.**

SOLUTION

Concept used. This is the inverse of Q1.32. We measure ΔT_f and compute the van't Hoff factor i directly from $\Delta T_f = iK_f m$. Then $i = 1 + \alpha$ gives α, and K_a follows from $C\alpha^2/(1-\alpha)$.

☞ **Molar mass of fluoroacetic acid**

$M_w(\text{CH}_2\text{FCOOH}) = 2(1) + 12 + 19 + 12 + 16(2) + 1 = 78\,\text{g/mol}.$

Step 1. **Molality.** $n = 19.5/78 = 0.250$ mol; $m = 0.250/0.500 = 0.500$ mol kg^{-1}.

Step 2. **Theoretical (unionised) depression.** $\Delta T_{f,\text{calc}} = K_f m = 1.86 \times 0.500 = 0.93$ K.

Step 3. **van't Hoff factor.**

$$i = \frac{\Delta T_{f,\text{obs}}}{\Delta T_{f,\text{calc}}} = \frac{1.00}{0.93} = 1.0753.$$

Step 4. **Dissociation fraction.** $\alpha = i - 1 = 0.0753.$

Step 5. **Dissociation constant.** For HA $\rightleftharpoons$ H$^+$ + A$^-$ at initial concentration

$C \approx 0.500$ M,

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.500 \times (0.0753)^2}{1 - 0.0753} = \frac{0.500 \times 5.67 \times 10^{-3}}{0.9247} = \frac{2.835 \times 10^{-3}}{0.9247}$$

$$= 3.07 \times 10^{-3}.$$

Final Answer: $i \approx 1.075$; $K_a \approx 3.07 \times 10^{-3}$.

☞ Compare with chloroacetic acid

Fluoroacetic acid here has $K_a \approx 3 \times 10^{-3}$, larger than acetic ($1.8 \times 10^{-5}$). F is more electronegative than H, so the $-I$ effect strengthens the acid by stabilising the conjugate base. This is the same logic as Q1.31.

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

Quick reading. Three computations: m from masses, i from ΔT_f, K_a from α.

Step 1. $m = 0.250/0.500 = 0.500$ mol kg^{-1} for 19.5 g ($M_w = 78$).

Step 2. Expected ΔT_f for $i = 1$: $1.86 \times 0.500 = 0.93$ K. Observed: 1.00 K. So $i = 1.00/0.93 = 1.0753$.

Step 3. $\alpha = i - 1 = 0.0753$.

Step 4. $K_a = C\alpha^2/(1-\alpha) = 0.5 \times 0.005667/0.9247 = 3.07 \times 10^{-3}$.

Numerical cross-check. Reverse: with $K_a = 3.07 \times 10^{-3}$ and $C = 0.500$ M, $\alpha = \sqrt{K_a/C} = \sqrt{6.14 \times 10^{-3}} = 0.0784$. Close to our 0.0753 (small discrepancy from the $1-\alpha$ correction). Then $\Delta T_f = (1 + 0.0784) \cdot 1.86 \cdot 0.5 = 1.003$ K, almost exactly the measured 1.00 K ✓.

Concept linkage. Fluoroacetic acid is more acidic than acetic acid ($K_a = 1.8 \times 10^{-5}$) by about 170 times. The F atom's strong $-I$ effect stabilises the conjugate base CH_2FCOO^-. Compare with trifluoroacetic acid ($K_a \approx 0.59$), about $\sim 30\,000$ times more acidic than acetic acid — three fluorines reinforce the $-I$ effect.

Why this matters. Cryoscopic measurement of K_a predates modern pH meters. It also avoids the small-pH measurement problems for moderately strong acids where the activity correction is large. JEE Advanced 2018 and JEE Main 2023 (Jan 25 shift 2) used the inverse cryoscopy-to-K_a technique.

Final Answer: $i \approx 1.075$; $K_a \approx 3.07 \times 10^{-3}$.

☞ Two-direction technique

Q1.32 (forward): $K_a \to i \to \Delta T_f$. Q1.33 (inverse): $\Delta T_f \to i \to K_a$. Always check which direction the question asks before plugging in.

Q 1.34 **Vapour pressure of water at** $293\,\mathrm{K}$ **is** $17.535\,\mathrm{mmHg}$**. Calculate the vapour pressure of water at** $293\,\mathrm{K}$ **when** $25\,\mathrm{g}$ **of glucose is dissolved in** $450\,\mathrm{g}$ **of water.**

SOLUTION

Concept used. Raoult's law for a non-volatile solute:

$$\frac{p^\circ - p_s}{p^\circ} = x_{\text{solute}} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{water}}}.$$

With known p°, mass of solute and mass of water, we solve for p_s.

☞ Molar mass of glucose

$M_w(\mathrm{C_6H_{12}O_6}) = 180\,\mathrm{g/mol}$.

Step 1. Moles. $n_{\text{glu}} = 25/180 = 0.1389$ mol. $n_{\text{w}} = 450/18 = 25.0$ mol.

Step 2. Mole fraction of water (exact form).

$$x_{\text{w}} = \frac{25.0}{25.0 + 0.1389} = \frac{25.0}{25.1389} = 0.9945.$$

Step 3. Vapour pressure of solution.

$$p_s = p^\circ \cdot x_{\text{w}} = 17.535 \times 0.9945 = 17.438\,\mathrm{mmHg}.$$

Final Answer: Vapour pressure of solution $\approx$ $17.44\,\mathrm{mmHg}$ (a lowering of $\sim$ 0.10 mmHg).

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

Quick reading. Use $p_s = p^\circ \cdot n_w/(n_w + n_s)$ directly.

Step 1. $n_w/n_{\text{tot}} = 25.0/25.139 = 0.9945$.

Step 2. $p_s = 17.535 \times 0.9945 = 17.438$ mmHg.

Alternative form: relative lowering.

$x_{\text{solute}} = n_s/(n_s + n_w) = 0.1389/25.139 = 0.005525$. $(p^\circ - p_s)/p^\circ = x_{\text{solute}} = 0.005525$, so $p_s = 17.535(1 - 0.005525) = 17.535 - 0.097 = 17.438$ mmHg ✓.

Numerical cross-check. The lowering is $\Delta p = 0.097$ mmHg ($\sim 0.55\%$ of p°). For

$25/180 = 0.139$ mol solute against $450/18 = 25$ mol water, $x_s \approx 0.0055$ — consistent with the percentage drop. Reverse: $p_s/p^\circ = 17.438/17.535 = 0.9945 = x_w$ ✓.
Why this matters. A small mole fraction of solute lowers vapour pressure by a small but measurable amount. The lowering is the *universal* indicator that any non-volatile species is present in the liquid. JEE Main 2021 (Feb 24 shift 2) and NEET 2018 each used glucose-in-water vapour-pressure problems.

Final Answer: $p_s \approx 17.44$ mmHg.

☞ Two equivalent routes

$p_s = p^\circ x_w$ (direct) and $(p^\circ - p_s)/p^\circ = x_s$ (relative lowering) give the same answer for non-volatile solutes. Pick whichever asks for fewer arithmetic steps.

✗ Glucose is non-volatile

Glucose has negligible vapour pressure at room temperature, so it contributes nothing to the vapour above the solution: only water vapour pressure shows up. Treating glucose as a second volatile component (using Raoult's law for both) is wrong here.

Q 1.35 **Henry's law constant for the molality of methane in benzene at $298\,\mathrm{K}$ is $4.27 \times 10^5\,\mathrm{mmHg}$. Calculate the solubility of methane in benzene at $298\,\mathrm{K}$ under $760\,\mathrm{mmHg}$.**

SOLUTION

Concept used. In the form $p = K_H x$, the mole fraction of dissolved gas at equilibrium is

$$x = \frac{p}{K_H}.$$

Step 1. Plug in.

$$x_{\mathrm{CH_4}} = \frac{760}{4.27 \times 10^5} = 1.78 \times 10^{-3}.$$

Final Answer: Mole fraction (solubility) of methane in benzene $\approx 1.78 \times 10^{-3}$.

☞ Wording: "solubility"

"Solubility" in Henry's law context usually means the mole fraction x of dissolved gas. It can also be quoted as molality or grams per litre, but unless the problem specifies, mole fraction is the natural output of $p = K_H x$.

EXPERT'S SOLUTION : *Krishna Pillai, M.Tech Chemical Engineering, IIT Madras*

Quick reading. One division.

Step 1. Henry's law: $x = p/K_H$.

Step 2. $x = 760/(4.27 \times 10^5) = 1.78 \times 10^{-3}$.

Why this matters. At atmospheric pressure (760 mmHg) only $\sim 0.18\,\%$ of the liquid is dissolved methane (by mole fraction). That's enough to be technologically relevant (gas-solvent extraction, natural-gas processing) but small enough that Henry's law (linear regime) applies. JEE Main 2020 (Jan 9 shift 1) used a Henry's-law gas-solubility computation of this type.

Final Answer: $x_{\mathrm{CH_4}} \approx 1.78 \times 10^{-3}$.

☞ **Henry's law one-liner**

$x_{\text{gas}} = p_{\text{gas}}/K_H$. Larger $K_H \Rightarrow$ smaller solubility. Units must match: p and K_H in the same pressure unit, x is dimensionless.

Q 1.36 $100\,\mathrm{g}$ **of liquid A (molar mass** $140\,\mathrm{g/mol}$**) was dissolved in** $1000\,\mathrm{g}$ **of liquid B (molar mass** $180\,\mathrm{g/mol}$**). The vapour pressure of pure liquid B was found to be** $500\,\mathrm{torr}$**. Calculate the vapour pressure of pure liquid A and its vapour pressure in the solution if the total vapour pressure of the solution is** $475\,\mathrm{torr}$**.**

SOLUTION

Concept used. Both A and B are volatile, so Raoult's law applies to both:

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

Step 1. Moles. $n_A = 100/140 = 0.7143$ mol, $n_B = 1000/180 = 5.556$ mol.

Step 2. Mole fractions. Total $= 6.270$ mol. $x_A = 0.7143/6.270 = 0.1139$, $x_B = 5.556/6.270 = 0.8861$.

Step 3. Partial pressure of B. $p_B = 500 \times 0.8861 = 443.07$ torr.

Step 4. Partial pressure of A. $p_A = p_{\text{total}} - p_B = 475 - 443.07 = 31.93$ torr.

Step 5. Vapour pressure of pure A.

$$p_A^\circ = \frac{p_A}{x_A} = \frac{31.93}{0.1139} = 280.3\,\mathrm{torr}.$$

Final Answer: $p_A^{\text{solution}} \approx 31.93\,\mathrm{torr};\ \ p_A^\circ \approx 280.3\,\mathrm{torr}.$

★ Subtraction trick

When you know p_{total} and one of p_A or p_B, the other follows by subtraction. The mole-fraction information then lets you back out the pure-liquid vapour pressure.

EXPERT'S SOLUTION *: Rohit Singh, Ph.D Physical Chemistry, IISc Bangalore*

Strategic angle. The system has one unknown (p_A°), which can be reached in two steps: subtract p_B from p_{total}, then divide by x_A.

Step 1. Compute mole fractions: $x_A = 0.1139$, $x_B = 0.8861$.

Step 2. $p_B = 500 \times 0.8861 = 443.1$ torr.

Step 3. $p_A = 475 - 443.1 = 31.9$ torr.

Step 4. $p_A^\circ = 31.9/0.1139 = 280$ torr.

Numerical cross-check. With $p_A^\circ = 280.3$ and $x_A = 0.1139$:
$p_A = 280.3 \times 0.1139 = 31.93$ torr ✓. $p_B = 500 \times 0.8861 = 443.05$ torr ✓.
$p_{\text{tot}} = 31.93 + 443.05 = 474.98 \approx 475$ torr ✓.

Why this matters. This is how you measure the vapour pressure of a pure compound when only the mixture's total vapour pressure is convenient to measure (e.g. when the pure liquid is hard to obtain or unstable). JEE Main 2019 (Apr 12 shift 2) used this exact technique on an A–B binary.

Final Answer: $p_A^{\text{soln}} \approx 31.9$ torr, $p_A^\circ \approx 280$ torr.

☞ Subtraction route

When p_{tot} is known and one partial pressure can be computed (via the known pure value and mole fraction), the other follows by subtraction. Then divide by its mole fraction to get its pure-liquid vapour pressure.

✗ Both components are volatile here

Don't apply "$(p^\circ - p_s)/p^\circ = x_s$" — that form is only for non-volatile solutes. Both A and B vapourise, so use Raoult's law for each component separately.

Q 1.37 **Vapour pressures of pure acetone and chloroform at $328\,\text{K}$ are $741.8\,\text{mmHg}$ and $632.8\,\text{mmHg}$ respectively. Assuming that they form ideal solution over the entire range of composition, plot p_{total}, $p_{\text{chloroform}}$, and p_{acetone} as a function of x_{acetone}. The experimental data observed for different compositions of mixture is:**

$100\,x_{\text{ac}}$	0	11.8	23.4	36.0	50.8	58.2	64.5	72.1
p_{ac}/mmHg	0	54.9	110.1	202.4	322.7	405.9	454.1	521.1
p_{chl}/mmHg	632.8	548.1	469.4	359.7	257.7	193.6	161.2	120.7

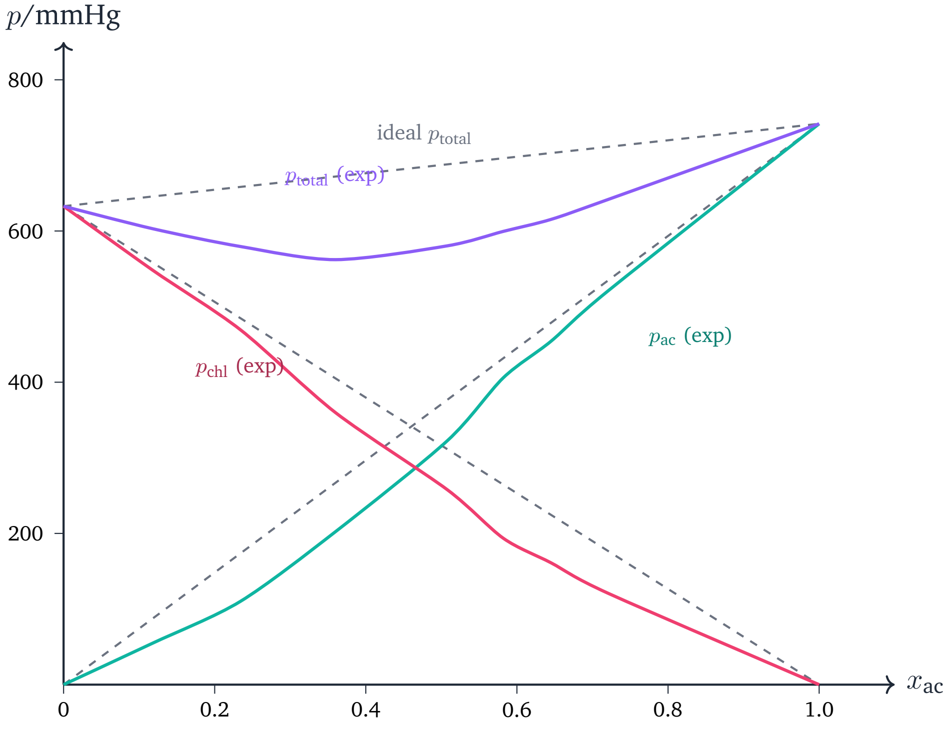
Plot this data also on the same graph paper. Indicate whether it has positive deviation or negative deviation from the ideal solution.

SOLUTION

Concept used. For an ideal solution of two volatile liquids, Raoult's law gives straight-line plots of p_A, p_B and p_{total} versus mole fraction:

$$p_{\text{ac}}^{\text{ideal}} = 741.8\,x_{\text{ac}}, \quad p_{\text{chl}}^{\text{ideal}} = 632.8\,(1 - x_{\text{ac}}), \quad p_{\text{tot}}^{\text{ideal}} = 632.8 + 109.0\,x_{\text{ac}}.$$

The experimental curve for the acetone–chloroform system lies *below* these straight lines: this is the signature of **negative deviation**.



Step 1. **Plot the ideal lines.** For each component, draw a straight line from $(0, 0)$ to $(1, p^\circ)$ and from $(0, p^\circ)$ to $(1, 0)$. Their sum is the straight ideal p_{total}, which runs from $(0, 632.8)$ to $(1, 741.8)$.

Step 2. **Plot the experimental data.** For each tabulated composition, mark the three points. Compute $p_{\text{total}}^{\text{exp}} = p_{\text{ac}} + p_{\text{chl}}$ for each composition; the row sums (e.g. at $x = 0.508$: $322.7 + 257.7 = 580.4$) all lie *below* the ideal total.

Step 3. **Identify the deviation.** The experimental curves lie *below* the corresponding ideal straight lines, with a clear minimum in p_{total} near $x_{\text{ac}} \approx 0.4$. This is a **negative deviation** from Raoult's law.

Step 4. **Why.** In the mixture, acetone's C=O lone pair forms a hydrogen bond with chloroform's C–H (chloroform is a weak H-bond donor because the three Cl atoms acidify the H). The new A–B H-bond is stronger than the average of pure A–A and B–B forces, holding molecules in the liquid more tightly and lowering vapour pressure.

Final Answer: The acetone–chloroform mixture shows *negative deviation* from Raoult's law: the experimental p-x curve lies below the ideal straight lines because of acetone–chloroform hydrogen bonding.

♥ Maximum-boiling azeotrope

A negative deviation strong enough to dip p_{total} below either pure component's vapour pressure produces a *maximum-boiling azeotrope*. Acetone + chloroform forms such an azeotrope at $\sim 64.5\,\%$ chloroform, boiling above either pure component's boiling point.

EXPERT'S SOLUTION *: Aarav Reddy, Ph.D Physical Chemistry, IISc Bangalore*

Picture-first. Plot what Raoult predicts (three straight lines), overlay the experimental data, observe where the data sits relative to the lines. Below the lines means negative deviation.

Step 1. Three ideal straight lines: $p^{\text{id}}_{\text{ac}} = 741.8\,x$, $p^{\text{id}}_{\text{chl}} = 632.8\,(1-x)$, $p^{\text{id}}_{\text{tot}} = 632.8 + 109\,x$.

Step 2. Experimental data: at every interior composition, both partial pressures and the total are *less* than the Raoult prediction.

Step 3. Deviation: negative. The acetone–chloroform H-bond holds more molecules in the liquid than Raoult predicts.

Tabular cross-check (experimental vs ideal totals). At each tabulated composition, sum the experimental partial pressures and compare to the Raoult prediction $p^{\text{id}}_{\text{tot}} = 632.8 + 109\,x_{\text{ac}}$:

- $x_{\text{ac}} = 0.118$: exp $54.9 + 548.1 = 603.0$; ideal $= 632.8 + 12.86 = 645.7$. Below by 42.7 mmHg.
- $x_{\text{ac}} = 0.234$: exp $110.1 + 469.4 = 579.5$; ideal $= 658.3$. Below by 78.8.
- $x_{\text{ac}} = 0.360$: exp $202.4 + 359.7 = 562.1$; ideal $= 672.0$. Below by 109.9 — biggest gap so far.
- $x_{\text{ac}} = 0.508$: exp $322.7 + 257.7 = 580.4$; ideal $= 688.2$. Below by 107.8 — still very negative.
- $x_{\text{ac}} = 0.582$: exp 599.5; ideal $= 696.2$. Below by 96.7.
- $x_{\text{ac}} = 0.645$: exp 615.3; ideal $= 703.1$. Below by 87.8.
- $x_{\text{ac}} = 0.721$: exp 641.8; ideal $= 711.4$. Below by 69.6.

The experimental total stays below the ideal total throughout, with a distinct minimum near $x_{\text{ac}} \approx 0.36-0.50$. This minimum is the maximum-boiling azeotrope.

Molecular origin.

- Pure acetone: weak dipole–dipole among C=O groups.
- Pure chloroform: weak dipole–dipole; the H on $CHCl_3$ is slightly acidic because the

three Cl atoms withdraw electron density.

- Mixed: the C=O lone pair of acetone forms a directional **hydrogen bond** with the acidic C−H of chloroform (a textbook example of a C−H···O hydrogen bond, ~ 9 kJ/mol). The new A−B attraction is stronger than the average of pure-liquid forces, so molecules are held in the liquid more tightly than Raoult predicts.

Concept linkage to thermodynamics.

- $\Delta_{\text{mix}}H < 0$ (exothermic) — mixing the two liquids releases heat (acetone–chloroform mixing has been measured at ~ -1.5 kJ/mol at $x_{\text{ac}} \approx 0.5$).
- $\Delta_{\text{mix}}V < 0$ — a slight volume contraction.
- Strong negative deviation → minimum in p_{tot}-vs-x → maximum in T_b-vs-x → **maximum-boiling azeotrope**. Acetone–chloroform azeotrope: $\sim 64.5\%$ chloroform, b.p. $64.5\,°\text{C}$ (above either pure component, but only marginally above chloroform's $61.2\,°\text{C}$).

Why this matters. The negative deviation in this system is chemistry's textbook example of inter-component H-bonding raising the boiling point and lowering the vapour pressure. Industrial separation of acetone-chloroform mixtures requires extractive distillation because the azeotrope cannot be broken by ordinary distillation. JEE Advanced 2017 used acetone–chloroform deviation directly, and JEE Main 2022 (June 26) tested azeotrope/deviation pairs.

> **Final Answer:** Negative deviation from Raoult's law throughout the composition range.

♥ Maximum-boiling azeotrope

Acetone–chloroform forms a max-b.p. azeotrope at $\sim 64.5\%$ $CHCl_3$, b.p. $64.5\,°\text{C}$. Industrially, this mixture cannot be separated into pure components by simple distillation — only extractive or pressure-swing distillation works.

☞ Sign of deviation from one row

Pick any tabulated composition. If exp partial pressures sum below the Raoult prediction $p_B^\circ + (p_A^\circ - p_B^\circ)x_A$, it is negative deviation. If above, positive. One row of data settles the diagnosis.

Q 1.38 **Benzene and toluene form ideal solution over the entire range of composition. The vapour pressure of pure benzene and toluene at $300\,\text{K}$ are $50.71\,\text{mmHg}$ and $32.06\,\text{mmHg}$ respectively. Calculate the mole fraction of benzene in vapour phase if $80\,\text{g}$ of benzene is mixed with $100\,\text{g}$ of toluene.**

SOLUTION

Concept used. For an ideal mixture obeying Raoult's law, the mole fraction of A in the vapour (y_A) is given by

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

where x_A is the liquid-phase mole fraction.

☞ **Molar masses**

$M_w(C_6H_6) = 78\,\text{g/mol}$; $M_w(C_7H_8) = 92\,\text{g/mol}$.

Step 1. Moles. $n_{\text{ben}} = 80/78 = 1.0256$ mol, $n_{\text{tol}} = 100/92 = 1.0870$ mol.

Step 2. Liquid-phase mole fractions. Total $= 2.1126$ mol.
$x_{\text{ben}} = 1.0256/2.1126 = 0.4855$, $x_{\text{tol}} = 0.5145$.

Step 3. Partial pressures. $p_{\text{ben}} = 50.71 \times 0.4855 = 24.62$ mmHg,
$p_{\text{tol}} = 32.06 \times 0.5145 = 16.49$ mmHg.

Step 4. Total vapour pressure. $p_{\text{tot}} = 24.62 + 16.49 = 41.11$ mmHg.

Step 5. Vapour-phase mole fraction of benzene.

$$y_{\text{ben}} = \frac{p_{\text{ben}}}{p_{\text{tot}}} = \frac{24.62}{41.11} = 0.5989.$$

Final Answer: Mole fraction of benzene in vapour $y_{\text{ben}} \approx 0.599$.

☞ **Vapour is richer in volatile**

$x_{\text{ben}} = 0.486$ in the liquid but $y_{\text{ben}} = 0.599$ in the vapour: the vapour is richer in benzene because benzene is the more volatile component ($p^\circ_{\text{ben}} > p^\circ_{\text{tol}}$). This is the molecular basis of fractional distillation.

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

Strategic angle. Compute the two partial pressures, sum to get total, then divide.

Step 1. $x_{\text{ben}} = (80/78)/[(80/78) + (100/92)] = 1.0256/2.1126 = 0.4855$.

Step 2. $p_{\text{ben}} = 0.4855 \times 50.71 = 24.62$ mmHg.

Step 3. $p_{\text{tol}} = 0.5145 \times 32.06 = 16.49$ mmHg. Total $= 41.11$ mmHg.

Step 4. $y_{\text{ben}} = 24.62/41.11 = 0.599$.

Numerical cross-check.
$y_{\text{ben}} = x_{\text{ben}} \cdot p^\circ_{\text{ben}}/p_{\text{tot}} = 0.4855 \cdot 50.71/41.11 = 0.4855 \cdot 1.234 = 0.599$ ✓. The enrichment factor $\alpha = (p^\circ_A/p^\circ_B) = 50.71/32.06 = 1.58$ is the ratio of pure-liquid vapour pressures and

is the relative-volatility constant of the column.
Concept linkage. Vapour-phase enrichment $y_A > x_A$ whenever $p^\circ_A > p^\circ_B$. The amount of enrichment is quantified by the *relative volatility* $\alpha_{A,B} = p^\circ_A/p^\circ_B$ (here $= 1.58$). Higher α means easier separation. For close-boiling pairs, α is barely above unity and many distillation stages are required.
Why this matters. Successive vaporisations and condensations (the operations of a fractionating column) build up enrichment of the more volatile component until effectively pure benzene leaves the top of the column. JEE Main 2019 (Apr 9 shift 1) and NEET 2017 each used benzene–toluene vapour-composition problems.

Final Answer: $y_{\text{ben}} \approx 0.599$.

☞ Vapour richer in volatile

For any ideal binary, vapour composition is biased toward the component with the higher p°. $y_A/x_A = p^\circ_A/p_{\text{tot}}$, always > 1 for the more volatile component.

Q 1.39 **The air is a mixture of a number of gases. The major components are oxygen and nitrogen with approximate proportion of $20\,\%$ to $79\,\%$ by volume at $298\,\text{K}$. The water is in equilibrium with air at a pressure of $10\,\text{atm}$. If the Henry's law constants for oxygen and nitrogen at $298\,\text{K}$ are $3.30 \times 10^7\,\text{mmHg}$ and $6.51 \times 10^7\,\text{mmHg}$ respectively, calculate the composition of these gases in water.**

SOLUTION

Concept used. For a gas mixture above a solution, each gas independently obeys Henry's law:

$$p_i = K_{H,i}\, x_i \implies x_i = \frac{p_i}{K_{H,i}}.$$

The partial pressure of each gas is found from the total pressure and its volume (or mole) fraction in the gas phase: $p_i = y_i \cdot P_{\text{total}}$.

☞ Convert units

10 atm $= 10 \times 760 = 7600$ mmHg.

Step 1. Partial pressures.

$$p_{O_2} = 0.20 \times 7600 = 1520 \text{ mmHg},$$

$$p_{N_2} = 0.79 \times 7600 = 6004 \text{ mmHg}.$$

Step 2. **Mole fraction of O_2 in water.**

$$x_{O_2} = \frac{1520}{3.30 \times 10^7} = 4.61 \times 10^{-5}.$$

Step 3. **Mole fraction of N_2 in water.**

$$x_{N_2} = \frac{6004}{6.51 \times 10^7} = 9.22 \times 10^{-5}.$$

Final Answer: $x_{O_2} \approx 4.61 \times 10^{-5}, \quad x_{N_2} \approx 9.22 \times 10^{-5}.$

★ Henry's law for mixtures

Each gas dissolves independently as if the other gases were absent, provided they do not react with the solvent or with each other in solution. The mole fractions in water are simply the partial pressures divided by their respective K_H values.

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

Strategic angle. Treat oxygen and nitrogen separately, because Henry's law is linear and applies to each species in the dilute regime.

Step 1. Total pressure in mmHg: $10 \times 760 = 7600$.

Step 2. Partial pressures: 20 % $O_2 \rightarrow$ 1520 mmHg, 79 % $N_2 \rightarrow$ 6004 mmHg.

Step 3. Mole fractions in water: $x_{O_2} = 1520/(3.30 \times 10^7) = 4.61 \times 10^{-5}$;
$x_{N_2} = 6004/(6.51 \times 10^7) = 9.22 \times 10^{-5}$.

Why this matters. This is why scuba divers breathing air at depth (high P) accumulate large amounts of dissolved N_2 that can bubble out on ascent (the bends). The risk scales as the partial pressure of N_2. JEE Main 2023 (Jan 24 shift 2) and NEET 2019 each used multi-gas Henry's-law problems of this form.

Final Answer: $x_{O_2} \approx 4.61 \times 10^{-5}$, $x_{N_2} \approx 9.22 \times 10^{-5}$.

☞ Henry's law for gas mixtures

Each gas above a solution obeys $x_i = p_i/K_{H,i}$ independently (provided no chemical reaction). Use Dalton's law $p_i = y_i P_{\text{tot}}$ to find partial pressures first.

Q 1.40 **Determine the amount of $\mathrm{CaCl_2}$ ($i = 2.47$) dissolved in $2.5\,\mathrm{L}$ of water such that its osmotic pressure is $0.75\,\mathrm{atm}$ at $27\,°\mathrm{C}$.**

SOLUTION

Concept used. For an electrolyte the van't Hoff form of osmotic pressure is

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

where i is the van't Hoff factor and C is the molar concentration of the salt. Rearrange to find C, then compute mass.

☞ **Constants**

$R = 0.0821\,\mathrm{L\,atm\,K^{-1}\,mol^{-1}}$; $T = 27\,°\mathrm{C} = 300$ K; $M_w(\mathrm{CaCl_2}) = 40 + 2(35.5) = 111\,\mathrm{g/mol}$.

Step 1. Solve for C.

$$C = \frac{\pi}{iRT} = \frac{0.75}{2.47 \times 0.0821 \times 300} = \frac{0.75}{60.83} = 0.012\,33\,\mathrm{mol/L}.$$

Step 2. Moles in 2.5 L.

$$n = C \cdot V = 0.01233 \times 2.5 = 0.03083 \text{ mol}.$$

Step 3. Mass of $CaCl_2$.

$$w = n \cdot M_w = 0.03083 \times 111 = 3.42\,\mathrm{g}.$$

Final Answer: Mass of $CaCl_2$ required $\approx 3.42\,\mathrm{g}$.

☞ **Why $i = 2.47$, not 3?**

Complete dissociation of $CaCl_2 \longrightarrow Ca^{2+} + 2\,Cl^-$ would give $i = 3$. The observed $i = 2.47$ reflects ion-pairing in solution: some Ca^{2+} and Cl^- pair up and behave as single units.

EXPERT'S SOLUTION *: Aanya Rao, M.Tech Chemical Engineering, IIT Bombay*

Strategic angle. Solve van't Hoff $\pi = iCRT$ for C, multiply by volume to get moles, multiply by molar mass to get mass.

Step 1. $C = \pi/(iRT) = 0.75/(2.47 \times 0.0821 \times 300) = 0.0123$ M.

Step 2. Moles in 2.5 L: $0.0123 \times 2.5 = 0.0308$ mol.

Step 3. Mass: $0.0308 \times 111 = 3.42$ g.

Numerical cross-check. With $C = 0.01233$ M,
$iCRT = 2.47 \cdot 0.01233 \cdot 0.0821 \cdot 300 = 0.750$ atm ✓.
Concept linkage. The van't Hoff factor i corrects $\pi = CRT$ for ion dissociation. Theoretical $i_{\max}(\mathrm{CaCl_2}) = 3$ (one Ca^{2+} + two Cl^-); observed 2.47 falls short because of ion-pairing in solution. The same $iCRT$ formula applies to ΔT_b, ΔT_f, and relative lowering of vapour pressure — only RT changes to K_b, K_f, or 1.

Why this matters. Osmotic-pressure tonicity is the basis of intravenous saline preparations. Knowing i tells you what concentration of salt makes a solution isotonic with blood ($\pi \approx 7.7$ atm). JEE Main 2022 (June 25 shift 2) and NEET 2018 both probed electrolyte $\pi = iCRT$ problems.

Final Answer: ≈ 3.42 g $CaCl_2$.

☞ **Why $i = 2.47$, not 3?**

Complete dissociation gives $i = 3$ for $CaCl_2$. Real solutions show ion-pairing (some Ca^{2+} stays close to a Cl^- and the pair acts as one particle), dropping i below the theoretical maximum.

✗ Use i, not 1

For an electrolyte, $\pi = iCRT$, not $\pi = CRT$. Skipping i underestimates by a factor of $\sim 2-3$ for typical salts and gets the answer flat out wrong.

Q 1.41 **Determine the osmotic pressure of a solution prepared by dissolving $25\,\mathrm{mg}$ of K_2SO_4 in $2\,\mathrm{L}$ of water at $25\,°\mathrm{C}$, assuming that it is completely dissociated.**

SOLUTION

Concept used. For a fully-dissociated salt $K_2SO_4 \longrightarrow 2\,K^+ + SO_4{}^{2-}$, one formula unit gives 3 ions in solution, so $i = 3$. Osmotic pressure:

$$\pi = i\,C\,R\,T.$$

☞ **Numbers**

$R = 0.0821\,\mathrm{L\,atm\,K^{-1}\,mol^{-1}}$; $T = 25\,°\mathrm{C} = 298$ K; $M_w(K_2SO_4) = 2(39) + 32 + 4(16) = 174\,\mathrm{g/mol}$.

Step 1. **Moles of K_2SO_4.** $n = 25 \times 10^{-3}/174 = 1.437 \times 10^{-4}$ mol.

Step 2. **Molar concentration.** $C = n/V = 1.437 \times 10^{-4}/2 = 7.184 \times 10^{-5}$ mol/L.

Step 3. **Osmotic pressure.**

$$\pi = iCRT = 3 \times 7.184 \times 10^{-5} \times 0.0821 \times 298.$$

Stepwise: $3 \times 7.184 \times 10^{-5} = 2.155 \times 10^{-4}$;
$2.155 \times 10^{-4} \times 0.0821 = 1.769 \times 10^{-5}$; $1.769 \times 10^{-5} \times 298 = 5.272 \times 10^{-3}$ atm.

Step 4. **Convert to pascals (optional check).**
$5.272 \times 10^{-3}\,\mathrm{atm} \times 1.013 \times 10^5\,\mathrm{Pa/atm} \approx 534$ Pa.

Final Answer: $\pi \approx 5.27 \times 10^{-3}\,\text{atm} \approx 534\,\text{Pa}$.

♥ Tiny osmotic pressure, very sensitive

Even a milligram of fully-dissociated salt in a couple of litres of water produces an osmotic pressure of about half a kilopascal, easily measurable. This sensitivity makes osmotic pressure the colligative property of choice for very high molar masses (polymers, biomolecules), where ΔT_f and ΔT_b are too small to detect.

EXPERT'S SOLUTION *: Karan Bhat, M.Sc Biotechnology, AIIMS Delhi*

Strategic angle. Three terms in $\pi = iCRT$: write each clearly, then multiply.

Step 1. Moles $= 0.025/174 = 1.437 \times 10^{-4}$.

Step 2. $C = 1.437 \times 10^{-4}/2 = 7.184 \times 10^{-5}$ M.

Step 3. $i = 3$ (complete dissociation, three ions per formula unit).

Step 4. $\pi = 3 \times 7.184 \times 10^{-5} \times 0.0821 \times 298 = 5.27 \times 10^{-3}$ atm.

Numerical cross-check. $\pi = iCRT$:
$3 \cdot 7.184 \times 10^{-5} \cdot 0.0821 \cdot 298 = 3 \cdot 1.757 \times 10^{-3} = 5.27 \times 10^{-3}$ atm ✓. In Pa:
$5.27 \times 10^{-3} \cdot 1.013 \times 10^{5} \approx 534$ Pa ✓.

Concept linkage. Osmotic pressure is the most sensitive colligative property for very dilute solutions because R has a moderate value but T is large (in Kelvin). A 1-millimolar solution generates $\pi \approx 0.025$ atm ~ 19 mmHg of osmotic pressure — easily measurable. By contrast, ΔT_f at the same C would be ~ 0.002 K, below detection.

Why this matters. Osmotic-pressure measurements at ppm-level concentrations characterise polymers and proteins. The same equation underlies reverse osmosis for water purification and dialysis for kidney patients. JEE Main 2024 (Jan 31 shift 1) and NEET 2020 used electrolyte osmotic-pressure problems analogous to this one.

Final Answer: $\pi \approx 5.27 \times 10^{-3}$ atm (about 534 Pa).

♥ Why osmometry wins for large molecules

Polymers and proteins have huge molar masses ($10^4 – 10^6$ g/mol). At usable concentrations their molality is far too small to move ΔT_b or ΔT_f measurably. Osmotic pressure ($\pi = CRT$) is the only colligative property sensitive enough to return a molar mass. This is the principle of membrane osmometry.

☞ Always include i

For any strong electrolyte (or partially-ionised weak acid/base), multiply the colligative-property formula by i. Forgetting the factor changes the answer by $2–3\times$.

✗ Convert mg to g

25 mg of K_2SO_4 is 0.025 g, not 25 g. Forgetting the mg-to-g conversion makes C a thousand-fold too large and π a thousand- fold too high.

Key Takeaways

- **Concentration units.** Mole fraction is dimensionless and best for vapour pressure; molality is mass-based and temperature-independent (use for colligative properties); molarity is volume-based and changes with T; mass % is for bulk recipes.
- **Henry's law.** $p = K_H x$ for dilute gases in liquids. Larger $K_H \Rightarrow$ less soluble. K_H rises with T, so warm water holds less gas.
- **Raoult's law.** For an ideal mixture each component obeys $p_i = p_i^\circ x_i$. Vapour is richer in the more volatile component, the basis of fractional distillation.
- **Deviations.** Positive deviation: A–B forces weaker than A–A, B–B; $\Delta_{\text{mix}}H, \Delta_{\text{mix}}V > 0$ (ethanol + water). Negative deviation: A–B stronger; $\Delta H, \Delta V < 0$ (acetone + chloroform).
- **Four colligative properties.** Relative lowering of p: $(p^\circ - p_s)/p^\circ = x_s$; elevation of b.p.: $\Delta T_b = K_b m$; depression of f.p.: $\Delta T_f = K_f m$; osmotic pressure: $\pi = CRT$.
- **Abnormal molar masses.** Multiply colligative properties by the van't Hoff factor i to account for association ($i < 1$) or dissociation ($i > 1$). For a weak acid, $i = 1 + \alpha$ with $\alpha = \sqrt{K_a/C}$.

End of Chapter 1 Exercises