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PHYSICAL

CH 04

Solutions — Raoult's Law & Colligative Properties

04

Concentration terms, Henry's and Raoult's laws, ideal and non-ideal solutions, azeotropes, the four colligative properties and the van't Hoff factor — with an exam trap gallery, graded MCQs and a one-page revision sheet.

WHAT YOU WILL BE ABLE TO DO

- Convert between molarity, molality and mole fraction, and know which change with temperature
- Use Henry's law, and Raoult's law for both liquid and vapour composition
- Classify a solution as ideal or showing positive or negative deviation, and explain azeotropes
- Solve all four colligative-property numericals, including finding molar mass
- Use the van't Hoff factor for electrolytes and associating solutes

INSIDE

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J Practice MCQs
K Advanced problems
R One-page revision

HOW TO USE THESE NOTES

IN ONE LINE The core idea of a section	**KEY IDEA** The concept to remember	**EXAM TRAP** Where marks are usually lost
SOLVED EXAMPLE Worked step by step	**CHECK YOURSELF** Quick self-test	**MEMORY HOOK** A line that sticks

SECTION A

The big picture

A

One cause, four effects.

IN ONE LINE

A non-volatile solute lowers the solvent's vapour pressure; that one change raises the boiling point, lowers the freezing point and creates osmotic pressure — all in proportion to the number of particles.

THINK OF IT LIKE THIS

Picture the surface of the liquid as a doorway. Solvent molecules escape through it to make vapour. Solute particles stand in the doorway and block some of the exits, so fewer solvent molecules escape. It doesn't matter whether the blocker is glucose or urea; only how many blockers there are.

KEY IDEA

"Colligative" means "depending on the collection": the **number** of particles, not their identity. That is why NaCl (two ions per formula unit) has nearly twice the effect of glucose at the same molality.

SECTION B

Concentration terms

B

Pick the right unit before you pick the formula.

Term	Definition	Changes with temperature?
Molarity (M)	mol solute per litre of solution	Yes (volume expands)
Molality (m)	mol solute per kg of solvent	No
Mole fraction (x)	mol of a component ÷ total mol	No
Mass percent	g solute per 100 g solution	No
ppm	g solute per 10^6 g solution	No

KEY IDEA

Molality and mole fraction depend only on masses, so they don't change with temperature. That is why ΔTb and ΔTf formulas use molality.

SOLVED EXAMPLE 01 — MOLALITY AND MOLE FRACTION

5.85 g NaCl is dissolved in 500 g water. Find the molality. Separately, find the mole fraction of solute in a 1 molal aqueous solution.

SOLUTION

1. mol NaCl = 5.85/58.5 = 0.100; molality = 0.100/0.500 kg = 0.200 mol kg^{-1}.
2. 1 molal: 1 mol solute per 1000 g water = 55.5 mol water.
3. x(solute) = 1/(1 + 55.5) = 0.0177.

ANSWER 0.200 mol kg^{-1}; x(solute) ≈ 0.0177.

SECTION C

Henry's law

How much gas dissolves in a liquid.

$$p = K(H) \times x$$

p = partial pressure of the gas above the solution; x = its mole fraction in solution

- **Higher K(H) → lower solubility.** K(H) rises with temperature, so gases are less soluble in warm water (fish suffer in warm ponds).
- Soft drinks are bottled under high CO_2 pressure; opening the bottle drops the pressure and CO_2 comes out.
- Divers breathing compressed air dissolve extra N_2 in their blood; surfacing too fast releases bubbles ("the bends"). Diving tanks use helium-diluted air.
- At high altitude, the low partial pressure of O_2 means less dissolved O_2 (anoxia).

SOLVED EXAMPLE 02 — GAS DISSOLVED IN WATER

K(H) for N_2 in water at 298 K is 76.48 kbar. Air above the water has $p(N_2)$ = 0.80 bar. How many moles of N_2 dissolve in 1 L of water?

SOLUTION

1. $x(N_2) = p/K(H) = 0.80/76{,}480 = 1.05 \times 10^{-5}$.
2. 1 L water = 55.5 mol. Since x is tiny, mol $N_2 \approx x \times 55.5$.

ANSWER About 5.8×10^{-4} mol N_2.

SECTION D

Raoult's law

D

Vapour pressure of a solution, for volatile and non-volatile solutes.

$$p(A) = x(A) \times p^\circ(A)$$
$$p(\text{total}) = x(A)p^\circ(A) + x(B)p^\circ(B)$$

Each volatile component contributes in proportion to its mole fraction

Vapour composition: the mole fraction of A in the vapour is y(A) = p(A)/p(total). The vapour is always **richer in the more volatile component** — the basis of fractional distillation.

$$(p^\circ - p) / p^\circ = x(\text{solute})$$

Non-volatile solute: relative lowering of vapour pressure = mole fraction of solute

SOLVED EXAMPLE 03 — TWO VOLATILE LIQUIDS

26 g heptane (p° = 105.2 kPa, M = 100) is mixed with 35 g octane (p° = 46.8 kPa, M = 114). Find the vapour pressure and the mole fraction of heptane in the vapour.

SOLUTION

1. n(heptane) = 0.260; n(octane) = 0.307; x(heptane) = 0.260/0.567 = 0.459.
2. p = 0.459 × 105.2 + 0.541 × 46.8 = 48.3 + 25.3 = 73.6 kPa.
3. y(heptane) = 48.3/73.6.

ANSWER p ≈ 73.6 kPa; y(heptane) ≈ 0.66 — the vapour is richer in the more volatile heptane.

SOLVED EXAMPLE 04 — MOLAR MASS FROM RLVP

10 g of a non-volatile solute dissolved in 90 g water lowers the vapour pressure by 2%. Find its molar mass.

SOLUTION

1. $(p^\circ - p)/p^\circ = 0.02 = n_2/(n_1 + n_2)$, with $n_1 = 90/18 = 5.0$.
2. $n_2 = 0.02 \times 5.0/0.98 = 0.102$ mol.
3. M = 10/0.102.

ANSWER M ≈ 98 g mol^{-1}.

CHECK YOURSELF

C1 Which unit of concentration changes when the solution is warmed?

C2 Why is the vapour above a benzene–toluene mixture richer in benzene?

Answers at the end of the chapter.

SECTION E

Ideal and non-ideal solutions

E

When Raoult's law holds, and what happens when it doesn't.

	Ideal	Positive deviation	Negative deviation
A–B attraction vs A–A, B–B	Equal	Weaker	Stronger
Vapour pressure	Obeys Raoult	Higher than predicted	Lower than predicted
ΔH(mix)	0	Positive (absorbs heat)	Negative (releases heat)
ΔV(mix)	0	Positive (expands)	Negative (contracts)
Examples	Benzene + toluene; n-hexane + n-heptane	Ethanol + acetone; CS_2 + acetone; ethanol + water	Chloroform + acetone; HNO_3 + water; phenol + aniline
Azeotrope type	None	Minimum-boiling	Maximum-boiling

THINK OF IT LIKE THIS

Positive deviation: the two liquids would rather be with their own kind, so molecules escape more easily (higher vapour pressure). Negative deviation: they like each other more than themselves — chloroform's H bonds to acetone's oxygen — so they hold on and escape less.

Azeotropes boil at constant composition, so fractional distillation can't separate them. About 95% ethanol + water is a minimum-boiling azeotrope (positive deviation); about 68% HNO_3 + water is maximum-boiling (negative deviation).

SECTION F

The four colligative properties

F

Same cause, four measurements.

$$\text{Relative lowering of VP} = x(\text{solute})$$

$$\Delta T_b = K_b \times m$$

$$\Delta T_f = K_f \times m$$

$$\pi = CRT$$

m = molality; C = molarity; R = 0.083 L bar K^{-1} mol^{-1}

Solvent	Kb (K kg mol^{-1})	Kf (K kg mol^{-1})
Water	0.52	1.86
Benzene	2.53	5.12
Camphor	—	≈ 40 (used for small samples)

$$M(\text{solute}) = K \times w(\text{solute}) \times 1000 / [\Delta T \times w(\text{solvent})]$$

Molar mass from ΔTb (use Kb) or ΔTf (use Kf); masses in grams

SOLVED EXAMPLE 05 — FREEZING POINT

1.0 g urea (M = 60) is dissolved in 100 g water. Find the freezing point (Kf = 1.86).

SOLUTION

1. m = (1.0/60)/0.100 = 0.167 mol kg^{-1}.
2. ΔTf = 1.86 × 0.167 = 0.31 K.

ANSWER Freezes at about −0.31 °C.

SOLVED EXAMPLE 06 — MOLAR MASS FROM BOILING POINT

1.8 g of a non-volatile solute in 100 g benzene raises the boiling point by 0.36 K (Kb = 2.53). Find M.

SOLUTION

1. M = 2.53 × 1.8 × 1000/(0.36 × 100).

ANSWER M ≈ 126.5 g mol^{-1}.

SECTION G

Osmosis and osmotic pressure

The colligative property that works best for big molecules.

Osmosis is the flow of **solvent** through a semipermeable membrane from the dilute side to the concentrated side. Osmotic pressure π is the pressure needed to stop it.

- **Isotonic** solutions have equal π (0.9% NaCl matches blood cells).
- **Hypertonic** outside → water leaves the cell → it shrinks (plasmolysis). **Hypotonic** outside → water enters → it swells and may burst.
- **Reverse osmosis:** apply pressure above π to push water out of salt water — desalination.
- **Why π for polymers and proteins?** Even a very dilute solution gives a large, measurable π, it's measured at room temperature (no denaturing), and it uses molarity directly.

SOLVED EXAMPLE 07 — **MOLAR MASS OF A PROTEIN**

1.26 g of a protein in 200 mL of solution has π = 2.57 × 10^{-3} bar at 300 K. Find M.

SOLUTION

1. π = (w/MV)RT, so M = wRT/(πV).
2. M = 1.26 × 0.083 × 300/(2.57 × 10^{-3} × 0.200).

ANSWER M ≈ 61,000 g mol^{-1}. (ΔTf for this solution would be only about 10^{-4} K — too small to measure.)

SECTION H

The van't Hoff factor

H

When the number of particles isn't the number of formula units.

i = observed colligative property / calculated (no dissociation)

ΔTf = i Kf m · ΔTb = i Kb m · π = iCRT

Behaviour	i	Example
Non-electrolyte	1	Glucose, urea, sucrose
Dissociates into n ions	1 < i ≤ n	NaCl → 2; $CaCl_2$ → 3; $K_4[Fe(CN)_6]$ → 5
Associates (n molecules → 1)	< 1	Ethanoic or benzoic acid dimerises in benzene: i → 0.5

Dissociation: α = (i − 1)/(n − 1)

Association: α = (1 − i)/(1 − 1/n)

SOLVED EXAMPLE 08 — DEGREE OF DISSOCIATION

0.10 m NaCl freezes at −0.348 °C (Kf = 1.86). Find α.

SOLUTION

1. Expected ΔTf = 1.86 × 0.10 = 0.186 K.
2. i = 0.348/0.186 = 1.87.
3. α = (1.87 − 1)/(2 − 1).

ANSWER α ≈ 0.87 (87% dissociated).

SOLVED EXAMPLE 09 — ASSOCIATION IN BENZENE

2.0 g benzoic acid (M = 122) in 25 g benzene lowers the freezing point by 1.62 K (Kf = 4.9). Find the degree of association.

SOLUTION

1. Observed M = 4.9 × 2.0 × 1000/(1.62 × 25) = 242 g mol^{-1}.
2. i = 122/242 = 0.504.
3. Dimerisation, n = 2: α = (1 − 0.504)/(1 − 0.5).

ANSWER α ≈ 0.99 — almost all of it exists as hydrogen-bonded dimers.

CHECK YOURSELF

C3 Which 0.1 m solution freezes lowest: glucose, NaCl or $CaCl_2$?

C4 Why does acetic acid show a molar mass near 120 in benzene?

Answers at the end of the chapter.

SECTION I

Exam trap gallery

The mistakes that cost the most marks in this chapter.

✗ TRAP 01 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Use molarity in ΔTf = Kf × m.	Use molality (mol per kg of solvent).

WHY Molality doesn't change with temperature; the K values are defined for it.

✗ TRAP 02 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
0.1 m NaCl and 0.1 m glucose have the same ΔTf.	NaCl gives nearly twice the ΔTf (i ≈ 2).

WHY Colligative properties count particles, not formula units.

✗ TRAP 03 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Higher K(H) means the gas is more soluble.	Higher K(H) means **less** soluble: x = p/K(H).
WHY K(H) is in the denominator.	

✗ TRAP 04 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
ΔTf is added to 0 °C.	The solution freezes **below** 0 °C: T = 0 − ΔTf.
WHY ΔTf is a depression.	

✗ TRAP 05 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
An azeotrope is a compound.	It's a mixture; its composition changes with pressure.
WHY It only boils at constant composition at one pressure.	

✗ TRAP 06 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Chloroform + acetone shows positive deviation.	Negative deviation (maximum-boiling azeotrope).
WHY H bonding between them makes A–B attraction stronger.	

✗ TRAP 07 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
i is always a whole number.	i is usually fractional (e.g. 1.87 for NaCl).
WHY Dissociation is incomplete, especially at higher concentration.	

✗ TRAP 08 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
In $\pi = CRT$, use R = 8.314 with C in mol L^{-1}.	Use R = 0.083 L bar K^{-1} mol^{-1} (or 0.0821 L atm) for π in bar (atm).
WHY Units must match: 8.314 needs SI units throughout.	

MEMORY HOOK

"**Count the crowd, not the faces**" — colligative = number of particles.

"**Molal for heat, molar for pressure**" — ΔTb/ΔTf use m; π uses C.

"**Big K(H), shy gas**" — high Henry's constant, low solubility.

"**Plus pushes out, minus holds in**" — positive deviation, higher VP; negative deviation, lower VP.

SECTION J

Practice MCQs

J

Levels: Easy checks recall, Moderate needs one reasoning step, Tough combines two ideas.

Q01 Which concentration term depends on temperature? [EASY]

(a) Molality (b) Mole fraction
(c) Molarity (d) Mass percent

Q02 The unit of the molal elevation constant Kb is: [EASY]

(a) K mol kg^{-1} (b) K kg mol^{-1}
(c) mol kg K^{-1} (d) K^{-1} kg mol^{-1}

Q03 Which method is best for finding the molar mass of a protein? [EASY]

(a) Elevation of boiling point (b) Depression of freezing point
(c) Osmotic pressure (d) Relative lowering of VP

Q04 A solution of chloroform and acetone shows: [EASY]

(a) positive deviation (b) negative deviation
(c) ideal behaviour (d) no deviation at any composition

Q05 Which 0.1 m aqueous solution has the highest boiling point? [EASY]

(a) Glucose (b) KCl
(c) K_2SO_4 (d) Urea

Q06 The van't Hoff factor of acetic acid fully dimerised in benzene is: [MODERATE]

(a) 2 (b) 1
(c) 0.5 (d) 0.25

Q07 The mole fraction of solute in a 1 molal aqueous solution is: [MODERATE]

(a) 0.0177 (b) 0.0180
(c) 0.1770 (d) 1.0000

Q08 A solution showing positive deviation from Raoult's law forms: [MODERATE]

(a) a maximum-boiling azeotrope (b) a minimum-boiling azeotrope
(c) no azeotrope (d) a solid solution

Q09 1.0 g urea (M = 60) in 100 g water: ΔTf is (Kf = 1.86): [MODERATE]

(a) 0.031 K (b) 0.31 K
(c) 3.1 K (d) 0.186 K

Q10 A 0.1 m solution of a salt AB_2 shows i = 2.6. The degree of dissociation is: [MODERATE]

(a) 0.6 (b) 0.8
(c) 0.9 (d) 0.53

Q11 Red blood cells placed in 2% NaCl solution will: [MODERATE]

(a) swell (b) burst
(c) shrink (d) remain unchanged

Q12 For an ideal solution, which is NOT true? [MODERATE]

(a) ΔH(mix) = 0 **(b)** ΔV(mix) = 0

(c) It obeys Raoult's law **(d)** ΔS(mix) = 0

Q13 In a mixture of heptane (p° = 105.2 kPa) and octane (p° = 46.8 kPa) with x(heptane) = 0.459, the mole fraction of heptane in the vapour is about: [TOUGH]

(a) 0.46 **(b)** 0.54

(c) 0.66 **(d)** 0.34

Q14 2 g benzoic acid in 25 g benzene gives ΔTf = 1.62 K (Kf = 4.9). The percentage association is about: [TOUGH]

(a) 50% **(b)** 75%

(c) 99% **(d)** 25%

Q15 10 g of a solute in 90 g water lowers the vapour pressure by 2%. Its molar mass is about: [TOUGH]

(a) 49 **(b)** 98

(c) 196 **(d)** 9.8

Answer key with explanations

Q01 **(c) Molarity** — Molarity uses solution volume, which expands on heating.

Q02 **(b) K kg mol^{-1}** — ΔTb = Kb × m, so Kb = K/(mol kg^{-1}) = K kg mol^{-1}.

Q03 **(c) Osmotic pressure** — π is large enough to measure for dilute solutions, at room temperature.

Q04 **(b) negative deviation** — Hydrogen bonding between the two makes A–B attraction stronger.

Q05 **(c) K_2SO_4** — K_2SO_4 gives 3 ions (i ≈ 3).

Q06 **(c) 0.5** — Two molecules become one particle: i = 1/2.

Q07 **(a) 0.0177** — 1/(1 + 55.5) = 0.0177.

Q08 **(b) a minimum-boiling azeotrope** — Higher vapour pressure → lower boiling point at the azeotropic composition.

Q09 **(b) 0.31 K** — m = 0.167; ΔTf = 1.86 × 0.167 = 0.31 K.

Q10 **(b) 0.8** — $AB_2 \rightarrow A^{2+} + 2B^-$, n = 3: α = (2.6 − 1)/(3 − 1) = 0.8.

Q11 **(c) shrink** — 2% NaCl is hypertonic compared with 0.9%; water leaves the cells.

Q12 **(d) ΔS(mix) = 0** — Mixing always increases entropy: ΔS(mix) > 0.

Q13 **(c) 0.66** — p(hep) = 48.3 kPa, p(total) = 73.6 kPa; y = 48.3/73.6 = 0.66.

Q14 **(c) 99%** — Observed M = 242; i = 0.504; α = (1 − 0.504)/0.5 = 0.99.

Q15 **(b) 98** — $n_2/(n_1 + n_2)$ = 0.02 with n_1 = 5 → n_2 = 0.102 → M = 98.

SECTION K

Advanced problems

K

TGT/PGT level: each needs two ideas from the chapter.

SOLVED EXAMPLE 10 — FREEZING POINT FROM OSMOTIC PRESSURE

A dilute aqueous solution has π = 2.49 bar at 300 K. Estimate its freezing point (Kf = 1.86; assume molality ≈ molarity).

SOLUTION

1. C = π/RT = 2.49/(0.083 × 300) = 0.100 mol L^{-1}.
2. For a dilute aqueous solution, m ≈ C = 0.100 mol kg^{-1}.
3. ΔTf = 1.86 × 0.100 = 0.186 K.

ANSWER About −0.19 °C. Any one colligative property predicts the others.

SOLVED EXAMPLE 11 — CHOOSING BETWEEN TWO SALTS

Which lowers the freezing point of water more per gram: NaCl (M = 58.5) or $CaCl_2$ (M = 111)? Assume complete dissociation.

SOLUTION

1. Particles per gram, NaCl: 2/58.5 = 0.0342 mol.
2. Particles per gram, $CaCl_2$: 3/111 = 0.0270 mol.

ANSWER NaCl gives more particles per gram, so it lowers the freezing point more per gram ($CaCl_2$ is still used on roads because it works at lower temperatures and releases heat as it dissolves).

Check-yourself answers

C1 Molarity.

C2 Benzene is more volatile (higher p°), and y = p(A)/p(total) favours the more volatile component.

C3 $CaCl_2$ (i ≈ 3).

C4 It dimerises through hydrogen bonds in benzene, so the number of particles halves and the apparent molar mass doubles.

QUICK REVISION

One-page revision

Read this page the night before the exam.

Concentration

- Molarity changes with T; molality, x, mass % don't
- 1 molal aqueous → x(solute) = 0.0177
- Use molality for ΔTb, ΔTf; molarity for π

Henry and Raoult

- p = K(H) x; big K(H) = less soluble
- p(A) = x(A) p°(A)
- Vapour richer in the more volatile liquid
- (p° − p)/p° = x(solute)

Deviations

- Positive: weaker A–B, higher VP, ΔH > 0, min-boiling azeotrope
- Negative: stronger A–B, lower VP, ΔH < 0, max-boiling azeotrope
- $CHCl_3$ + acetone negative; ethanol + acetone positive

Colligative

- ΔTb = i Kb m; ΔTf = i Kf m; π = iCRT
- Water: Kb 0.52, Kf 1.86
- $M = K\, w_2\, 1000/(\Delta T\, w_1)$
- π is best for proteins and polymers

van't Hoff factor

- Dissociation: α = (i − 1)/(n − 1)
- Association: α = (1 − i)/(1 − 1/n)
- Dimer in benzene → i ≈ 0.5
- 0.1 m $CaCl_2$ > NaCl > glucose for ΔTf

Osmosis

- Solvent moves dilute → concentrated
- Isotonic 0.9% NaCl; hypertonic shrinks cells
- Reverse osmosis desalinates water
- Memory: count the crowd, not the faces

END OF NOTES · RAMGOVINDYADAV.COM