Solutions

A solution is a homogeneous mixture of two or more chemically non-reacting substances whose composition can be varied within certain limits.

Solvent : ~~solute~~ component in larger amount.
Solute : the component in smaller amount.
Binary solution : one solute + one solvent.

Types of Solutions

Based on the physical state of solute & solvent, 9 types of solutions are possible :

1. Gas in gas : air (O_2 + N_2 + ...)
2. Gas in liq : O_2 in water, soda
3. Gas in sol : H_2 in Pd, Pt
4. Liq in gas : moisture in air
5. Liq in liq : alcohol in water
6. Liq in sol : amalgam (Hg in Na)
7. Sol in gas *: camphor in air
8. Sol in liq : salt in water
9. Sol in sol : alloys (brass, bronze)

Most common type : solid / liquid in liquid.

Concentration of Solutions

Concentration = amount of solute in a given quantity of solution / solvent. Several methods:

(1) Mass Percentage (w/w)

w/w % = (mass of solute / mass of soln) x 100

*

<-e.g. 10 % glucose soln : 10 g glucose in
<-90 g water (total 100 g soln).

(2) Volume Percentage (v/v)

v/v % = (vol. of solute / vol. of soln) x 100

35% v/v aq. ethylene glycol : antifreeze in car radiators (freezes at -17.6 C).

(3) Mass by Volume (w/V)

w/V % = (mass of solute / vol. soln) x 100

<-used in medicine & pharmacy.

Note : w/V depends on temperature (V changes).

Concentration Units (contd.)

(4) Parts per Million (ppm)

For very dilute solutions (trace amounts).

$$ppm = (mass\ solute\ /\ mass\ soln) \times 10^6$$

e.g. 5.8 g of dissolved O2 in 1000 kg sea water = 5.8 ppm. 1 ppm F- in drinking water prevents tooth decay ; 1.5 ppm causes mottling. Pollutants in air also expressed in ppm.

(5) Mole Fraction (x)

$$x_A = n_A / (n_A + n_B)$$

<-mole fraction
<-of A

For binary mixture : $x_A + x_B = 1$

useful in relating P, V to composition
(~~Henry~~ Dalton's law, Raoult's law).

Independent of temperature. No units.

Molarity & Molality

(6) Molarity (M)

Moles of solute dissolved per litre of solution.

$$M = n_{solute} / V \text{ (in L)}$$

<- unit : mol/L
<- = M

Also $M = (w_B \times 1000) / (M_B \times V \text{ mL})$

Drawback : depends on T (volume expands / contracts with T). Hence NOT temp-independent.

(7) Molality (m)

Moles of solute per kg of solvent.

$$m = n_{solute} / W_{solvent} \text{ (kg)}$$

<- unit : mol / kg
<- = m

Also $m = (w_B \times 1000) / (M_B \times W_A \text{ g})$

Mass independent of T => molality is temperature ~~dependent~~ independent.

Preferred in colligative property calculations.

Solved Example 1

Q. Calculate molarity of solution containing 5 g NaOH in 450 mL of solution.

Solution :

$M_{NaOH} = 23 + 16 + 1 = 40$ g/mol

Moles of NaOH = 5 / 40 = 0.125 mol

Volume = 450 mL = 0.450 L

Using definition of molarity :

M = (moles of solute) / (vol. in L)

= 0.125 / 0.450 = 0.278 mol/L

Final answer : M = 0.278 M

Quick check

1 L of soln contains 0.278 mol = 0.278 × 40 = 11.1 g NaOH. 450 mL would contain 11.1 × 0.45 = 5.0 g. Verified.

Solved Example 2 :

Q. A solution of glucose in water is 10% w/w. Calculate mole fraction of glucose and water.

Solution :

Take 100 g of solution.

Mass of glucose = 10 g ; mass of water = 90 g.

M of glucose ($C_6H_{12}O_6$) = 180 g/mol

M of water (H_2O) = 18 g/mol

$n_{glu} = 10 / 180 = 0.0556$ mol

$n_{H20} = 90 / 18 = 5.00$ mol

Mole fraction of glucose :

$$x_{glu} = 0.0556 / (0.0556 + 5.00)$$

$$= 0.0556 / 5.0556 = 0.011$$

$x_{H20} = 1 - 0.011 = 0.989$

Answer : $x_{glu} = 0.011$; $x_{H20} = 0.989$

Solubility

Solubility = max amount of a substance that dissolves in a given solvent at a specified T.

Depends on : nature of solute / solvent, temperature and pressure.

Solid in Liquid

Saturated solution : solute - dissolved solute in dynamic equilibrium with un~~disolved~~ dissolved solute.

Solute (s) <=> Solute in solution

<-dynamic eqm

Like dissolves like :

- polar solute -- polar solvent (NaCl - H_2O)
- non-polar -- non-polar (naphthalene - C_6H_6)

Effect of T

If dissolution endothermic (delta H > 0) :

solubility increases with T (KNO_3).

If exothermic (delta H < 0) :

solubility decreases with T ($Ce_2(SO_4)_3$).

Pressure : negligible effect on solid solubility.

Solubility of Gas in Liquid

Strongly affected by Temperature & Pressure.

Henry's Law

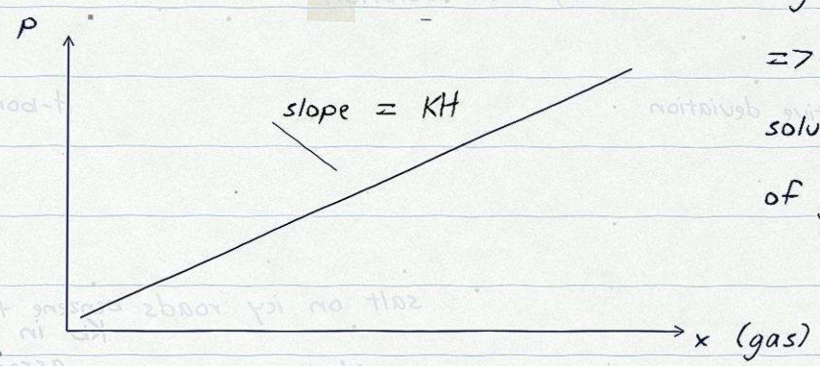
At constant T, solubility of a gas in a liquid is directly proportional to its partial pressure.

$$p = K_H \ x$$

<- KH = Henry's law
<- constant.

p = partial pressure of gas above soln
x = mole fraction of gas in soln

Plot : p vs x



Higher KH => lower solubility of gas.

Henry's Law - Applications

KH varies with T & gas nature

KH (gas) increases with T => solubility of gas decreases with rise in T.

(Aquatic life prefers cold water - more dissolved O_2.)

Some KH values (293 K)

Gas	KH / kbar
He	144.97
H_2	69.16
N_2	76.48
O_2	34.86
CO_2	1.67 (least KH, most soluble)

Real-life uses

1. Soda water : sealed at high p CO_2.
2. Scuba divers : He + O_2 mix, not air, to avoid the 'bends' (N_2 bubbles in blood on rapid ascent).
3. High altitudes : low pO_2 => anoxia. Climbers suffer weakness (low O_2 in blood).

Solved Example 3

Q. N_2 gas is bubbled through water at 293 K. If $p(N_2) = 0.987$ bar, calculate moles of N_2 dissolved in 1 L water. $K_H(N_2) = 76.48$ kbar.

Solution :

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

$x_{N2} = p / K_H$

$= 0.987 / (76480) = 1.29 \times 10^{-5}$

1 L water = 1000 g => 1000/18 = 55.55 mol

$x_{N2} \quad n_{N2} / n_{H2O}$ (since $n_{N2} << n_{H2O}$)

$n_{N2} = x_{N2} \times n_{H2O}$

$= 1.29 \times 10^{-5} \times 55.55$

$n(N_2) = 7.16 \times 10 \quad -4$ mol

Very little N_2 dissolves at 1 atm in pure water - because $K_H(N_2)$ is high.

Vapour Pressure - Raoult's Law

Vapour Pressure (VP)

Pressure exerted by vapour in equilibrium with its liquid at a given temperature.

Raoult's Law (liq-liq solution)

For a solution of volatile liquids, the partial VP of each component is directly proportional to its mole fraction in the solution.

$$p_A = p_A^* \, x_A \qquad p_B = p_B^* \, x_B$$

<- p^* = VP of
<- pure component

By Dalton's law of partial pressures :

$$p_{total} = p_A + p_B = p_A^* x_A + p_B^* x_B$$

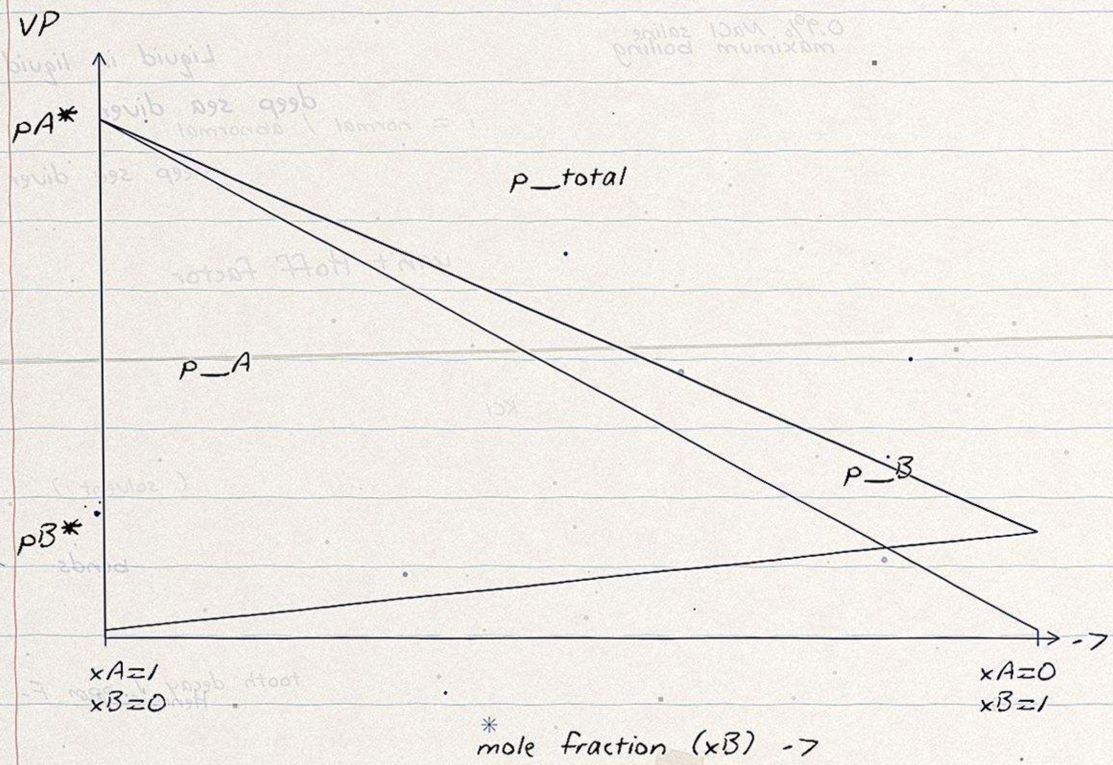
Since $x_A = 1 - x_B$:

$$p_{total} = p_A^* + (p_B^* - p_A^*) \, x_B$$

=> p_total varies linearly with xB.

VP vs Mole Fraction Plot

For an ideal binary solution :



All three plots are STRAIGHT lines for an ideal solution (obeys Raoult's law over all compositions and at all temperatures).

Ideal & Non-ideal Solutions

Ideal Solution

Obeys Raoult's law for ALL compositions and all temperatures. Conditions :

1. $p_A = p_A^* x_A$ and $p_B = p_B^* x_B$
2. $\Delta_{mix} H = 0$ (no heat change)
3. $\Delta_{mix} V = 0$ (no vol. change)
4. $F(A-A) = F(B-B) = F(A-B)$

Examples : n-hexane + n-heptane

benzene + toluene

CCl_4 + $SiCl_4$ (chlorides)

Non-ideal Solution

Does NOT obey Raoult's law.

$F(A-B) \neq F(A-A), F(B-B)$ => shows deviation.

Two types :

1. + ve dev : $F(A-B) < F(A-A), F(B-B)$

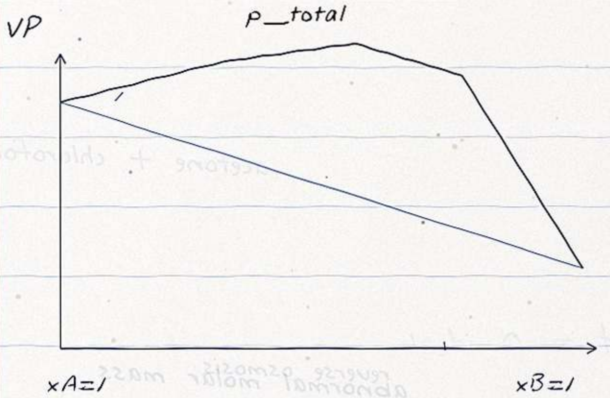
   VP higher than predicted by Raoult's law.

2. - ve dev : $F(A-B) > F(A-A), F(B-B)$

   VP lower than predicted by Raoult's law.

Deviation Plots

(a) Positive Deviation



Examples :

ethanol + acetone

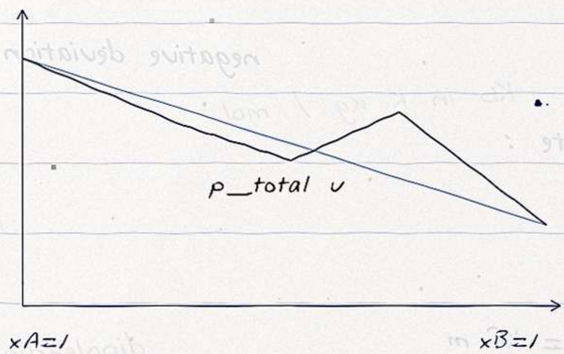
CCl_4 + C_6H_6

CS_2 + acetone

EtOH + H_2O

H-bonding in pure ethanol breaks => more vapours.

(b) Negative Deviation



Examples :

$CHCl_3$ + acetone

HCl + H_2O

HNO_3 + H_2O

Note : New H-bond btwn $CHCl_3$ & CH_3-CO-CH_3 => VP lowered.

Azeotropes

Liquid mixtures that distill at a constant boiling temperature without change in composition (vapour & liquid have same x).

Cannot be separated by simple distillation.

Two Kinds

(1) Minimum BP : + ve deviation systems
e.g. EtOH + H_2O at 95.4% EtOH boils at 351.15 K (< both pure components).

(2) Maximum BP : - ve deviation systems
e.g. HNO_3 (68%) + H_2O boils at 393.5 K (> both pure components).

Summary Table

Type	VP	delta H	delta - V	Azeotrope
Ideal	Raoult	0	0	none
+ dev	higher	> 0	> 0	Min-BP
- dev	lower	< 0	< 0	Max-BP

Solid Solute in Liquid Solvent

Non-volatile solute does NOT contribute to VP.

So p_solution = p1 = p1* x1   (Raoult)

where 1 = solvent ; non-vol. solute (2) has p2 = 0.

Relative Lowering of VP

VP of solvent in solution < VP of pure solvent.

$$(p_1^* - p) / p_1^* = x_2$$

<-depends only on
<-x2 (colligative)

Derivation :

$$p_1 = p_1^* x_1 = p_1^* (1 - x_2)$$
$$p_1^* - p_1 = p_1^* x_2$$
$$(p_1^* - p) / p_1^* = x_2$$

For dilute solution (n2 << n1) :

$$x_2 \quad n_2 / n_1 = (w_2/M_2) / (w/M)$$

$$\Rightarrow (p_1^* - p)/p_1^* = (w_2 M) / (M_2 w)$$

Allows molar mass determination of solute.

Colligative Properties

Properties of dilute solutions that depend ONLY on the number of solute particles, and NOT on their nature.

Four colligative properties :

1. Relative lowering of VP
2. Elevation of boiling point
3. Depression of freezing point
4. Osmotic pressure

(2) Elevation of BP

BP of solvent rises when a non-volatile solute is added. delta T_b = Tb - Tb*.

$$\text{delta } T_b = K_b \, m$$

<- Kb = molal BP
<- elev. const.

Kb units : K kg / mol (or C kg / mol).

$$K_b = (R\, M_1\, T_b^{*2}) \,/\, (1000 \text{ delta } H_{vap}^{*})$$

Kb (water) = 0.52 K kg/mol ; Kb (C6H6) = 2.53

Depression of Freezing Point

FP of solvent lowers when a non-volatile solute is added. delta T_f = Tf* - Tf.

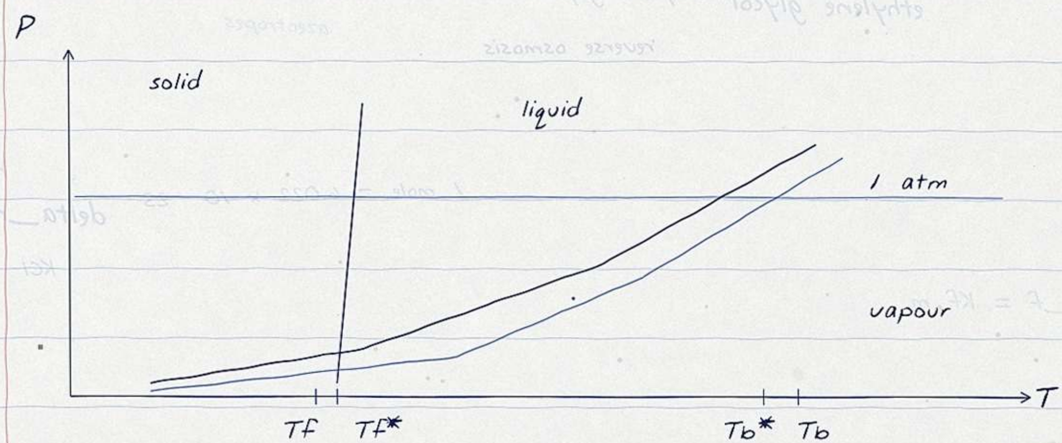
$$\text{delta } T_f = K_f\, m$$

<- Kf = molal FP
<- depr. const.

$$K_f = (R\, M_1\, T_f^{*2}) \,/\, (1000 \text{ delta } H_{fus})$$

Kf (water) = 1.86 K kg/mol ; Kf (C6H6) = 5.12

Phase diagram (qualitative)



Solution curve sits below pure solvent curve.

Osmosis & Osmotic Pressure

Osmosis : spontaneous flow of solvent molecules from a pure solvent (or dilute soln) to a concentrated soln through a semipermeable membrane (SPM).

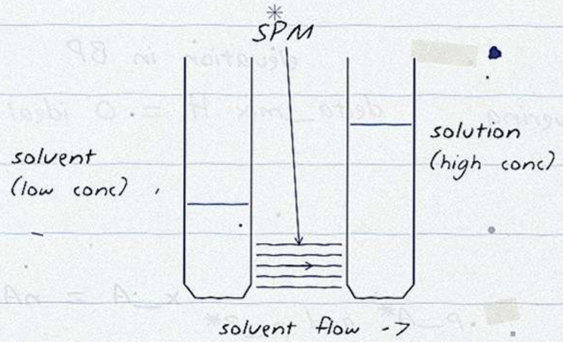
Osmotic pressure (pi) = extra pressure that must be applied on the solution side to JUST stop osmosis.

$$\pi = C R T = (n_2/V) R T$$

<-Van't Hoff <-equation

C = molar conc. (mol/L) ; R = 0.0821 L atm/mol K

T in Kelvin ; pi in atm.



h gives a measure of osmotic pressure.

Osmosis - Terminology & Uses

Isotonic, Hyper-, Hypotonic

① Isotonic : two soln of equal pi.

e.g. 0.9% NaCl & blood plasma at 310 K.

② Hypertonic : soln with higher pi.

Water exits cell -> shrinks (crenation).

③ Hypotonic : soln with lower pi.

Water enters cell -> bursts (haemolysis).

Reverse Osmosis

If P_applied > pi on the solution side,
solvent flows from solution -> pure side.
Used in ~~desolinization~~ desalination of sea water.

Why pi is preferred (not delta Tb / Tf)

(i) Magnitude of pi is large => measurable even for very dilute solutions.

(ii) Measured at room T (unlike BP / FP).

(iii) Suitable for proteins, polymers which decompose at high T.

Solved Example 4

Q. 18 g of glucose (C6H12O6) is dissolved in 1 kg of water in a saucepan. At what T will water boil at 1 atm ? Kb(H2O) = 0.52 K kg/mol.

Solution :

$M(C_6H_{12}O_6) = 6(12) + 12(1) + 6(16) = 180$ g/mol

moles of glucose = 18 / 180 = 0.10 mol

mass of solvent = 1 kg

m = 0.10 / 1 = 0.10 mol / kg

Using delta T_b = Kb x m :

delta T_b = 0.52 x 0.10 = 0.052 K

Boiling point of pure water = 373.15 K

T_b (soln) = 373.15 + 0.052 = 373.20 K

So water boils at 373.20 K (100.05 C).

Solved Example 5

Q. 1.00 g of a non-electrolyte solute dissolved in 50 g of benzene lowers the FP by 0.40 K. Kf(benzene) = 5.12 K kg/mol. Find M2.

Solution :

Use formula relating delta Tf with M2 :

$$\Delta T_f = K_f \times (1000\ w_2) / (M_2\ w)$$

$$M_2 = (K_f \times 1000 \times w_2) / (\Delta T_f \times w)$$

Substitute : Kf = 5.12, w2 = 1.00 g, delta Tf = 0.40, w1 = 50 g.

$$M_2 = (5.12 \times 1000 \times 1.00) / (0.40 \times 50)$$

$$= 5120 / 20$$

$$M\_2 = 256 \text{ g / mol}$$

Likely S_8 (8 × 32 = 256). Sulphur dissolves in C_6H_6.

Solved Example 6

Q. 200 cm3 of an aqueous soln of a protein contains 1.26 g. of the protein. The osmotic pressure of this soln at 300 K is 2.57×10^{-3} bar. Calculate the molar mass of the protein.

Solution :

$$pi = (w_2 R T) / (M_2 V)$$
$$\Rightarrow M_2 = (w_2 R T) / (pi V)$$

Convert units :

$w_2 = 1.26$ g

$V = 200$ mL $= 0.200$ L

$R = 0.0831$ L bar / mol K

$T = 300$ K

$pi = 2.57 \times 10^{-3}$ bar

$$M_2 = (1.26 \times 0.0831 \times 300) / (2.57e{-3} \times 0.200)$$

$$= 31.41 / (5.14 \times 10^{-4})$$

$$M_2 = 6.11 \times 10^{4} \text{ g / mol}$$

Typical for biomolecules. Osmotic method works.

Abnormal Molar Mass

Molar mass calculated from a colligative property is the ' colligative ' or ' apparent ' molar mass M2 (apparent).

If solute DISSOCIATES (e.g. NaCl, KCl) :

- # of particles > # of formula units
- observed delta T > calculated delta T
- apparent M2 < true M2.

If solute ASSOCIATES (e.g. C_6H_5COOH in C_6H_6) :

- # of particles < # of formula units
- observed delta T < calculated delta T
- apparent M2 > true M2.

Van't Hoff factor (i)

i = (observed coll. prop) / (calc. coll. prop)

i = (calc. M_2) / (observed M_2)

i = (No. of particles after dissoc / assoc) / (No. of partic

i > 1 : dissociation ; i < 1 : association.

Modified Colligative Formulas

Including Van't Hoff factor i :

$$(p_1^* - p) / p_1^* = i\, x_2$$

$$\text{delta } T_b = i\, K_b\, m$$

$$\text{delta } T_f = i\, K_f\, m$$

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

Degree of dissoc / assoc (alpha)

For dissoc : A_n -> n A (n = particles after)

$$\text{alpha} = (i - 1) / (n - 1)$$

For assoc : n A -> A_n (1 particle from n)

$$\text{alpha} = (1 - i)(n) / (n - 1)$$

Examples : i (NaCl) 2 ; i ($BaCl_2$) 3

i (C_6H_5COOH in C_6H_6) 0.5 (dimer)

Solved Example 7

Q. 2 g of benzoic acid (C_6H_5COOH) is dissolved in 25 g of benzene which shows a depression in FP of 1.62 K. $K_f(C_6H_6)$ = 4.9 K kg/mol. Calculate i and degree of association.

Solution :

$M\ (C_6H_5COOH) = 122\ g\ /\ mol$

$m = (2\ /\ 122) \times (1000\ /\ 25) = 0.656\ mol/kg$

$\text{delta } T_f\ (\text{calc}) = K_f\ m = 4.9 \times 0.656 = 3.22\ K$

$\text{delta } T_f\ (\text{obs}) = 1.62\ K$

$i = 1.62\ /\ 3.22 = 0.503$

Since $i < 1$ => association (forms dimer, $n=2$)

$\text{alpha} = (1 - i) \times n\ /\ (n - 1) = (1 - 0.503) \times 2\ /\ (2$

$= 2 \times 0.497 = 0.994$ 99.4 %

Nearly all benzoic acid dimerises in benzene.

Solved Example 8

Q. Calculate the osmotic pressure at 300 K of a 0.0100 M aqueous KCl solution. Assume complete dissociation. R = 0.0821 L atm/mol K.

Solution :

KCl -> K+ + Cl- ; 2 ions => i = 2.

pi = i C R T

pi = 2 x 0.0100 x 0.0821 x 300

= 2 x 0.0100 x 24.63

= 0.493 atm

pi = 0.493 atm

Compare with non-electrolyte (glucose) at same C : pi = 0.246 atm. So KCl gives 2x more pi.

Because 1 mol KCl -> 2 mol particles.

Chapter Summary

Key formulae

* $M = n / V(L)$; $m = n / W(kg)$
* $x_A = n_A / (n_A + n_B)$
* Henry : $p = K_H x$
* Raoult : $p_i = p_i^* x_i$
* $(p^* - p)/p^* = x_2$ (rel. lower)
* delta $T_b = i K_b m$
* delta $T_f = i K_f m$
* pi = $i C^* R T$
* $alpha_{dissoc} = (i - 1) / (n - 1)$

Important constants

Kb (H2O) = 0.52 K kg/mol

Kf (H2O) = 1.86 K kg/mol

Kb (C6H6) = 2.53 K kg/mol

Kf (C6H6) = 5.12 K kg/mol

R = 0.0821 L atm/(mol K) = 0.0831 L bar/(mol K)

Common pitfalls

1. molarity changes with T ; molality doesn't.
2. forget Van't Hoff i for electrolytes !
3. mass of SOLVENT in molality, not solution.
4. R values for atm vs bar differ - check units.