Colligative properties of the solutions

Colligative properties

- Physical chemical properties of solutions made by a solvent and non-volatile solutes
- They depend on the **number** of molecules in a given volume of solvent and not on the identity (e.g. size or mass) of the molecules

- Lowering of the vapour pressure (Raoult's law)
- Elevation of boiling point
- Depression of freezing point
- Osmotic pressure

Raoult's law

- The vapour pressure of an ideal solution is dependent on the vapour pressure of each chemical component and on their mole fraction

- The vapour pressure is the pressure of a gas in equilibrium with its own liquid phase
- When we add a solute to the liquid, the vapour pressure varies proportionally to the actual concentration of the solute

$$P_{solution} = P_0 x_0 + P_1 x_1 \qquad (a)$$

- Where “0” refers to the solvent and “1” to the solute

Raoult's law

$$P_{solution} = P_0 x_0 + P_1 x_1$$

- Whenever the solute is non volatile → $P_1 = 0$

$$P_{solution} = P_0 x_0 \qquad (b)$$

- Therefore $P_{solution} < P_0$ of the pure solvent
- Since x0+x1 = 1, let's rearrange equation (b) as follows:

$$P_{solution} = P_0(1-x_1) = P_0 - P_0 x_1$$

$$P_0 - P_{solution} = \Delta P = P_0 x_1$$

- Hence the decrease of the solvent vapour pressure (ΔP) is proportional to the mole fraction of the solute (x_1)

Boiling point elevation and freezing point depression

- Both properties are proportional to the lowering of the vapour pressure of the solution

- Boiling $Point_{solution}$ = Boiling $Point_{solvent}$ + ΔT_b

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

- Freezing $Point_{solution}$ = freezing $Point_{solvent}$ – ΔT_f

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

K_b is the ebullioscopic constant; K_f is the cryoscopic constant; the concentration is expressed in molality

What is "i"?

- "*i*" is the van't Hoff factor **[1+α(ν-1)]**
- Where **α** is the **dissociation constant** and **ν** is the total **number of ions** present in the solution
- "*i*" is a correction factor which accounts for the real concentration of solutes in solutions
- From its definition $\alpha = \frac{n_{dissociated}}{n_{total}}$, α is a dimensionless number and its value is $0 \leq \alpha \leq 1$

Osmotic pressure

- This is the pressure which needs to be applied to a solution to prevent the inward flow of water across a **semipermeable membrane**
- The phenomenon of osmotic pressure arises from the tendency of a pure solvent to move through a semipermeable membrane and into a solution containing a solute to which the membrane is impermeable.
- This process is of vital importance in biology as the cell's membrane is selective towards many of the solutes found in living organisms.

Osmotic pressure

- The laws governing the osmotic pressure of solution were formalized by van't Hoff, among others
- The osmotic pressure of a solution at constant temperature is directly **proportional** to its **concentration**
- The osmotic pressure of a solution is directly proportional to absolute **temperature**
- The osmotic pressure units are *atm*

$$\pi V = nRTi \rightarrow \quad \pi = CRTi$$

Where:

C is the molar concentration of the solution,

R is the ideal gas constant,

T is the absolute temperature and

"***i***" is van't Hoff factor : $[1+\alpha(\nu-1)]$

Chemical nature of solutes

- Non volatile solutes can be divided into two main classes:

Electrolytes

- ionic bonds
- highly heteropolar co-valent bonds
- water breaks their bonds

Covalent compounds

- covalent bonds
- water dissolves them without breaking

Exercise 1

- Calculate the osmotic pressure of a solution 0.1 M of urea at 25°C.

Urea is a covalent compound → does not dissociate into water → since $\alpha=0$, then $i=[1+\alpha(\nu-1)]=1$

$$\pi = CRTi = 0.1 \cdot 0.082 \cdot 298 \cdot 1 = 2.44 \text{ atm}$$

Exercise 2

- Calculate the osmotic pressure of a solution 0.5 M of magnesium chloride ($MgCl_2$) at 25°C.

$MgCl_2 \rightarrow Mg^{2+} + 2Cl^-$ electrolyte = salt

$\alpha=1$ and $\nu=3$ $\rightarrow i = [1+\alpha(\nu-1)] = [1+1(3-1)] = 3$

$\Pi = CRTi = 0.5 \cdot 0.082 \cdot 298 \cdot 3 = 36.65$ atm

Exercise 3

- Calculate the osmotic pressure of a solution made by dissolving 1.5g of barium chloride ($BaCl_2$) in 400ml of water at 298K.

$BaCl_2 \rightarrow Ba^{2+} + 2Cl^-$ $\alpha=1; \nu=3$

$\pi = CRTi = (g/FW \cdot V)RT[1+a(v-1)] =$

$= (1.5/208 \cdot 0.4) \cdot 0.082 \cdot 298 \cdot 3 = 1.32 \text{ atm}$

Exercise 4

- The osmotic pressure of $CaCl_2$ is 5 atm at 32°C. Calculate the molar concentration and the osmolar concentration.

$CaCl_2 \rightarrow Ca^{2+} + 2Cl^-$ $\alpha=1; \nu=3 \rightarrow i=3$

$\pi = CRTi$ $\rightarrow C = \pi / RTi = 5 / 0.082 \cdot 305 \cdot 3 = 0.067$ M

$Ci = \pi / RT = 5 / 0.082 \cdot 305 = 0.2$ osM $\rightarrow$ this is the real concentration felt by the solution

Exercise 5

Calculate the osmotic pressure at 27°C of a solution made by sodium sulfate (Na_2SO_4) 0.5M and glycerol 1.5M

$Na_2SO_4 \rightarrow 2Na^+ + SO_4^{2-}$ hence α=1 and ν=3

$C_3H_5(OH)_3$ covalent organic compound, α=0

$$C_{tot} = C_{Na2SO4} \cdot i + C_{glycerol} = 0.5 \cdot 3 + 1.5 = 3.0 \text{ osM}$$

$$\pi = C_{tot}RT = 3.0 \cdot 0.082 \cdot 300 = 73.8 \text{ atm}$$

Exercise 6

- The blood osmotic pressure is 7.65 atm at 37°C. Calculate how many grams of glycerol can be dissolved in 0.5L of water to obtain a solution isotonic with blood.

T= 37+273 = 310K
Glycerol is a covalent compound, hence i=1

$C = \pi / RT = 7.65 / 0.082 \cdot 310 = 0.3M$

$C = n/V = g/PM \cdot V \quad \Rightarrow \quad g = C \cdot FW \cdot V = 0.3 \cdot 92 \cdot 0.5 = 13.8g$

Exercise 7

- Calculate the formula weight of a covalent compound, whose solution at 2%w/v has an osmotic pressure of 3 atm at 25°C.

T= 25 +273 = 298K

C = π/RT = 3/ 0.082·298 = 0.123 M

C = n/V = g/FW·V

Hence FW = g/C·V = 2/ 0.123·0.1 = 162.6 Da

Exercise 8

- The blood osmotic pressure is 7.65 atm at 37°C. How many grams of glucose are dissolved in 250ml of water ready to be injected intravenously?

Glucose is a covalent compound → i=1
the formula is $C_6H_{12}O_6$, hence FW=180

T= 37 +273 = 310K

$C = \pi/RT = 7.65/ 0.082 \cdot 310 = 0.3M$

$C = n/V = g/FW \cdot V$

$g = C \cdot FW \cdot V = 0.3 \cdot 180.16 \cdot 0.25 = 13.51g$

Exercise 9

How many grams of sodium chloride are necessary to have 1L of a solution with osmotic pressure of 126.29atm at 27°C?

$NaCl \rightarrow Na^{+} + Cl^{-}$ hence $\alpha=1$, $\nu=2$

$i=[1+\alpha(\nu-1)] = 2$

$\pi = CRTi = gRTi / FW \cdot V$

$$g = \frac{FW\,\pi\,V}{RTi} = \frac{58.44 x 126.29 x 1}{0.082 x 300 x 2} = \frac{7380.39}{49.2} = 150g$$

Exercise 10

- Calculate the formula weight of a covalent compound, whose solution made by 300g in 1 L has an osmotic pressure of 25.85 atm at 0°C.

$$\pi = \mathrm{CRT}i \qquad \Rightarrow \pi = \frac{gRT}{FW\ V}$$

$$FW = \frac{gRT}{\pi\ V} = \frac{300\text{x}0.082\text{x}273}{25.85\text{x}1} = \frac{6715.8}{25.85} = 259.79$$