Solutions -- Chapter 13

The Solution Process

1. **Why do things dissolve?**

    - driving force toward more random state (entropy)

    - attractive forces between solute and solvent (enthalpy)

    "*like dissolves like*"

    (ionic and polar substances tend to be water soluble)

2. **Heats of Solution (ΔH_{soln})**

    ΔH_{soln} is a combination of two opposing effects:

    Lattice Energy (E_L)
    endothermic (a positive ΔH value)
    energy required to separate solid particles

    Hydration (solvation) Energy (E_H)
    exothermic (a negative ΔH value)
    energy gained as solute particles are surrounded
    by solvent molecules

    $\therefore$ $\Delta H_{soln} \approx E_L + E_H$ (ΔH_{soln} can be positive or
    negative)

3. **Solubility -- How much will dissolve?**

    units are usually: g solute per 100 g of solution

    "saturated" solution: maximum amount of solute is
    dissolved

    solute(undissolved) $\rightleftharpoons$ **solute**(dissolved)

4. **Effect of Temperature on Solubility**

    most substances are more soluble at higher temperature

5. Effect of Pressure on Solubility

no significant effect for solid or liquid solutes, but major effect with gaseous solutes dissolved in liquid solvents

Henry's Law: gases are more soluble at higher pressure (e.g., carbonated beverage)

$$C_g \propto P_g \quad \text{or} \quad C_g = k_g P_g \quad \text{or} \quad C_1/C_2 = P_1/P_2$$

Concentrations of Solutions

1. Molarity (M)

M = moles of solute / liter of *solution*

2. Mole Fraction (and mole percent)

$$X_A = \text{moles A} / [\text{moles A} + \text{moles B} + \ldots]$$

mole % $= X_A \times 100\%$

mixtures of gases: $X_A \propto n_A \propto P_A$ (constant temp)

so, $X_A = P_A / P_{total}$

3. Weight (or Mass) Fraction (and weight percent)

$WF_A = \text{mass A} / \text{mass of solution}$

Wt % $= WF_A \times 100\%$

e.g., a 5.00% (by weight) solution of NaCl contains:

5 g NaCl in 100 g of solution (5 g NaCl and 95 g H_2O)

related terms: parts per million (and parts per billion):

ppm = mass fraction x 10^6 **ppb** = mass fraction x 10^9

4.   **Molality (m)   --   don't confuse it with Molarity (M) ! ! !**

   m = moles solute / kg of *solvent*

   e.g., molality of above 5.00% NaCl solution?

   m   =   [(5.00 g NaCl) x (1 mole NaCl / 58.4 g NaCl)] / (0.095 kg)
        =   0.90 mole NaCl / kg   =   0.90 m

5.   **Conversions between concentration methods**

   Example: Commercial hydrobromic acid, HBr, is 40.0% by
                      weight. The density of this solution is 1.38 g/mL.
                      Calculate the molality, molarity, and mole fraction of
                      this HBr solution.

   40.0% HBr means that 100 g of solution contains:
            40.0 g HBr and 60.0 g H_2O

   moles HBr = 40.0 g x (1 mole / 80.9 g) = 0.494 mole
   moles H_2O = 60.0 g x (1 mole / 18.0 g) = 3.333 mole

   X_{HBr} = 0.494 / (0.494 + 3.333) = 0.129 (or 12.9 mole %)

   m = moles HBr / kg H_2O = 0.494 mole / 0.060 kg = 8.23 m

   to find molarity, need volume of solution (from density):

   volume of 100 g of soln = 100 g x (1 mL / 1.38 g) = 72.5 mL
   M = mole HBr / L of soln = 0.494 mole / 0.0725 L = 6.82 M

Colligative Properties
   (depend on number of solute particles)

1.   **Vapor Pressure   (related to mole fraction of solvent)**

   Vapor pressure of solution is always less than the pure solvent.

For solutions of *non-volatile* solutes, **Raoult's Law** applies:

$$P_{solution} = X_{solvent} \cdot P^{\circ}_{solvent}$$

OMIT -- mixtures of two or more volatile components
(pp 597-599)

2. **Freezing Point Depression and Boiling Point Elevation**
(related to *molality* of the solution)

change in freezing and boiling points:

$$\Delta t_f = K_f m \qquad\qquad \Delta t_b = K_b m$$

where K_f and K_b are properties of the solvent:

K_f = molal freezing point depression constant
K_b = molal boiling point elevation constant

e.g., for water: $K_f = 1.86\ °C / m$ and $K_b = 0.51\ °C / m$

Problem:
A solution of 6.400 g of an unknown compound in 100.0 g of
benzene (C_6H_6) boils at 81.7°C. Determine molecular mass of
the unknown.

Data for benzene: $K_f = 5.07\ °C / m$ $\quad t_f = 5.07\ °C$
$K_b = 2.53\ °C / m$ $\quad t_b = 80.2\ °C$

$\Delta t_b = 81.7 - 80.2 = 1.5\ °C$

$m = \Delta t_b / K_b = (1.5\ °C) / (2.53\ °C / m) = 0.593\ m$
$\quad = 0.593\ mole / kg$

(0.100 kg) x (0.593 mole / kg) = 0.0593 mole
molecular mass = g / mole = 6.40 g / (0.0593 mole)
$\quad\quad\quad = 108\ g / mole$

3.   Osmotic Pressure   (see Figure 13.16)

   osmosis --   passage of solvent through a "semipermeable"
                   membrane into a solution

   osmotic pressure (Π) --   back pressure required to stop
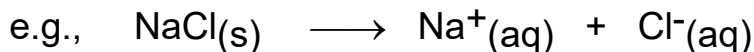   osmosis

   $$\Pi \propto M \quad \text{(at constant temp)}$$

      more generally:

   $$\Pi V = nRT \qquad \text{(the van't Hoff equation)}$$

Osmotic pressure measurements (and the van't Hoff equation) are very
useful for determining molecular masses of unknowns, especially large
molecules, e.g., polymers, proteins, etc.

4.   Dissociation of Solutes

   e.g., $NaCl_{(s)} \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)}$

      # moles of ions = 2 times moles of NaCl

   so, colligative properties are about twice as large

Colloidal Dispersions

   Colloid   --   fluid suspension of very small particles
                  ($\sim$ nanometers) -- not a true solution

   Types and examples of colloids -- Table 13.10

   common examples: soaps, milk, whipped cream, fog, jellies,
                      paint, etc.

how soaps work -- *micelle* formation

long hydrocarbon "tail"
hydrophobic

O

O^- Na^+

anionic "head"
hydrophilic

^-O_2C CO_2^- CO_2^-

^-O_2C CO_2^-

^-O_2C CO_2^-

^-O_2C CO_2^-

^-O_2C CO_2^-

^-O_2C CO_2^- CO_2^-

micelle