

## Chem 103

Lecture 2c  
Chemical Equilibrium 4

## Last time

- Aspects of equilibrium problem solving and 5% rule; determining the dominant species.
- Le Chatelier's Principle
- A 10-minute bonus quiz!

## Today

- Pick up graded pop quiz
- Key for quiz: 1C 2B 3C 4E 5A 6B
- Chapter 14 – intro to solutions
- Solution concentrations
- Henry's Law
- Colligative properties

## Le Chatelier's Principle

Le Chatelier's Principle: A system at equilibrium responds to a stress by adjusting to minimize that stress.

3 examples which are initially at equilibrium:

- a)  $A(aq) + B(aq) \rightleftharpoons AB(aq)$  initially at equilibrium  
If you add A to the system, it will favor the forward reaction to lower the concentration of A. Increase in A is the "stress".
- b)  $A(g) + B(g) \rightleftharpoons AB(g)$ ; compress the system (pressure increases). The forward reaction is favored to relieve the pressure.
- c)  $A + B \rightleftharpoons AB + \Delta$ . (exothermic) If raise temperature, reverse reaction is favored, to "absorb" the additional heat.

## Chapter 14: Solutions

What are solutions?

-*homogeneous* mixtures of 2 or more pure substances

Examples of solutions:

- solids in liquids;
- liquids in liquids
- Solids in solids,
- gases in liquids

## Interactions change in dissolving process

Dissolution = process of dissolving a solute into a solvent to form a solution

Interactions between molecules (or ions) disrupted or formed.  
Consider a solid crystal dissolving in a liquid solvent:

Solvent - solvent interactions are broken ( $\Delta H_{\text{vaporization}} > 0$ )

Solute-solute interactions are broken ( $\Delta H_{\text{lattice}} > 0$ )

Solute-solvent interactions are formed. ( $\Delta H_{\text{solvation}} < 0$ )

## Strength of interactions determine dissolving process

These can reduce solubility:

Strong solute-solute interactions

Strong solvent-solvent interactions

These can increase solubility:

Strong solute-solvent interactions

## Like dissolves like!

Rule of thumb: Like substances dissolve like substances and unlike substances do not dissolve unlike substances.

Main example: polar substances dissolve polar substances but not nonpolar substances

**Oil and water don't mix!**  
They are *immiscible*.

**Oil dissolves in gasoline. They are miscible.**  
**Sugar dissolves in water but not in oil.**

## Enthalpy of solution, $\Delta H_{\text{soln}}$

$$\begin{aligned}\Delta H_{\text{soln}} &= \sum \Delta H_i \\ &= \Delta H_{\text{solvent}} + \Delta H_{\text{solute}} + \Delta H_{\text{solvation}}\end{aligned}$$

Recall the signs!  $\Delta H_{\text{solvent}}$  (+),  $\Delta H_{\text{solute}}$  (+) and  $\Delta H_{\text{solvation}}$  (-)

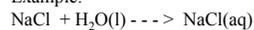
Note:  $\Delta H_{\text{soln}}$  can be + (endothermic) or - (exothermic)

(See Figure 14.4)

Usually, **exothermic** is more favorable. But **entropy** change also factor affecting favorability of a reaction or process.

## Solution of ionic solid in liquid

Example:



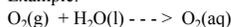
$$\begin{aligned}\Delta H_{\text{soln}} &= \Delta H_{\text{solvent}} + \Delta H_{\text{solute}} + \Delta H_{\text{solvation}} \\ &= (\text{positive}) + (\text{large positive}) + (\text{large negative}) \\ &\Rightarrow \text{usually endothermic.}\end{aligned}$$

What happens to solubility if you raise the temperature?

According to Le Chatelier's principle, solubility of solid would increase! (for endothermic case)

## Solution of a gas in water

Example:



$$\begin{aligned}\Delta H_{\text{solution}} &= \Delta H_{\text{solvent}} + \Delta H_{\text{solute}} + \Delta H_{\text{solvation}} \\ &= (\text{positive}) + (0) + (\text{negative}) \\ &= \text{negative (exothermic)}\end{aligned}$$

What happens to solubility if you raise the temperature?

According to Le Chatelier's principle, solubility would decrease! Gases dissolve less in warm water than in cold.

Trout love cold mountain streams but die in warm pond. Why?

What is thermal pollution?

## Henry's Law

Solubility of a gas in a liquid is proportional to the partial pressure of the gas on the liquid surface:

$$s_{\text{g}} = k_{\text{H}} P_{\text{g}}$$

Example:  $\text{O}_2$  has  $k_{\text{H}} = 1.26 \times 10^{-3} \text{ M atm}^{-1}$  (at  $25^\circ\text{C}$ )

If the  $\text{O}_2$  mole fraction in air is 0.21, what is the molar solubility of  $\text{O}_2$  in an aquarium at  $25^\circ\text{C}$ ?

$$s_{\text{O}_2} = k_{\text{O}_2} P_{\text{O}_2} = 1.26 \times 10^{-3} \text{ M atm}^{-1} (1.0 \text{ atm})(0.21) = 2.65 \times 10^{-4} \text{ M}$$

## Concentration units

Review of concentration units:

1 molar (M) = 1 mole solute/ liter soln

1 molal (m) = 1 mole solute/ kg solvent

1 % (m/v) = (1 g solute/g soln) x 100%  
(same as =g solute/100g soln)

1 ppm = (1 g solute/g soln) x 10<sup>6</sup>  
(same as =g solute/10<sup>6</sup>g soln)  
(for dilute aqueous solutions: 1 ppm = 1mg solute/L soln)

## Example Problem

What is the molality of a 1.20 M NaCl solution whose density is 1.0200 g/mL? (FW of NaCl = 58.5 g/mol)

Solution:

M = mol solute/L soln, m = mol solute/kg solvent

Assume 1.0 L: #mol NaCl = 1.20, mass soln

= 1.0200 g/mL(1000mL/L)(1kg/1000g) = 1.0200 kg

Kg solvent = kg solution – kg NaCl = 1.0200 kg – 0.0585kg

=0.9615 kg; m = 1.20 mol/.9615kg = 1.25 m

## Example Problem #2

What is the ppm Ca<sup>2+</sup> in a 2.50 L solution containing 1.20 CaCl<sub>2</sub>?

(FW's: CaCl<sub>2</sub> = 111.1 g/mol)

Solution: recall that ppm ≈ 1 mg/L

g Ca<sup>2+</sup> = 1.20 CaCl<sub>2</sub> (1mol/111.1)(1 mol Ca<sup>2+</sup>/1mol CaCl<sub>2</sub>)(40.1g

Ca<sup>2+</sup>/mol Ca<sup>2+</sup>) = 0.433 g

ppm Ca<sup>2+</sup> = 0.433g (1000mg/g)/L = 433 ppm Ca<sup>2+</sup>

## Colligative properties

Colligative properties = physical properties of solutions which depend upon the concentration of solute particles.

4 main examples:

- Bolling point elevation
- Freezing point depression
- Vapor Pressure lowering
- Osmotic pressure

## Boiling point elevation

$$\Delta T_b = k_b m_{\text{solute}}$$

Where  $\Delta T_b$  = change in boiling point

$K_b$  = molal boiling pt elev'n const.

and, m = molality of solute particles

## Freezing point depression

$$\Delta T_f = k_f m_{\text{solute}}$$

Where  $\Delta T_f$  = change in freezing pt

$K_f$  = molal freezing pt elev'n const.

and, m = molality of solute particles

### Vapor pressure lowering

$$P_1 = X_1 P_1^\circ \text{ (Raoult's Law)}$$

Where  $P_1$  = vapor pressure of a solvent in a liquid solution.

$X_1$  = mole fraction of that solvent in the solution

$P_1^\circ$  = vapor pressure of that solvent when it is pure solvent.

### Osmotic pressure

$$\pi = iMRT \text{ (across semipermeable membrane)}$$

Where  $\pi$  = osmotic pressure

$i$  = "van't Hoff factor", a correction factor to account for actual # particles in solution

$M$  = molarity of solute

$R = 0.0821 \text{ atmL/molK}$

$T$  = temperature in K