Chem 103

Lecture 2b
Chemical Equilibrium 3

Last time

- ICE method of calculating equilibrium values given certain initial conditions.
- Reaction Quotient, Q
- Using Q to predict favored direction of reaction
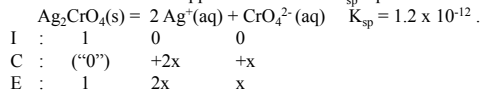- Special types of equilibria and their K's.
- Sample Calculations.

Today

- Aspects of equilibrium problem solving and 5% rule; determining the dominant species.
- Le Chatelier's Principle
- Chapter 14 – intro to solutions
- Solution concentrations
- But first: A 10-minute bonus quiz!

Sample solubility problem #1a)

Silver chromate, Ag_2CrO_4 , a sparingly soluble compound, has a *solubility product, K_{sp}* , of 1.2×10^{-12} . What is the *molar solubility* of Ag_2CrO_4 in pure water?

Solution: Use the ICE approach: Write the K_{sp} equilibrium:
$$Ag_2CrO_4(s) = 2\,Ag^+(aq) + CrO_4^{2-}\,(aq) \quad K_{sp} = 1.2 \times 10^{-12} .$$
I :   1   0   0
C :   ("0")   +2x   +x
E :   1   2x   x
(note: above, we let x = $[CrO_4^{2-}]$ and so $[Ag^+]$ = 2x)
$K_{sp} =[Ag^+]^2[CrO_4^{2-}]/1 = (2x)^2(x) = 4x^3 = 1.2 \times 10^{-12}$
Or, $x^3 = 3.0 \times 10^{-13}$ Take cube root of both sides:
=> x = 6.7×10^{-5}M = $[CrO_4^{2-}]$ => $[Ag^+]$ =2x = 1.3×10^{-4} M

Aspects of problem solving: 5% rule

What is the "5% Rule"?   By convention: approximations allowed within 5% limit.
For example if you have $(2.5 \times 10^{-2} -x)\, x^2 = 2.5 \times 10^{-8}$, what is x?
Rearranging:
   $x^3 - 2.5 \times 10^{-2}\, x^2 + 2.5 \times 10^{-8} =0$; Hard to solve! Why?
  - because it is a 3rd order polynomial equation (i.e. x^3 is highest order).

Approximations can make calculations easier (or even possible!)
Assume that x << 2.5×10^{-2} => then above equation becomes:
$(2.5 \times 10^{-2} -x)\, x^2 \approx   (2.5 \times 10^{-2})\, x^2 = 2.5 \times 10^{-8}$. (This is easy to solve)

$x^2 = 2.5 \times 10^{-8} / (2.5 \times 10^{-2}) = 1.0 \times 10^{-6}$ => x = 1.0×10^{-3}
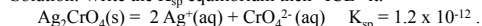
Verify that x < 2.5×10^{-2} : $\dfrac{(1.0 \times 10^{-3})(100\%)}{(2.5 \times 10^{-2})}$ = 4% OK since it's less than 5%

Note: x is dropped only when it is added or subtracted from a relatively much larger number

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Sample solubility problem #1b

Silver chromate, Ag_2CrO_4, a sparingly soluble compound, has a *solubility product, K_{sp}*, of 1.2×10^{-12} . What is the *molar solubility* of Ag_2CrO_4 in 0.10M $AgNO_3$?

Solution: Write the K_{sp} equilibrium then "ICE" it:
$$Ag_2CrO_4(s) = 2\,Ag^+(aq) + CrO_4^{2-}\,(aq) \quad K_{sp} = 1.2 \times 10^{-12} .$$
I :   1   0.10   0
C :   ("0")   +2x   +x
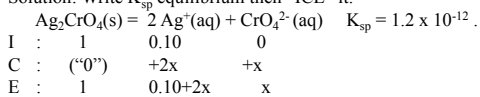E :   1   0.10+2x   x
(note the presence of Ag^+ from the start)
$K_{sp} =[Ag^+]^2[CrO_4^{2-}]/1 = (0.10+2x)^2(x) = 1.2 \times 10^{-12}$
Hard to solve because 3rd order polynomial!

Sample solubility problem #1b…

Silver chromate, Ag_2CrO_4 , a sparingly soluble compound, has a *solubility product, K_{sp}* , of 1.2×10^{-12} . What is the *molar solubility* of Ag_2CrO_4 in 0.10M $AgNO_3$?

Solution: Write K_{sp} equilibrium then "ICE" it:

$\qquad Ag_2CrO_4(s) = 2\ Ag^+(aq) + CrO_4{}^{2-}(aq) \qquad K_{sp} = 1.2 \times 10^{-12}$.

I	:	1	0.10	0
C	:	("0")	+2x	+x
E	:	1	0.10+2x	x

Assuming 2x<<0.10 so that 0.10+2x ≈ 0.10 gives us:

$K_{sp} = [Ag^+]^2[CrO_4{}^{2-}]/1 \approx (0.10)^2(x) = 1.2 \times 10^{-12}$

Now easy to solve: $x = 1.2 \times 10^{-12} /0.010 = 1.2 \times 10^{-10} <<0.10$!

For quadratic equations

Quadratic equations contain 2nd order polynomials , i.e. the highest order is x^2. It can be written in the form:

$\qquad a x^2 + bx + c = 0$

If after approximating, you find that x>5%, you need to re-calculate the solution using the quadratic equation below:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

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) $A(aq) + B(aq) <==> AB(aq)$ 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) $A(g) + B(g) <==> AB(g)$; compress the system (pressure increases).   The forward reaction is favored to relieve the pressure .

c) $A + B <==> AB + \Delta.$ (exothermic)   If raise temperature, reverse reaction is favored, to "absorb" the additional heat.

Le Chatelier's Principle…

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

Look at Q for 2 of the previous examples:

a) $A(aq) + B(aq) <==> AB(aq)$ If [A] increases. $Q=[AB]/([A][B])$ decreases. Thus forward reaction is favored.

b) $A(g) + B(g) <==> AB(g)$; compressing system increases all pressures by x: $(1+x)P_A$, $(1+x)P_B$ and $(1+x)P_C$.

$K = P_C/P_A P_B$ becomes: $Q = (1+x)P_A / (1+x)^2 P_A P_B$

$= (P_C/P_A P_B)/(1+x) < K$ so that forward is favored

Le Chatelier's Principle…

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

Remember the connection between L.Chatelier's principle and Q (reaction quotient).

Example: A tank of gas contains H_2 (g) , C(s) and CH_4(g) at equilibrium : $C(s) + 2H_2(g) <=> CH_4(g)$. Predict what happens when:

a) more solid carbon, C, is added to system.

b) Ar(g) is added to the tank, raising the overall pressure.

Le Chatelier's Principle…

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

(see Conceptual Exercise 13.11 , (page 491 in "Principles…") to note the various scenarios one may encounter in applying Le Chatelier's principle.)

Chapter 14: Solutions

What are solutions?
-*homogeneous* mixtures of 2 or more pure substances

Examples of solutions:
a) solids in liquids;
b) liquids in liquids
c) Solids in solids,
d) 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 ($\Delta H_{vaporization} > 0$)

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

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

Strength of interactions determin 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, ΔH_{soln}

$\Delta H_{soln} = \sum \Delta H_i$

$\qquad = \Delta H_{solvent} + \Delta H_{solute} + \Delta H_{solvation}$

Recall the signs! $\Delta H_{solvent}$ (+) , ΔH_{solute}(+) and $\Delta H_{solvation}$ (-)
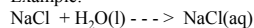
Note: ΔH_{soln} can be + (endothermic) or - (exothermic)

(See Figure 14.4)

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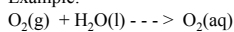
Solution of ionic solid in liquid

Example:
$NaCl + H_2O(l) - - - > NaCl(aq)$

$\Delta H_{soln} = \Delta H_{solvent} + \Delta H_{solute} + \Delta H_{solvation}$
$\qquad = (positive) + (large\ positive) + (large\ negative)$
$=> $ usually endothermic.

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:
$O_2(g) + H_2O(l) - - - > O_2(aq)$

$\Delta H_{solution} = \Delta H_{solvent} + \Delta H_{solute} + \Delta H_{solvation}$
$= (positive) + (0) + (negative)$
$= negative \ (exothermic)$

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:

$$s_g = k_H P_g$$

Example: O_2 has $k_H = 1.26 \times 10^{-3}$ M atm^{-1} (at 25°C)

If the O_2 mole fraction in air is 0.21, what is the molar solubility of O_2 in an aquarium at 25°C?
$s_{O2} = k_{O2} P_{O2} = 1.26 \times 10^{-3}$ M atm^{-1} (1.0 atm)(0.21)=2.65x10^{-4}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 10^6
   (same as =g solute/10^{6}g soln)
   (for dilute aqueous solutions: 1 ppm = 1mg solute/L soln)

answer to today's pop quiz

1 C
2 B
3 C
4 E
5 A
6 B