

Chem 201 Lecture 3a

Review of equilibria
 K_{sp} , common ion effect,
 K_f , Sample calculations

Last time

Dixon's Q-test
Gravimetry

Today

Review Equilibria and Thermodynamics
Types of equilibria: K_{sp} and K_f
Volumetric analysis

Homework "correlation"

HW #3 Due 7/13
7th edition: (as is)
8th edition (instead of ch 27, do: ch **26**
15, 17, 18, **23**) The rest of the
correlations will be emailed to you.

Review Equilibria, K expression

For $aA + bB \rightleftharpoons cC + dD$
 $K_{eq} = \frac{[\text{products}]}{[\text{reactants}]}$
 $K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$
Note: for solids and liquids, use 1
For solutions, use M
For gases, use partial pressures (in Bar)

Manipulating K's

If $A \rightleftharpoons B$ $K = K_1$; $B \rightleftharpoons C$ $K = K_2$
1) What is K' for $B \rightleftharpoons A$? $K' = ?$
 $K' = 1/K_1$
2) What's K'' for $2A \rightleftharpoons 2B$?
 $K'' = K_1^2$
3) What's K''' for $A \rightleftharpoons C$?
 $K''' = K_1 K_2$

Review Thermodynamics

ΔG = free energy change
 ΔH = enthalpy change ($\Delta H < 0$ exothermic)
 ΔS = entropy change
 $\Delta G = \Delta H - T\Delta S$
Favored rxn: $\Delta G < 0$ unfavored: $\Delta G > 0$
If $\Delta G = 0$, system is at equilibrium

Le Chatelier's Principle

A system initially at equilibrium, subjected to a "stress" will respond to minimize that "stress".



Examples:

[B] increase : product is favored (forward is favored)

[A] decrease: reactant is favored (reverse favored)

P_c increased: reactant is favored (reverse favored)

A or D are added or subtracted: neither favored

Temp is increased: forward is favored

Relation of ΔG , K and Q:

$\Delta G = \Delta G^\circ + RT \ln Q$ (Q=reaction quotient)

If $Q = K_{eq}$, $\Delta G = 0$ and we have:

$\Delta G^\circ = -RT \ln K_{eq}$ or $K_{eq} = 10^{-\Delta G^\circ/RT}$

From Q, we can predict favored direction:

$Q > K_{eq}$, reverse favored

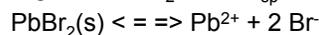
Since $\Delta G = \Delta G^\circ + RT \ln Q > \Delta G^\circ + RT \ln K = 0$

Similarly: $Q < K_{eq}$, forward is favored

Types of equilibria: solubility product, K_{sp}

K_{sp} -used for sparingly soluble ionic substances.

E.g. $PbBr_2$, $K_{sp} = 7.9 \times 10^{-6}$



$$(s)(2s)^2/1 = 7.9 \times 10^{-6} \Rightarrow s = (1.98 \times 10^{-6})^{1/3}$$

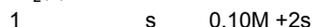
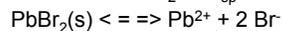
$$s = 1.3 \times 10^{-2} \text{ M} \quad (s = \text{molar solubility, saturated})$$

If $Q = K$; saturated, if $Q > K$, supersaturated

Common ion effect

If add $PbBr_2$ to 0.10M NaBr, what is solubility?

Recall: $PbBr_2$, $K_{sp} = 7.9 \times 10^{-6}$



$$(s)(.10+2s)^2/1 = 7.9 \times 10^{-6}; \text{ using 5\% rule we get:}$$

$$\Rightarrow s \approx (7.9 \times 10^{-6}) / (0.10)^2 = 7.9 \times 10^{-4}$$

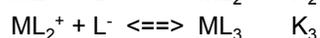
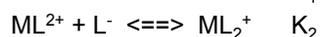
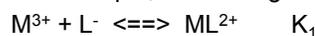
Note: $(100\%)(7.9 \times 10^{-4}) / (0.10) = 0.79\% < 5\%$

Note: presence of *common ion* lowers solubility

Types of equilibria: K_f

K_f = complex ion formation constant

for example, M^{3+} and ligands L^- :

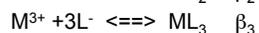
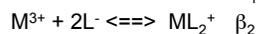
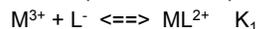


Note that K_1 , K_2 and K_3 are "step-wise formation constants".

Types of equilibria: K_f

K_f = complex ion formation constant

For the previous example, M^{3+} and ligands L^- :



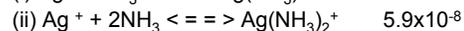
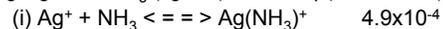
Note that β_2 and β_3 are "cumulative formation constants".

Note: $\beta_n = K_1 K_2 \dots K_n$

K_f example: $Ag(NH_3)_2^+$

K_f = complex ion formation constant

Eg Ag^+ and NH_3 (ligand) β (cumulative):



$K_2 = ?$ for: $Ag(NH_3)^+ + NH_3 \rightleftharpoons Ag(NH_3)_2^+$

Do (ii)-(i): $K_2 = K_{ii}/K_i = (5.9 \times 10^{-8}) / (4.9 \times 10^{-4}) = 1.2 \times 10^{-4}$

K_2 is a "step-wise formation constant".

(another way: $\beta_2 = K_1 K_2$ so $K_2 = \beta_2 / K_1$

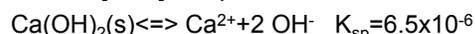
$= (5.9 \times 10^{-8}) / (4.9 \times 10^{-4}) = 1.2 \times 10^{-4}$)

Consider $Ca(OH)_2$

K_{sp} for $Ca(OH)_2$ is 6.5×10^{-6}

K_f for $Ca(OH)^+$ is $10^{-1.3}$

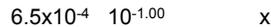
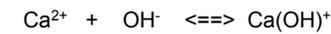
What is $[Ca^{2+}]$ in a pH 13.00 buffer?



$$s \approx (6.5 \times 10^{-6}) / (10^{-1.00})^2 = 6.5 \times 10^{-4}$$

$[Ca(OH)^+] = ?$ Use K_f equilibrium

K_f equilibrium calculation



$$K_f = [Ca(OH)^+] / [Ca^{2+}][OH^-]$$

$$10^{-1.3} = x / (6.5 \times 10^{-4})(10^{-1.00}); \quad x = 3.3 \times 10^{-6}$$

(n.b. both equilibria satisfied at same time)

As $[OH^-]$ increases, dissolved Ca^{2+} increases due to complex formation

Total dissolved Ca = $[Ca^{2+}] + [Ca(OH)^+]$

Protic Acids

Bronsted-Lowry definition

Salts can be acidic or basic

Conjugate acids and bases

Self-ionization of water

pH = $-\log[H^+]$ (approx)

Strengths of acids and bases