

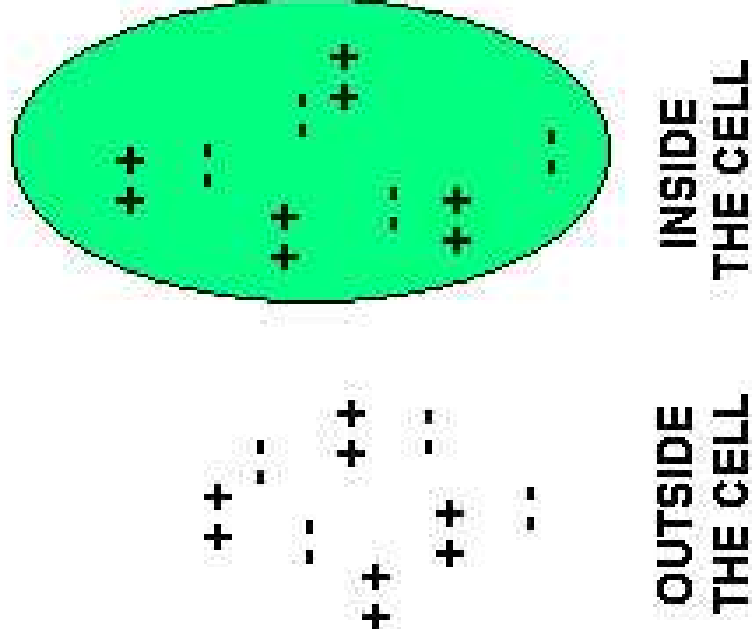
Chapter 6 Homework

Due Wednesday, February 4, 2009

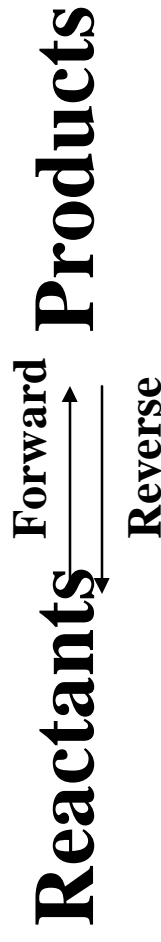
Chapt. 6: 6-5, 6-7, 6-8, 6-19, 6-30,
6-36, 6-42, 6-48, 6-49

Chapter 6: Chemical Equilibrium

Chemical equilibrium provides the basis for determining what species are present as well as how much of each species is present.



The thermodynamic equilibrium constant



$$K = [C]^c [D]^d / [A]^a [B]^b$$

Note: = same as \leftrightarrow

$$K = k_{\text{forward}} / k_{\text{reverse}}$$

When $K > 1$, then the reaction is favored (will most likely occur).

K is a **thermodynamic** term, so if the **kinetics** are not good then the reaction may take a very long time to occur.

Standard State Issues

$$K = [\text{C}]^c[\text{D}]^d / [\text{A}]^a[\text{B}]^b$$

- Since K values are dimensionless, so all concentrations are actually a ratio to the the standard state concentration (1 M for solutions and 1 bar for gases).
- To keep units consistent, all concentrations are expressed in M and all pressures in bars.
- For all pure solids or liquids at std. state, the concentration is 1 M. So, for pure solids and liquids, the concentration is 1 and can be dropped out of the calculation.

**What is, exactly, the term
inside brackets?**

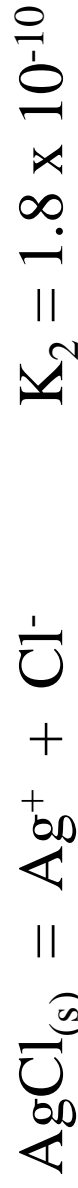
$$K = [C]^c[D]^d / [A]^a[B]^b$$

- **[C] is the ratio of activities of component C at equilibrium to standard state activity of C.**
- **At the present, we will assume the concentration is equivalent to the activity.**

Manipulating equilibrium constants

- **Add the reactions, multiply the equilibrium constants**
- **Reverse the reaction, take $1/K$**
- **Multiply reaction by n , take K^n**

Example: Determining the equilibrium constant of two R_x



(reaction of interest)

$$K_3 = K_1 \times K_2 = (2.0 \times 10^3) (1.8 \times 10^{-10}) = 3.6 \times 10^{-7}$$

What does the K values tell you about AgCl??

Thermodynamic Terms Associated w/Equilibrium

Enthalpy => Related to the heat of the reactions.

$$\text{Symbol is } \Delta H = H_{\text{products}} - H_{\text{reactants}}$$

When ΔH is negative - the reaction is exothermic (heat given off).

When ΔH is positive - the reaction is endothermic (heat absorbed).

Entropy => Related to the disorder of the reaction.

$$\text{Symbol is } \Delta S = S_{\text{products}} - S_{\text{reactants}}$$

When ΔS is positive - the products are more disordered than reactants.

When ΔS is negative - the products are less disordered than reactants.

Gibbs Free Energy: $\Delta G = \Delta H - T \Delta S$

Gibbs Free Energy combines Enthalpy and Entropy.

If ΔG is negative, then reaction is favored.

So...

if $\Delta H = -$ and $\Delta S = +$, then R_x is favored.

if $\Delta H = +$ and $\Delta S = -$, then R_x is NOT favored.

What if $\Delta H = -$ AND $\Delta S = -$, ΔG must be calculated.

Relationship of free energy and equilibrium constant:

$$\mathbf{K = e^{-(\Delta G^\circ/RT)}} \quad \text{where } \mathbf{R} \text{ is gas constant} \quad \mathbf{T} \text{ is temperature (K)}$$

Le Chatelier's Principle

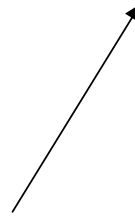
- *If, to a system at equilibrium, a stress be applied, the system will react so as to relieve the stress.*
- *Examples: add reactants, take away products*



<http://onsager.bd.psu.edu/~jircitano/equilibrium.html>

Le Chatelier's Principle in Action

If more A is added:



Then the consequence is the R_x proceeds “more” to the right (in the forward direction) to offset the additional “A”.

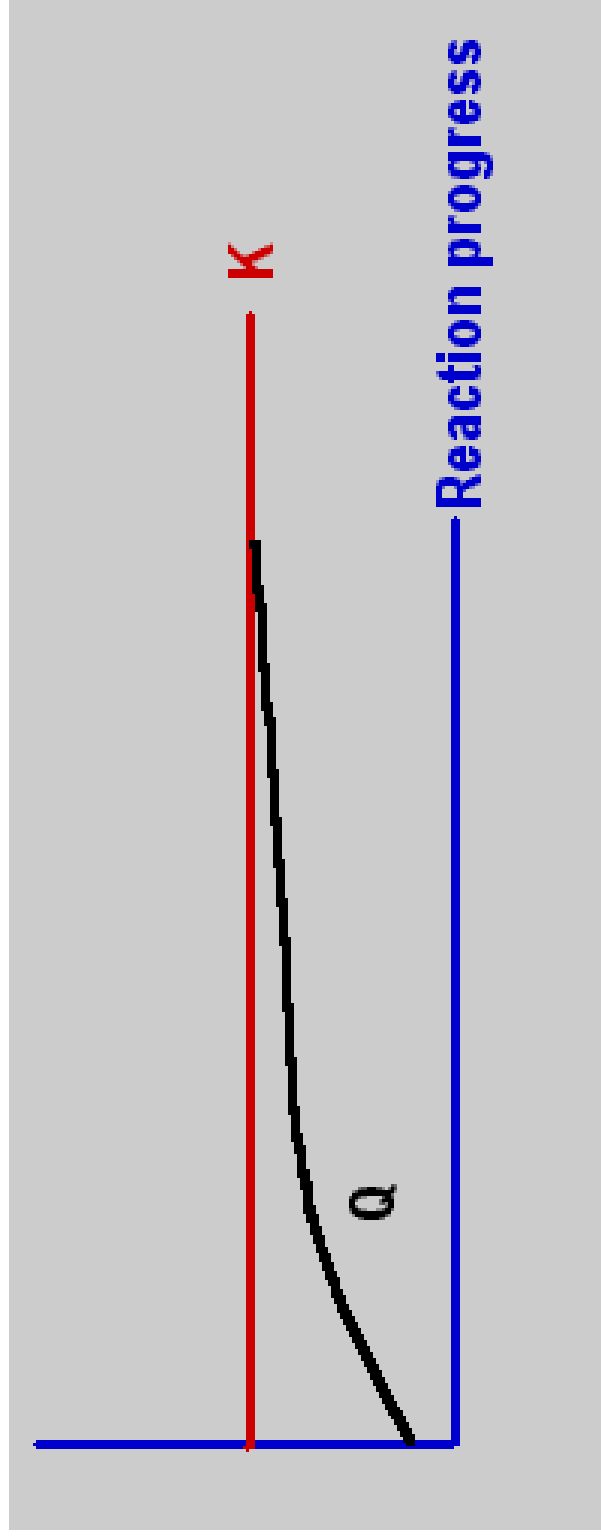
The reaction quotient, Q , can be used to compare the effects of Le Chatelier's Principle to the equilibrium state (K).

$$Q = [\mathbf{C}]^c[\mathbf{D}]^d / [\mathbf{A}]^a[\mathbf{B}]^b$$

Note: activities do not have to be at equilibrium

Relationship between K and Q

- K : ratios of activities at equilibrium to the standard state activity
- Q : ratios of activities under non-equilibrium conditions to the



Solubility Product $\Rightarrow K_{sp}$

K_{sp} is the equilibrium constant that describes the reaction of a solid dissolving (dissolution).



but the $[\text{CaSO}_{4(s)}]$ is 1 at std state, so $K = [\text{Ca}^{2+}] [\text{SO}_4^{2-}] = K_{sp}$

$$K_{sp} \text{ 's: } \text{CaSO}_4 = 2.4 \times 10^{-5}$$

$$\text{SrSO}_4 = 3.2 \times 10^{-7}$$

$$\text{BaSO}_4 = 1.1 \times 10^{-10}$$

Using K_{sp} to determine concentrations in solution



How many grams of $\text{La}(\text{IO}_3)_3$ will dissolve in 250.0 mL of water?

$$K_{\text{sp}} \text{ for } \text{La}(\text{IO}_3)_3 = 1.0 \times 10^{-11}$$

Common Ion Effect:

A salt will be less soluble if one of its constituents ions is already present in the solution.



Recall: For CaSO_4 , $K = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = K_{\text{sp}}$
if you add CaSO_4 water, you will have $[\text{Ca}^{2+}] = [\text{SO}_4^{2-}]$.

However, if you have one of the ions already present in the water, (for example Ca^{2+}) then less of the CaSO_4 will dissolve so $[\text{Ca}^{2+}] > [\text{SO}_4^{2-}]$.

How does the presence of 0.050 M LiIO_3 change how many grams of $\text{La}(\text{IO}_3)_3$ will dissolve in 250 mL?

