CHEMICAL EQUILIBRIA

CHEM 251 SDSU

CHEMICAL REACTIONS

- The 18th century view of chemical reactions was that they proceeded as a result of elective affinities.

- If: A + BC ➞ AB + C then compound A was said to have a greater affinity for B than C.

- The implication of this was that reactions were presumed to proceed only in one direction and to do so to completion; the reaction AB + C would not yield A + BC.

- Claude Berthollet realize that this was not the case when he found sodium carbonate precipitating onto limestone ($CaCO_3$) at the edge of a lake in Egypt.

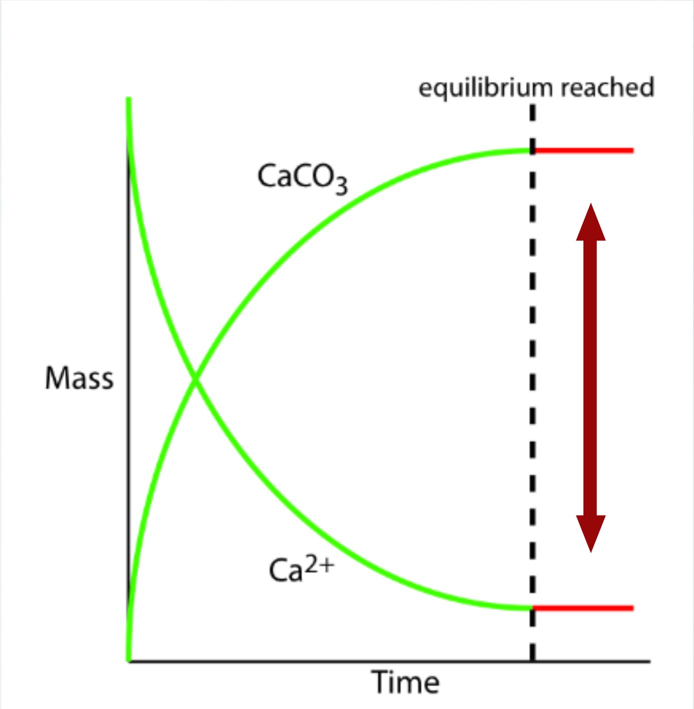
EQUILIBRIUM

$$Na_2CO_3(s) + CaCl_2(aq) \rightleftharpoons 2NaCl(aq) + CaCO_3(s)$$

- The figure to the right describes the changes in the forms of calcium over the course of the reaction above.

- In an equilibrium the free calcium ion is not completely consumed, some always remains free in solution once the equilibrium is reached.

- Importantly, though the system appears to be at a steady state to our eyes, it is in fact dynamic, with calcium carbonate constantly dissociating and calcium ions precipitating as calcium carbonate.



CHEMICAL EQUILIBRIA

- There are several prominent equilibria that will be investigated during this semester, each is related to a specific type of reaction:
    - Precipitation reactions (K_{sp})
    - Acid-base reactions (K_a or K_b)
    - Complexation reactions (K_f)
    - Oxidation-reduction (redox) reactions

THERMODYNAMICS

- For a given reaction: $aA + bB \rightleftharpoons cC + dD$
- The initial conditions of the system will determine the direction of the reaction.
- Thermodynamics can be used to evaluate the initial conditions as well as attempt to understand the equilibrium conditions.
- The direction of a reaction is the one that **lowers** the overall free energy of the system.
- At constant temperature and pressure (typical bench top reaction conditions) the free energy of the system is given by the **Gibb's Free Energy** function (ΔG).

EQUILIBRIUM & FREE ENERGY

- $\Delta G = \Delta H - T\Delta S$ When **ΔG** has a value other than **zero** the reaction will proceed in one direction or the other.

- Only when the value of **$\Delta G=0$** will the reaction be at **equilibrium**.

- As the concentrations of the reaction species determines the equilibrium we can express the ΔG value in terms of their concentrations.

- $\Delta G = \Delta G° + RT(\ln Q)$

  - $\Delta G°$ is the Gibb's free energy when all reaction components are at their **standard state**.

  - The standard state is 1 mol/L concentration; 1 atm partial pressure for gasses and all pure solids and liquids are given a value of 1.

EQUILIBRIUM & FREE ENERGY

- aA + bB ⇌ cC + dD

- $\Delta G = \Delta G° + RT(\ln Q)$

- Q is the reaction quotient and it accounts for the non-standard concentrations and partial pressures of the reaction components.

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

- As equilibrium is reached when $\Delta G=0$, we can see that this condition will arise only when: $\Delta G° = -RT(\ln K)$

- At equilibrium Q is replaced with K; the equilibrium constant.

$$K = \frac{[C]^c_{eq}[D]^d_{eq}}{[A]^a_{eq}[B]^b_{eq}}$$

- The direction of a reaction is indicated by the value of Q. If Q > K, the reaction goes to the left; if Q < K the reaction goes to the right.

SAMPLE PROBLEM

The reaction below is at equilibrium under the listed conditions. Based on this information, which direction will the reaction go under the "unstable" conditions?

$$AgNO_{3(aq)} + H_3PO_{4(aq)} \rightleftharpoons HNO_{3(aq)} + Ag_3PO_{4(s)}$$

	$AgNO_{3(aq)}$	$H_3PO_{4(aq)}$	$HNO_{3(aq)}$	$Ag_3PO_{4(s)}$
At equilibrium:	3.7 mM	1.03 mM	27.8 mM	4.67 g
Unstable:	2.9 μM	4.92 mM	9.01 mM	15.8 g