

Lowry-Brønsted acids

- loss or gain of protons
 - Lewis acid accepts an electron pair
- strong vs. weak acids
 - low vs. high pK_a
- Carbonic acid is a special case of a weak acid
 - controls the pH of most natural waters

Complex ions and ion pairs

- ion pair—soluble weak association of two charged ions.
 - Outer sphere—ligand does not replace water
- complex ion—metal and ligand (other than water) form a soluble “species”
 - Inner sphere—ligand replaces water
- solvation complex—metal plus primary hydration sheath (ligand is water)

Types of complexes

- monodentate—one bond
 - Cu-acetate
- bidentate—two bond
 - Cu-oxalate
- polydentate (chelates)
 - Cu-citrate
 - Cu-EDTA
- $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$

Metal-fulvate interactions

- Strong sites (type 1)—inner sphere multidentate
 - dominate at low metal/high fulvate conc.
 - two carboxylic or phenol/carboxylic groups
- Weak sites (type 2)—outer sphere and monodentate
 - important when type 1 sites become saturated
 - H bonding or single bond with carboxylic group

Lewis acids and bases

- A Lewis base has at least one pair of valence electrons that are not already being shared in a covalent bond.
- A Lewis base (ligand) can be negatively charged or neutral.
- Examples: NO_3^- , Cl^- , NH_3 , C_2H_4
- A Lewis acid accepts electrons.
- All Lewis acids are metals and + charged.

Soft acids and bases

- "Soft" acids and bases are polarizable
 - electron cloud will shift in bonding
 - tendency to form more covalent bonds
 - tendency towards lower charge density
 - tendency towards a larger size
- Examples:
 - S^{2-} and other reduced S groups
 - Hg^{2+} , Cd^{2+}

Hard acids and bases

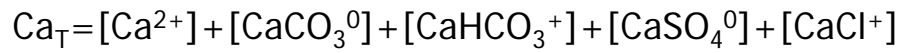
- "Hard" acids and bases are not polarizable
 - tendency to have a high charge density
 - tendency towards small size
 - Tendency to form more electrostatic bonds
- Examples:
 - NO_3^- , PO_4^{3-} , F^-
 - All earth and alkaline earth metals, Al^{3+}

Hard and soft

- In nature, soft Lewis acid and bases tend to form bonds with each other.
 - e.g. Hg^{2+} forms a strong bond with reduced S groups on soil organic matter
- In soil solution, most acids and bases are hard and most of the interaction is electrostatic.
- Soft acids and bases tend to form stronger bonds and do not remain soluble.

Speciation

- Analysis of soil solution gives total ion concentration. This is the sum of:
 - free (hydrated) ion
 - complexed ion



Speciation Modeling

- Computer programs
 - GEOCHEM
 - MINTEQA2
 - SOILCHEM

Equilibrium models
Thermodynamic database

Methods of elemental analysis

- Atomic absorption spectroscopy (AAS)
 - measures absorbance of a specific wavelength
 - flame (higher throughput, less sensitive)
 - graphite furnace (most sensitive)
- ICP-AES
 - inductively coupled plasma atomic emission spectroscopy
 - multielement / wider linear range / more sensitive than flame AAS

Interferences

- Chemical—the element must be in an atomic form (no molecules). More of a problem with AAS (lower heat).
- Ionization—for absorbance, the element must not lose its electrons
- Matrix—samples and standards should match
- Spectral—absorption or emission lines overlap or are too close.