Lecture 2: Chemistry and Chemical Reactions

Oxidation state

- Number of electrons lost (or gained) by an element when forming an ion or chemical bond

Determining the oxidation state of an element in a compound:

1. An element bonded to itself has an oxidation state of zero (supersedes the other rules)
2. Hydrogen (H) is always +1
3. Oxygen (O) is always -2
4. The sum of the oxidation states of all elements in the compound must add up to the total charge on the compound

Examples: O_2 gas, CO_2, CH_4, CH_2O (organic matter), SO_4^{2-}

Charge Balance

- Water contains positively charged (cations) and negatively charged (anions) dissolved ions
- Charge balance – Positive and negative charges <u>must</u> cancel each other out
- Solute charge is represented in terms of equivalents per volume (e.g., eq/L or meq/L for milliequivalents per liter)
- eq/L = mol/L x solute charge

Unit Conversion

One of the most important skills you will ever learn is how to convert between different units.

Examples:

(a) What is the molarity (mol L^{-1}) of $\mathbf{Mg^{2+}}$ in a solution prepared as 50 mg L^{-1} $MgCl_2 \cdot 6H_2O$?
(b) What is the molarity (mol L^{-1}) of $\mathbf{Cl^-}$ in a solution prepared as 50 mg L^{-1} $MgCl_2 \cdot 6H_2O$?

First, what is the molecular mass (g/mol) of $MgCl_2$-$6H_2O$? 203.31 g/mol

(c) (50 mg $MgCl_2$-$6H_2O$ / L)(1 g / 1000 mg)(1 mol $MgCl_2$-$6H_2O$ / 203.31 g $MgCl_2$-$6H_2O$)(1 mol Mg / 1 mol $MgCl_2$-$6H_2O$) = 2.5 x 10^-4 mol/L

(d) (50 mg MgCl2-6H2O / L)(1 g / 1000 mg)(1 mol MgCl2-6H2O / 203.31 g MgCl2-6H2O)(2 mol Cl / 1 mol MgCl2-6H2O) = 4.9 x 10^-4 mol/L

Are these charge balanced? Yes! Cl^- has one equivalent per mol (eq/mol) and Mg^{2+} has two equivalents per mol.

(e) (4.9 x 10^{-4} mol/L Cl-) x (1 eq/mol) = 4.9 x 10^{-4} eq/L
(f) (2.5 x 10^{-4} mol/L Mg^{2+}) x (2 eq/mol) = 4.9 x 10^{-4} eq/L

*note that the 2.5 and 4.9 are rounded, so it's actually like 2.45

Geochemical Models

Steps to build a model:

1. Define the system
2. Define the identity and quantity of the constituents (reactants and products) in the system
3. Write a balanced equation for the chemical reaction of interest

1. Define the system
    a. Closed System – composition is fixed; no mass transfer (box)
    b. Open System – mass can enter and leave the system via fluxes (box + arrows)
2. Define the constituents
    a. Example constituents (ensure they are expressed in comparable units)
        i. Water
        ii. Minerals
        iii. Gases (defined by their partial pressure)
        iv. Solutes (defined by their concentration; e.g., mass/volume)
3. Write a balanced equation for the chemical reaction of interest

    Reactants → Products $\qquad$ $aA + bB \rightarrow cC + dD$

    a. Start with an unbalanced equation of reactants and products
    b. Make an element inventory
    c. Adjust the numbers in front of the reactants and products until balanced on either side of the arrow
    d. Assuming the reaction takes place with water as a solvent, add H^+, OH^- and H_2O as needed to balance the equation (but only if H_2O participates in the reaction)
    e. Double check for **mass balance** and **charge balance**!

    Examples:
    NaCl --> (in water) → Na+ + Cl-
    $MgCl_2$ → (in water)→ Mg(2+) + 2 Cl(-)
    Fe(3+) + H_2O → FeOOH (then balance the elements…) Fe(3+) + 2 H2O → FeOOH + 3 H+

Chemical Reactions

Types of chemical reactions
1. Dissolution/precipitation
2. Acid-base
3. Adsorption/desorption
4. Oxidation-reduction (redox)

*reactions can be more than one type

1. Dissolution reaction: $A_{\nu A}B_{\nu B\,(s)} \rightarrow \nu_A A^{qA}{}_{(aq)} + \nu_B B^{qB}{}_{(aq)}$
    a. A – element
    b. νA – stoichiometric amount of A
    c. qA – charge on the ion A

Examples:
a. $NaCl_{(s)}$ → Na + Cl
b. $CaCO_{3\,(s)} + CO_2 + H_2O$ → Ca + HCO_3^-

2. Precipitation reaction: $\nu_A A^{qA}{}_{(aq)} + \nu_B B^{qB}{}_{(aq)} \rightarrow A_{\nu A}B_{\nu B\,(s)}$

Examples:
a. $Ca^{2+}{}_{(aq)} + SO_4^{2-}{}_{(aq)} + H_2O$ → gypsum

3. Acid-base reaction: $HA + B \rightarrow A^- + HB^+$

Brønsted-Lowry definition: transfer of a proton from an acid (the proton donor) to a base (the proton acceptor)

Examples (which are the acid, base, conjugate acid, conjugate base?)

a. $HCl + H_2O \rightarrow Cl^- + H_3O^+$
b. $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$
c. $CaCO_3 + H_2SO_4 \rightarrow H_2CO_3 + Ca^{2+} + SO_4^{2-}$

4. Surface complexation reactions
    a. Adsorption – the adhesion of a substance (e.g., solute) onto a surface
    b. Desorption – the release of a substance from a surface into solution

$\equiv S\text{-}O^- + H^+ \rightarrow \equiv S\text{-}OH$ $\equiv S\text{-}OH + H^+ \rightarrow \equiv S\text{-}OH_2^+$

$\equiv S\text{-}K^+ + H^+ \rightarrow \equiv S\text{-}H^+ + K^+$

Inner-sphere complex – ion forms a chemical bond with the surface at a specific site
Outer-sphere complex – electrostatic interaction between ion and charged surface; ion remains in hydration shell

5. Redox (oxidation-reduction) reactions
    a. Transfer of electrons from e- donor (reducing agent) to e- acceptor (oxidizing agent)
    OILRIG – oxidation is loss, reduction is gain

Oxidation half reaction: $A^0 \rightarrow A^+ + e^-$ Reduction half reaction: $B^0 + e^- \rightarrow B^-$