Notes 4-3: Ch. 4.3-4.4: Acid-Base Reactions; Oxidation Number, Half-Reactions

- Arrhenius Acids & Bases
  - Arrhenius Acids produce H^+ in aqueous solutions: HCl (aq) → H^+ (aq) + Cl^- (aq)
  - Arrhenius Bases produce OH^- in aqueous solutions: NaOH (aq) → Na^+ (aq) + OH^- (aq)
- Brønsted Acids & Bases
  - Brønsted Acids *donate* protons (H^+): HCl (aq) + H_2O (*l*) → H_3O^+ (aq) + Cl^- (aq)
    - H_3O^+ is *hydronium* ion, better representation of species than H^+
  - Brønsted Bases *accept* protons: NH_3 (aq) + H_2O (*l*) → NH_4^+ (aq) + OH^- (aq)
    - H_2O is *amphoteric*–it behaves as both an acid and a base
    - Any $R_3N + H^+ \rightarrow R_3NH^+$
  - Acids classified by number of protons:
    - Monoprotic has one proton:
      - Strong monoprotic acids: HCl, HBr, HI, $HClO_4$, HNO_3
      - All others weak: HF, HNO_2, CH_3COOH (any acid ending in COOH), etc.
    - Polyprotic acids: Diprotic has two protons: H_2SO_4, $H_2C_2O_4$
      - H_2SO_4 is strong, but only for first dissociation:
        - Polyprotic acids dissociate one at a time in H_2O:
          - $H_2SO_4 + H_2O \rightarrow HSO_4^- + H_3O^+$
          - $HSO_4^- + H_2O \rightarrow SO_4^{2-} + H_3O^+$
          - Intermediate species (HSO_4^-) amphoteric
      - All others weak: H_2SO_3, H_2CO_3, etc.
    - Triprotic has three protons: H_3PO_4 (none strong)
      - Both intermediate species ($H_2PO_4^-$, HPO_4^{2-}) amphoteric
  - Strong bases: Hydroxides of alkali metals (e.g. NaOH), $Ca(OH)_2$, $Sr(OH)_2$, & $Ba(OH)_2$ (same as exceptions to OH^- solubility rules). Cations for "b" on periodic table
- Neutralization Reactions: Double Replacement w/acid & base (one usually strong)
  - acid + base → water + salt (any ionic compound not containing H^+ or OH^-)
  - HBr (aq) + KOH (aq) → KBr (aq) + H_2O (*l*)
    - Ionic equation: H^+ (aq) + Br^- (aq) + K^+ (aq) + OH^- (aq) → K^+ (aq) + Br^- (aq) + H_2O (*l*)
    - Net ionic equation: H^+ (aq) + OH^- (aq) → H_2O (*l*)
  - Be careful—weak acids & bases do NOT dissociate:
    - HF (aq) + NaOH (aq) ⇌ NaF (aq) + H_2O (*l*)
      - Ionic equation: HF (aq) + Na^+ (aq) + OH^- (aq) ⇌ Na^+ (aq) + F^- (aq) + H_2O (*l*)
      - Net ionic equation: HF (aq) + OH^- (aq) ⇌ F^- (aq) + H_2O (*l*)
    - H_2SO_3 (aq) + 2 LiOH (aq) → 2 H_2O (*l*) + Li_2SO_3 (aq)
      - Ionic equation: H_2SO_3 (aq) + 2 Li^+ (aq) + 2 OH^- (aq) → 2 H_2O (*l*) + 2 Li^+ (aq) + SO_3^{2-} (aq)
      - Net ionic equation: H_2SO_3 (aq) + 2 OH^- (aq) → 2 H_2O (*l*) + SO_3^{2-} (aq)
- Oxidation-Reduction (Redox) Reactions
  - Many reactions involve transfer of electrons:
    - One species loses electrons, it is *oxidized* (Losing Electrons is Oxidation-LEO)
    - One species gains electrons, it is *reduced* (Gaining Electrons is Reductions-GER)
      - Mnemonic: LEO the Lion says GER
    - Ox-Red occur simultaneously and MUST occur together—can't have one without the other.

- Oxidation Number
  - Bookkeeping location of electrons: Number of charges an atom would have *if electrons were transferred completely*.
    - Rules: since sharing electrons is involved, electronegativity is important.
      - Write ox. number for *single* atom

Rules for Assigning Oxidation Numbers

1. All atoms in their elemental state (H_2 gas, Li metal, solid C) have an oxidation number of 0.
2. All monatomic ions (whether aqueous or in a solid ionic compound) have an oxidation number equal to their charge (e.g. K^+, Br^-, Fe^{3+}, S^{2-}).
3. All neutral compounds have a net oxidation number of 0. All polyatomic ions have a net oxidation number equal to their charge (e.g. in NO_3^-, the sum of the oxidation numbers of N and the 3 O atoms must equal –1).
4. Fluorine is the most electronegative element, so in compounds its oxidation number is *always* –1.
5. Oxygen's oxidation number is *usually* –2, except:
    a. When combined with F (which is more electronegative), F is –1 and O follows rule 3.
    b. In peroxides (O_2^{2-}) its oxidation number is –1 (e.g. Na_2O_2)
    c. In superoxides (O_2^-) its oxidation number is –½ (rare) (e.g. KO_2)
6. Hydrogen has oxidation number +1 in all compounds except metal hydrides, such as LiH, and specialty compounds such as sodium borohydride, $NaBH_4$, where its oxidation number is –1 since it is more electronegative.
7. The oxidation number of all other atoms in a species must be determined according to the above rules. For example, in NO_3^-, the oxidation number of each O is –2 and the sum of the oxidation numbers must be –1, so the oxidation number of N must be +5).
    a. In any binary compound, the more electronegative atom is assigned its normal negative charge. E.g. in SCl_6, Cl is assigned –1, so S is +6 since the molecule is neutral.

Practice: Find the oxidation number of the underlined atom in the following species:

0	0	+3 –1	–1	+1 –1	+2 –1	+4 –2	–3 +1
$\underline{Co}$	$\underline{O}_2$	$\underline{Fe}Cl_3$	$Ca\underline{Br}_2$	$H_2\underline{O}_2$	$\underline{O}F_2$	$\underline{C}O_2$	$\underline{C}_2H_6$
+7 -2	+1 +5 –2	+5 –1	+1 +6 –2	+2 +5 –2	+1 +6–2		
$\underline{Mn}O_4^-$	$H\underline{Cl}O_3$	$\underline{P}Cl_5$	$Na_2\underline{Cr}_2O_7$	$Ca(\underline{N}O_3)_2$	$H_2\underline{S}O_4$		

- Half Reactions
    - Redox reactions can be separated into oxidation and reduction half-reactions
    - Half reactions show electron transfer explicitly.
    - e.g. $2\ Na + Cl_2 \rightarrow 2\ NaCl$
        - Assign oxidation numbers: $2\ Na^0 + Cl_2^0 \rightarrow 2\ Na^+Cl^-$
        - Split into ox & red ½-reactions, balance mass, then balance charge using electrons
        - Oxidation Reaction: Na is *oxidized*: $Na \rightarrow Na^+ + e^-$
        - Reduction Reaction: Cl_2 is *reduced*: $Cl_2 + 2\ e^- \rightarrow 2\ Cl^-$

          Note: charge must balance but does not need to be 0
        - Na donates electrons to Cl_2 as it is oxidized—Na reduces Cl_2 so it is *reducing agent*
        - Cl_2 accepts electrons from Na as it is reduced—Cl_2 oxidized Na so it is *oxidizing agent*
        - To recombine, need to equalize electrons:

$[Na \rightarrow Na^+ + e^-]\times 2 \Rightarrow 2\ Na \rightarrow 2\ Na^+ + 2\ e^-$

$Cl_2 + 2\ e^- \rightarrow 2\ Cl^-$

Multiply by 2 to equalize & cancel electrons when

$2\ Na + Cl_2 + 2e^- \rightarrow 2\ Na^+ + 2\ Cl^- + 2e^-$

Cancel electrons and combine ions to get original equation.