CHEM 103
Redox Reactions

Lecture Notes
March 7, 2006
Prof. Sevian

Agenda

- Go over group problem
- Acids & bases
  - What you need to know about pH
  - Recap weak vs. strong acids/bases, and neutralization reactions
  - Recap how metal carbonates react with acids
- Oxidation-reduction (redox) reactions
  - How to recognize these reactions
  - Determining oxidation numbers of elements within a compound
  - Comparative reactivity (activity)
- Solution concentration
- Titration as a way to do stoichiometry

Breakdown of chemistry skills needed to do group problem

- Translate from name to chemical formula
- Identify insoluble compounds using solubility rules
- Understand the difference between ions that are dissolved in water (aq) vs. ions that are in crystalline state (s)
- Recognize states of matter (mixture vs. pure, phases of pure matter)
- Complete a reaction, using the fact that ion charges don't change in an exchange reaction
- Recognize that H-OH is the same as H_2O
- Balance a reaction
- Simplify by crossing out spectator ions

Strong vs. Weak Acids

- Strong acids (pH 1 to 4) are strong electrolytes
  - Only a few common acids are strong

    HCl, HBr, HI, HNO_3, H_2SO_4, $HClO_4$ (*memorize these*)
  - A few other less common acids are strong (you do not need to memorize these)

    e.g., **$HClO_3$, $HBrO_3$** and some others
- Weak acids (pH 5-7) are weak electrolytes
  - It is safe to assume that all other acids are weak

    Most common weak acids:

    HF, HNO_2, $HClO_2$, HSO_3, CH_3COOH

Symbolic Representation

How Can You Recognize a Base?

- Chemical formula contains hydroxide ion (OH^-)
  - Sodium hydroxide: **$NaOH$**
  - Calcium hydroxide: **$Ca(OH)_2$**
  - Aluminum hydroxide: **$Al(OH)_3$**
  - Beware chemical formulas that look like they contain hydroxide ion. Organic alcohol group (-OH) is same atoms, but doesn't ionize to form **OH^-** ions.

    methanol **CH_3OH**, ethanol **CH_3CH_2OH**, phenol **C_6H_5OH**
- Substance reacts with water to form hydroxide ions
  - Ammonia: $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$
  - Other amines (chemicals with $-NH_2$ functional group)

Strong vs. Weak Bases

- Strong bases (pH 11 to 14) are strong electrolytes
  - All bases containing the hydroxide ion (OH^-) are strong

    Most common strong bases:

    $NaOH$, KOH, $LiOH$, $Ca(OH)_2$, $Mg(OH)_2$
- Weak bases (pH 7-10) are weak electrolytes
  - Bases that do not contain the hydroxide ion (OH^-) are weak

    Most common weak bases:

    NH_3, CH_3NH_2, $C_6H_5NH_2$
- Organic alcohols are not bases
  - Organic molecules that contain an alcohol functional group (-OH) do not ionize to form hydroxide ions

What happens to pH when you mix acid and base solutions? Neutralization rxn

Acid + Base $\rightarrow$ Salt + Water

$(H^+)(anion^-) + (cation^+)(OH^-) \rightarrow (cation^+)(anion^-) + (H^+)(OH^-)$

This reaction occurs if the Base contains OH^- (in other words, only strong bases)

Strong acid + Strong base (strong acid ionizes nearly completely):

$HCl + NaOH \rightarrow NaCl + H_2O$

$H_2SO_4 + KOH \rightarrow KHSO_4 + H_2O$

Weak acid + Strong base (weak acid is mostly present as whole molecule):

$HF + NaOH \rightarrow NaF + H_2O$

$CH_3COOH + KOH \rightarrow KCH_3COO + H_2O$

What you need to know about pH

- You do not need to learn how to calculate pH right now (if you want to learn, see the lecture notes from last lecture)
- You do need to know the general regions of the pH scale (strong acid, weak acid, neutral, weak base, strong base)

When a metal carbonate reacts with an acid: two-step process

1. $MgCO_3\ (s) + 2\ HCl\ (aq) \rightarrow MgCl_2\ (aq) + H_2CO_3\ (aq)$
   (exchange rxn)
2. $H_2CO_3\ (aq) \rightarrow H_2O\ (l) + CO_2\ (g)$
   (carbonic acid is unstable)

Sum reaction:

$MgCO_3\ (s) + 2\ HCl\ (aq) \rightarrow MgCl_2\ (aq) + H_2O\ (l) + CO_2\ (g)$

Net ionic equation:

$MgCO_3\ (s) + 2\ H^+\ (aq) \rightarrow Mg^{2+}\ (aq) + H_2O\ (l) + CO_2\ (g)$

Net Ionic Equations of Weak vs. Strong Acid + Strong Base Reactions Differ

Strong acid examples (acid ionizes nearly completely):

$HCl + NaOH \rightarrow NaCl + H_2O$

$H^+\ (aq) + \cancel{Cl^-}\ (aq) + \cancel{Na^+}\ (aq) + OH^-\ (aq) \rightarrow \cancel{Na^+}\ (aq) + \cancel{Cl^-}\ (aq) + H_2O\ (l)$

Net ionic equation: $H^+\ (aq) + OH^-\ (aq) \rightarrow H_2O\ (l)$

$H_2SO_4 + KOH \rightarrow KHSO_4 + H_2O$

$H^+\ (aq) + \cancel{HSO_4^-}\ (aq) + \cancel{K^+}\ (aq) + OH^-\ (aq) \rightarrow \cancel{K^+}\ (aq) + \cancel{HSO_4^-}\ (aq) + H_2O\ (l)$

Net ionic equation: $H^+\ (aq) + OH^-\ (aq) \rightarrow H_2O\ (l)$

Net Ionic Equations of Weak vs. Strong Acid + Strong Base Reactions Differ

Weak acid examples (acid is mostly present as whole molecule):

$HF + NaOH \rightarrow NaF + H_2O$

$HF\ (aq) + \cancel{Na^+}\ (aq) + OH^-\ (aq) \rightarrow \cancel{Na^+}\ (aq) + F^-\ (aq) + H_2O\ (l)$

Net ionic equation: $HF\ (aq) + OH^-\ (aq) \rightarrow F^-\ (aq) + H_2O\ (l)$

$CH_3COOH + KOH \rightarrow KCH_3COO + H_2O$

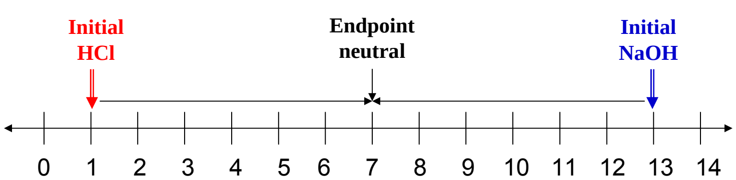
$CH_3COOH\ (aq) + \cancel{K^+}\ (aq) + OH^-\ (aq) \rightarrow \cancel{K^+}\ (aq) + CH_3COO^-\ (aq) + H_2O\ (l)$

Net ionic equation: $CH_3COOH\ (aq) + OH^-\ (aq) \rightarrow CH_3COO^-\ (aq) + H_2O\ (l)$

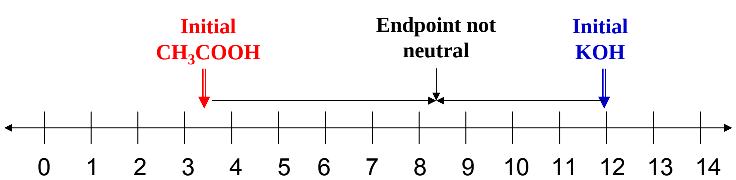
The difference between strong and weak acid-base reactions:
Strong acid present as ions, so it cancels out of net ionic equation.
Weak acid present as molecules, so doesn't cancel out of net ionic equation.

Neutralization: What happens to pH?
It approaches neutral pH

Ex 1: $\mathbf{HCl + NaOH \rightarrow NaCl + H_2O}$ (strong acid + strong base)
(equal concentrations of **HCl** and **NaOH** mixed in equal molar quantities)



Ex 2: $\mathbf{CH_3COOH + KOH \rightarrow KCH_3COO + H_2O}$ (weak acid + strong base)
(equal concentrations of $\mathbf{CH_3COOH}$ and **KOH** mixed in equal molar quantities)



Grouping Reactions

- Exchange rxns: no oxidation number change
  - Precipitation rxns
  - Acid-base rxns
    - Acid + Base → Salt + Water
    - Gas-forming rxns
- Redox rxns: oxidation numbers change
  - Single replacement (*e.g.*, many electrochemistry reactions)
  - Formation of compound from elements (*e.g.*, synthesis of sulfuric acid anhydride)
  - Decomposition of compound into elements (*e.g.*, producing pure metals from metal ores)
  - Combustion

What are oxidation numbers?

- A charge (sometimes real, sometimes fake) that can be assigned to each atom in a compound
  - In charged particles (ions within ionic solid, ions dissolved in water), the charge is real
  - In molecules (which are neutral), atoms don't have real charges
- Measures electron density that resides on the individual atom
  - Caveat: if the atom is in a molecule, and there is more than one of a particular kind of atom, in reality each one doesn't have the same electron density
- A model that provides an accounting method for explaining electron transfer in redox reactions

How to assign oxidation numbers

- Oxidation numbers sum to zero if compound is neutral, and total charge on ion if not neutral
- Atoms in free, neutral elements have oxidation number zero (0)

  Zn (*s*), **Ar** (*g*), $\mathbf{O_2}$ (*g*), $\mathbf{S_8}$ (*s*), **Ag** (*s*), $\mathbf{N_2}$ (*g*)

- Charged ions have oxidation number equal to their charges

  $\mathbf{FeCl_3}$ (*s*), $\mathbf{FeCl_2}$ (*s*), $\mathbf{Na^+}$ (*aq*), $\mathbf{Al^{3+}}$ (*aq*), $\mathbf{AlBr_3}$ (*s*)

- Oxygen, when in a compound or ion, nearly always has oxidation number -2 (exception: peroxides)

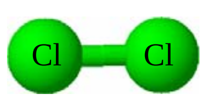
  $\mathbf{Al_2O_3}$ (*s*), **MgO** (*s*), $\mathbf{SO_4^{2-}}$ (*aq*), $\mathbf{NO_3^-}$ (*aq*); Exceptions: $\mathbf{H_2O_2}$ (*l*), $\mathbf{Na_2O_2}$ (*s*)

- Hydrogen, when in a compound or ion, nearly always has oxidation number +1 (exception: hydrides)

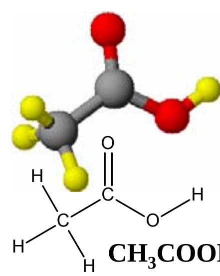
  HCl (*l*), $\mathbf{H_2SO_3}$ (*aq*), $\mathbf{CH_3COO^-}$ (*aq*); Exceptions: $\mathbf{CaH_2}$ (*s*), **NaH** (*s*)

Practice with oxidation numbers

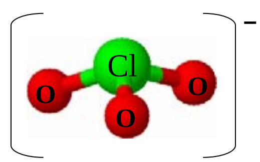
Identify oxidation numbers for each atom



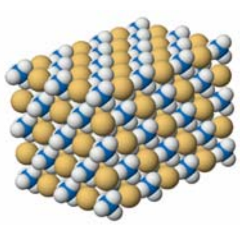
$\mathbf{Cl_2}$ (*g*)



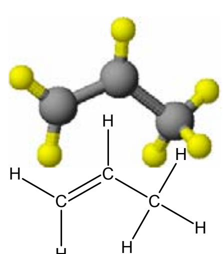
$\mathbf{CH_3COOH}$ (*aq*)



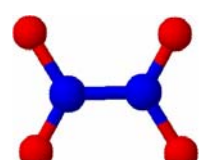
$\mathbf{ClO_3^-}$ (*aq*)



$\mathbf{NH_4Cl}$ (*s*)



$\mathbf{C_3H_6}$ (*g*)



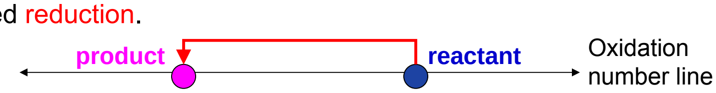
$\mathbf{N_2O_4}$ (*g*)

Redox Reactions
Macroscopic View

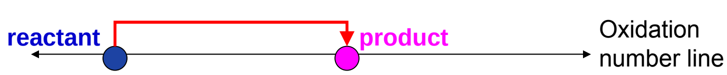
- Two distinct changes occur (*e.g.*, a new solid forms and a new ionic species appears in solution)
- Two half-reactions can be separated in such a way as to produce electrical current
- Some examples
  - Iron (III) oxide + aluminum (thermite reaction)
    http://www.jce.divched.org/JCESoft/CCA/samples/cca7thermite.html
  - Sodium + chlorine
    http://jchemed.chem.wisc.edu/JCESoft/CCA/CCA0/Movies/NACL1.html
  - Magnesium + carbon dioxide
    http://jchemed.chem.wisc.edu/JCESoft/CCA/CCA0/MOVIES/MAGCO2.html

Redox Reactions
Particle Level

- Process involved in a redox reaction is electron transfer
- Electron is transferred from a “donor” to an “acceptor”
- Electrons are negatively charged
- When the “acceptor” receives the electron, its oxidation number decreases (because electrons are negative). This part of the process is called reduction.



- When the “donor” loses the electron, its oxidation number increases (because electrons are negative). This part of the process is called oxidation.



- The two parts of the process can only happen simultaneously, but they can be separated so that the electrons must travel through a wire.

Redox Reactions
Symbolic Representation

http://www.jce.divched.org/JCESoft/CCA/samples/cca7thermite.html

Thermite reaction: Iron (III) oxide + aluminum

$$\mathbf{Fe_2O_3}\,(s) + \mathbf{Al}\,(s) \rightarrow ?$$

+3 -2 0

What are the products?

$$\mathbf{Fe_2O_3}\,(s) + \mathbf{Al}\,(s) \rightarrow \mathbf{Fe}\,(s) + \mathbf{Al_2O_3}\,(s)$$

+3 0 0 +3

reduction

oxidation

- Fe_2O_3 gets reduced to Fe metal. It gets reduced by Al. Therefore, Al is the reducing agent.
- Al metal gets oxidized to Al_2O_3. It gets oxidized by Fe_2O_3. Therefore, Fe_2O_3 is the oxidizing agent.

Redox Reactions
Symbolic Representation

http://jchemed.chem.wisc.edu/JCESoft/CCA/CCA0/Movies/NACL1.html

Sodium + chlorine

$$\mathbf{Na}\,(s) + \mathbf{Cl_2}\,(g) \rightarrow ?$$

0 0

What are the products?

$$2\,\mathbf{Na}\,(s) + \mathbf{Cl_2}\,(g) \rightarrow 2\,\mathbf{NaCl}\,(s)$$

0 0 +1 -1

oxidation

reduction

- Cl_2 gas gets reduced to Cl^- ions in NaCl crystals. It gets reduced by Na metal. Therefore, Na metal is the reducing agent.
- Na metal gets oxidized to Na^+ ions in NaCl crystals. It gets oxidized by Cl_2 gas. Therefore, Cl_2 gas is the oxidizing agent.

Ranking reactivity of metals with other metal cations in aqueous solution

- Called the activity series
- Metals that are higher are more reactive, *i.e.*, will react more readily than those below them
- Example: which reaction will occur?

  Mg (s) + Ni^{2+} (aq)

  or

  Ni (s) + Mg^{2+} (aq)

TABLE 4.5 Activity Series of Metals in Aqueous Solution

Metal	Oxidation Reaction
Lithium	$Li(s) \longrightarrow Li^{+}(aq) + e^{-}$
Potassium	$K(s) \longrightarrow K^{+}(aq) + e^{-}$
Barium	$Ba(s) \longrightarrow Ba^{2+}(aq) + 2e^{-}$
Calcium	$Ca(s) \longrightarrow Ca^{2+}(aq) + 2e^{-}$
Sodium	$Na(s) \longrightarrow Na^{+}(aq) + e^{-}$
Magnesium	$Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^{-}$
Aluminum	$Al(s) \longrightarrow Al^{3+}(aq) + 3e^{-}$
Manganese	$Mn(s) \longrightarrow Mn^{2+}(aq) + 2e^{-}$
Zinc	$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^{-}$
Chromium	$Cr(s) \longrightarrow Cr^{3+}(aq) + 3e^{-}$
Iron	$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^{-}$
Cobalt	$Co(s) \longrightarrow Co^{2+}(aq) + 2e^{-}$
Nickel	$Ni(s) \longrightarrow Ni^{2+}(aq) + 2e^{-}$
Tin	$Sn(s) \longrightarrow Sn^{2+}(aq) + 2e^{-}$
Lead	$Pb(s) \longrightarrow Pb^{2+}(aq) + 2e^{-}$
Hydrogen	$H_2(g) \longrightarrow 2H^{+}(aq) + 2e^{-}$
Copper	$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^{-}$
Silver	$Ag(s) \longrightarrow Ag^{+}(aq) + e^{-}$
Mercury	$Hg(l) \longrightarrow Hg^{2+}(aq) + 2e^{-}$
Platinum	$Pt(s) \longrightarrow Pt^{2+}(aq) + 2e^{-}$
Gold	$Au(s) \longrightarrow Au^{3+}(aq) + 3e^{-}$

Ease of oxidation increases

Another example: silver and copper

Which reaction will occur, based on the metal activity series?

Ag (s) + Cu^{2+} (aq) or Ag^{+} (aq) + Cu (s)

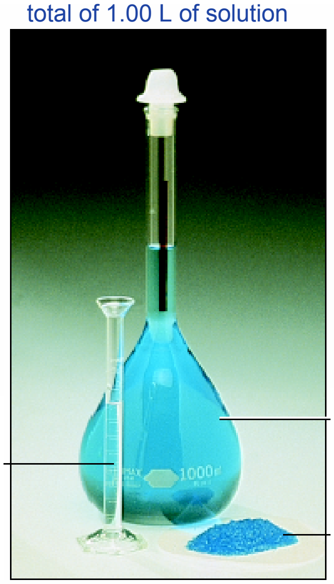
http://media.pearsoncmg.com/ph/esm/esm_brown_chemistry_10/irc/Chapter_04/Present/eMedia_Library/Movies/Chapter_04/Present/eMedia_Library/FormationofSilverCrystals/FormationofSilverCrystals.html

Net ionic reaction is:

Solution Concentration

- Many reactions of interest occur in aqueous solution
- To be able to quantify how much of a chemical reacts, and how much product is made, it is necessary to know quantities in moles
- In pure materials, the concentration of particles can be presented as density
- In mixtures that are aqueous solutions, the concentration of the particles of interest (solute) is usually presented as molarity
- Concentration just means how many particles (of interest) are present in a given amount of space
- Since Molarity = moles solute / Liter of solution, if you know the molarity and the volume of solution, you can find the moles of solute

Copper (II) sulfate solution has 25.0 g of $CuSO_4{\bullet}5H_2O$ (FW 250. g/mol) included in a total of 1.00 L of solution



From Chemistry & Chemical Reactivity 5th edition by Kotz / Treichel. C 2003. Reprinted with permission of Brooks/Cole, a division of Thomson Learning: www.thomsonrights.com. Fax 800-730-2215.

How to Calculate Concentration of a Solution

Need to know:

- Amount of solute (in mol)
- Amount of solution (in L)

$$\text{Molarity} = \frac{mol\ \text{of solute}}{L\ \text{of solution}}$$

$$= \frac{\left(25.0\ g \times \frac{1\ mol}{250.\ g}\right)}{1.00\ L}$$

$$= 0.100\ \frac{mol}{L} = 0.100\ M$$

Variations on the Theme

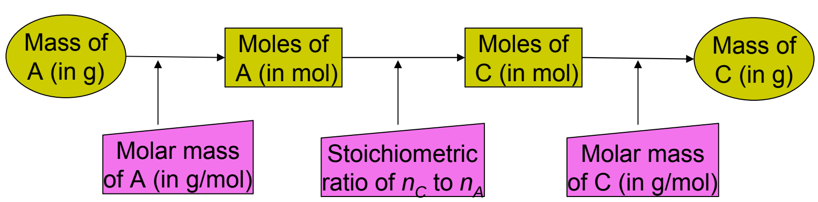
- Three variables:
  - Concentration of solution (molarity)
  - Amount of solute (moles or grams)
  - Volume of solution (liters)
- Given any two, you can always calculate the third
  - What is the concentration of a solution made by mixing ... (solute amount) into water to make a (certain number of liters) of solution?
  - How much solute (grams?) would be required to make (certain number of liters) of a (specify concentration) molar solution?
  - What volume of a (specify concentration) molar solution must be used to obtain (solute amount)?

Reminder: Stoichiometry

$$n_A\,\mathrm{A} + n_B\,\mathrm{B} \rightarrow n_C\,\mathrm{C} + n_D\,\mathrm{D}$$

<u>A typical scenario</u>

Given mass of chemical A, find mass that could be produced of chemical C.



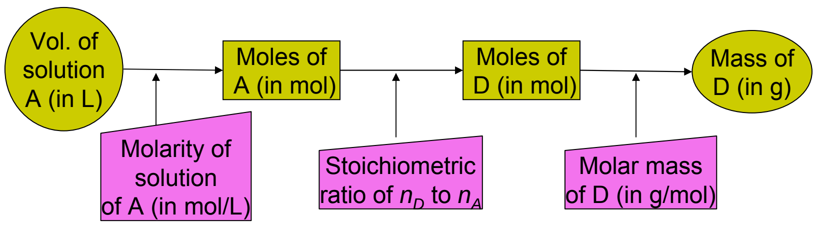
$$\text{mass of A (in } g) \times \frac{1\,mol\ \text{A}}{\text{molar mass of A}\,(g)} \times \frac{n_C\ mol\ \text{C}}{n_A\ mol\ \text{A}} \times \frac{\text{molar mass of C}\,(g)}{1\,mol\ \text{C}} = \text{mass of C (in } g)$$

Solution Stoichiometry

$$n_A \text{ A } (aq) + n_B \text{ B } (aq) \rightarrow n_C \text{ C } (aq) + n_D \text{ D } (s)$$

A typical scenario

Given volume of a certain molar solution of chemical A, find mass that could be produced of chemical D.



$$\text{volume of solution of A (in } L) \times \frac{\text{molarity of solution A } (mol)}{1\, L} \times \frac{n_D\ mol\ \text{D}}{n_A\ mol\ \text{A}} \times \frac{\text{molar mass of D } (g)}{1\, mol\ \text{D}} = \text{mass of D (in } g)$$

Acid-Base Titration

$$n_A \text{ Acid } (aq) + n_B \text{ Base } (aq) \rightarrow n_S \text{ Salt } (aq) + n_W\ H_2O\ (l)$$

A typical scenario

Given volume of a certain molar solution of Acid, find concentration of the Base solution if certain volume of Base used.