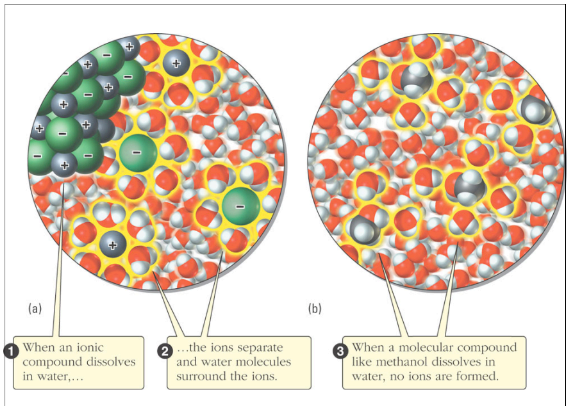
Aqueous Reactions & Sol'n Stoichiometry

Chapter 5

Properties of Aqueous Solutions

- Electrolytic Properties
  - ionic - conduct electricity (electrolytes)
  - non-ionic - do not conduct electricity (non-electrolytes)
- Ionic Compounds in Water
  - electrolytes
  - dissociate when dissolved in water
- Molecular Compounds in Water
  - non-electrolytes
  - do not dissociate when dissolved in water

    exceptions: those that react with water (e.g. NH_3, HCl)
- Strong and Weak Electrolytes
  - strong - dissociate completely
  - weak - dissociate only partly



Precipitation Reactions

occur when the mixed solutions contain a combination of ions which form a sparingly soluble (or insoluble) compound

Solubility Guidelines for Ionic Compounds

- solubility - amount of substance that can be dissolved in 1 L of water at 25°C
- substances with solubility < 0.01 mol/L considered **insoluble**

Predicting Precipitation Reactions

when two ionic compounds are mixed in aqueous solution - check the solubilities of the compounds formed when the ions “switch partners”

- if either of the new compounds is insoluble (or slightly soluble) - precipitation occurs
- if both new compounds are insoluble - two precipitation reactions occur
- if both new compounds are soluble - no precipitation occurs

Solubility Rules

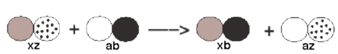
TABLE 5.1 Solubility Rules for Ionic Compounds

Usually Soluble	
Group 1A, ammonium NH_4^+, Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+	All Group 1A (alkali metal) and ammonium salts are soluble.
Nitrates, NO_3^-	All nitrates are soluble.
Chlorides, bromides, iodides, Cl^-, Br^-, I^-	All common chlorides, bromides, and iodides are soluble except AgCl, Hg_2Cl_2, $PbCl_2$; AgBr, Hg_2Br_2, $PbBr_2$; AgI, Hg_2I_2; PbI_2.
Sulfates, SO_4^{2-}	Most sulfates are soluble; exceptions include $CaSO_4$, $SrSO_4$, $BaSO_4$, and $PbSO_4$.
Chlorates, ClO_3^-	All chlorates are soluble.
Perchlorates, ClO_4^-	All perchlorates are soluble.
Acetates, CH_3COO^-	All acetates are soluble.

Solubility Rules (cont'd)

Usually Insoluble	
Phosphates, PO_4^{3-}	All phosphates are insoluble except those of NH_4^+ and Group 1A elements (alkali metal cations).
Carbonates, CO_3^{2-}	All carbonates are insoluble except those of NH_4^+ and Group 1A elements (alkali metal cations).
Hydroxides, OH^-	All hydroxides are insoluble except those of NH_4^+ and Group 1A (alkali metal cations). $Sr(OH)_2$, $Ba(OH)_2$, and $Ca(OH)_2$ are slightly soluble.
Oxalates, $C_2O_4^{2-}$	All oxalates are insoluble except those of NH_4^+ and Group 1A (alkali metal cations)
Sulfides, S^{2-}	All sulfides are insoluble except those of NH_4^+ Group 1A (alkali metal cations), and Group 2A (MgS, CaS, and BaS are sparingly soluble).

Exchange Reactions



- also known as metathesis
- cations exchange with each other
- driving force for exchange
  - formation of a precipitate
  - generation of a gas
  - production of a weak electrolyte
  - production of nonelectrolyte

Example 1

Predict whether or not a precipitate will form when the following two solutions are mixed:

(a) $AgNO_3$ (aq) + NaCl (aq)

(b) $Pb(NO_3)_2$ (aq) + KI (aq)

(c) $Ba(ClO_3)_2$ (aq) + Li_2SO_4 (aq)

(d) $BaCl_2$ (aq) + NaOH (aq)

Ionic Equations

molecular equation:

$Pb(NO_3)_2$ (aq) + 2 KI (aq) $\rightarrow$ PbI_2 (s) + 2 KNO_3 (aq)

complete ionic equation:

$Pb^{2+}(aq) + 2\ NO_3^-(aq) + 2\ K^+(aq) + 2\ I^-(aq) \rightarrow PbI_2(s) + 2\ K^+(aq) + 2\ NO_3^-(aq)$

$Pb^{2+}(aq) + 2\ NO_3^-(aq) + 2\ K^+(aq) + 2\ I^-(aq) \rightarrow PbI_2(s) + 2\ K^+(aq) + 2\ NO_3^-(aq)$

net ionic equation:

$Pb^{2+}(aq) + 2\ I^-(aq) \rightarrow PbI_2(s)$

net ionic equation shows only ions and molecules directly involved in reaction

Example 2

An aqueous solution of sodium carbonate is mixed with an aqueous solution of calcium chloride. A white precipitate immediately forms. Write a net ionic equation to account for this. What are the spectator ions?

Acid and Base Reactions

Acids

– substances that ionize or react in water to increase concentration of H^+ ions (protons)
  - HCl and HNO_3 - monoprotic acids
  - H_2SO_4 - diprotic acid

  $H_2SO_4\ (aq) \rightarrow H^+\ (aq) + HSO_4^-\ (aq)$

  $HSO_4^-\ (aq) \leftrightarrow H^+\ (aq) + SO_4^{2-}\ (aq)$

– strong acids

  HNO_3, H_2SO_4, $HClO_3$, $HClO_4$, HCl, HBr, HI

– weak acids

  all others including (but not limited to) HF, CH_3COOH, HCOOH, $H_2C_2O_4$, H_3PO_4

Acid and Base Reactions (cont'd)

Bases

– H^+ ion acceptors

– react with H^+ ions to form water

  $H^+\ (aq) + OH^-\ (aq) \rightarrow H_2O\ (\ell)$

– increase $[OH^-]$ when dissolved in water

  $NaOH\ (aq) \rightarrow Na^+\ (aq) + OH^-\ (aq)$

  $NH_3\ (aq) + H_2O\ (\ell) \leftrightarrow NH_4^+\ (aq) + OH^-\ (aq)$

– strong bases

  include $Ba(OH)_2$ and hydroxides of the alkali metals (NaOH, KOH, etc.), the soluble ionic hydroxides

– weak bases

  all slightly soluble or insoluble hydroxides and other compounds like NH_3, etc.

Reactions of Acids

- neutralization reaction (acid + base $\rightarrow$ salt + water)
- acid + carbonate (or HCO_3) $\rightarrow$ salt + water + CO_2 gas
- acid + metal oxide $\rightarrow$ salt + water
- acid + metal $\rightarrow$ salt + H_2 gas

Reactions of Bases

- base + ammonium salt → salt + water + NH_3 gas
- base + non-metal oxide → salt + water

Oxidation-Reduction Reactions

- characterized by transfer of electrons
- oxidation
  - loss of electrons during reaction
  - oxidation number increases (becomes more positive)
- reduction
  - gain of electrons during reaction
  - oxidation number decreases (becomes more negative)

Oxidation-Reduction Reactions

$$Fe_{(s)} + 2\,H^{+}_{(aq)} \rightarrow Fe^{2+}_{(aq)} + H_{2\,(g)}$$

Oxidation Numbers

determined by following a simple set of rules

1. oxidation number of atoms in neutral molecule must add up to zero; those in an ion must add up to charge on the ion
2. Group I elements --> +1
   Group II elements --> +2
   Group II elements --> +3
3. fluorine always -1 in compounds
   other halogens -1, *except* in compounds with oxygen or other halogens
4. hydrogen is +1 *except* in metal hydrides (e.g. LiH) – rule 2 takes precedence here
5. oxygen is -2 in compounds; *exceptions:* compounds with F (#3) and compounds with O–O bonds (#2 and #4)
6. elemental form --> 0

Example 3

Assign oxidation numbers to the atoms in the following:

(a) $NaCl$

(b) ClO^-

(c) $Fe_2(SO_4)_3$

(d) SO_2

(e) I_2

(f) $KMnO_4$

(g) CaH_2

Redox Reactions (cont'd)

Revisit reaction between metal and acid (or metal salt)

$$A + BX \rightarrow AX + B$$

$$Zn\ (s) + 2\ HBr\ (aq) \rightarrow ZnBr_2\ (aq) + H_2\ (g)$$
$$Mn\ (s) + Pb(NO_3)_2\ (aq) \rightarrow Mn(NO_3)_2\ (aq) + Pb\ (s)$$

These are displacement reactions

$$Mg\ (s) + 2\ HCl\ (aq) \rightarrow MgCl_2\ (aq) + H_2\ (g)$$

Redox Reactions (cont'd)

Metals can be oxidized by aqueous solutions of various salts

$$Fe\ (s) + Ni(NO_3)_2\ (aq) \rightarrow Fe(NO_3)_2\ (aq) + Ni\ (s)$$

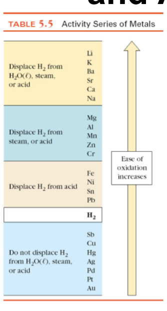
Net ionic equation:

$$Fe\ (s) + Ni^{2+}\ (aq) \rightarrow Fe^{2+}\ (aq) + Ni\ (s)$$

Remember: Whenever one substance is oxidized another must be reduced

All metals will not be oxidized by acids or metal salt. How do we determine which will??

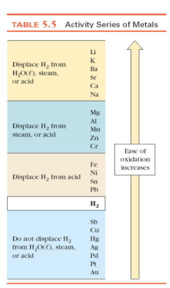
Redox Reactions and Activity Series



- metals at top most easily oxidized
- any metal on list can be oxidized by any metal ion below it

Example 4

Which of the following metals will be oxidized by $Pb(NO_3)_2$: Zn, Cu, Fe?



Concentrations of Solutions

concentration - amount of solute dissolved in a given quantity of solvent or solution

$$\text{molarity (M)} = \frac{\text{moles solute}}{\text{volume of sol'n in liters}}$$

1.00 M --> 1.00 mol solute / 1 L sol'n

Example 5

Calculate the molarity of a solution prepared by dissolving 10.0 g of $AgNO_3$ in enough water to make 250.0 mL of solution.

Dilution

Sometimes you want to take a concentrated solution and make a more dilute solution of it. When you do this, the moles of solute remain constant throughout the process.

$$M_i V_i = M_f V_f$$

Example 6

A flask contains 625 mL of 3.05 M calcium nitrate solution. What volume of 15.8 M $Ca(NO_3)_2$ contains the same number of moles of $Ca(NO_3)_2$ as this solution?

Example 7

What is the molar concentration of nitrate ions in 3.05 M calcium nitrate?

Example 8

How many milliliters of 4.5 M HCl are required to prepare 200 mL of 0.75 M HCl?

Example 9

(a) Describe how to prepare 0.500 L of 0.0250 M aqueous solution of potassium dichromate

Example 9 (cont'd)

(b) Describe how to dilute the solution from part (a) to obtain a solution with a final concentration of 0.0140 M.

Example 10

When the orange salt potassium dichromate is added to a solution of concentrated hydrochloric acid, it reacts according to the following net ionic equation:

$K_2Cr_2O_7 + 14\ HCl \rightarrow 2\ K^+ + 2\ Cr^{3+} + 8\ Cl^- + 7\ H_2O + 3\ Cl_2$

Suppose that 6.20 g of $K_2Cr_2O_7$ reacts with 100.0 ml of concentrated HCl (13.0 M). Calculate the final concentration of Cr^{3+} ion that results and the number of moles of chlorine gas produced.

Example 10 (cont'd)

$K_2Cr_2O_7 + 14\ HCl \rightarrow 2\ K^+ + 2\ Cr^{3+} + 8\ Cl^- + 7\ H_2O + 3\ Cl_2$

Titrations

- chemical reactions of solution of known concentration with solution of unknown concentration

$$HCl + NaOH \rightarrow NaCl + H_2O$$

- point at which stoichiometrically equivalent amounts of HCl and NaOH are brought together is called the equivalence point (endpoint)
- typically use an indicator that changes color at the equivalence point

Example 11

What is the molarity of a solution of sodium hydroxide if it requires 23.97 mL of that solution to reach the phenolphthalein endpoint when adding it to a solution containing 0.5333 g of $KHC_8H_4O_4$?

$$KHC_8H_4O_4 + NaOH \rightarrow NaKC_8H_4O_4 + H_2O$$

Example 12

The indicator methyl red turns from yellow to red when the solution in which it is dissolved changes from basic to acidic. A 25.00 mL volume of a sodium hydroxide solution is titrated with 0.8367 M HCl. It takes 22.48 mL of this acid to reach a methyl red endpoint. Find the molarity of the sodium hydroxide solution.

$$HCl + NaOH \rightarrow NaCl + H_2O$$