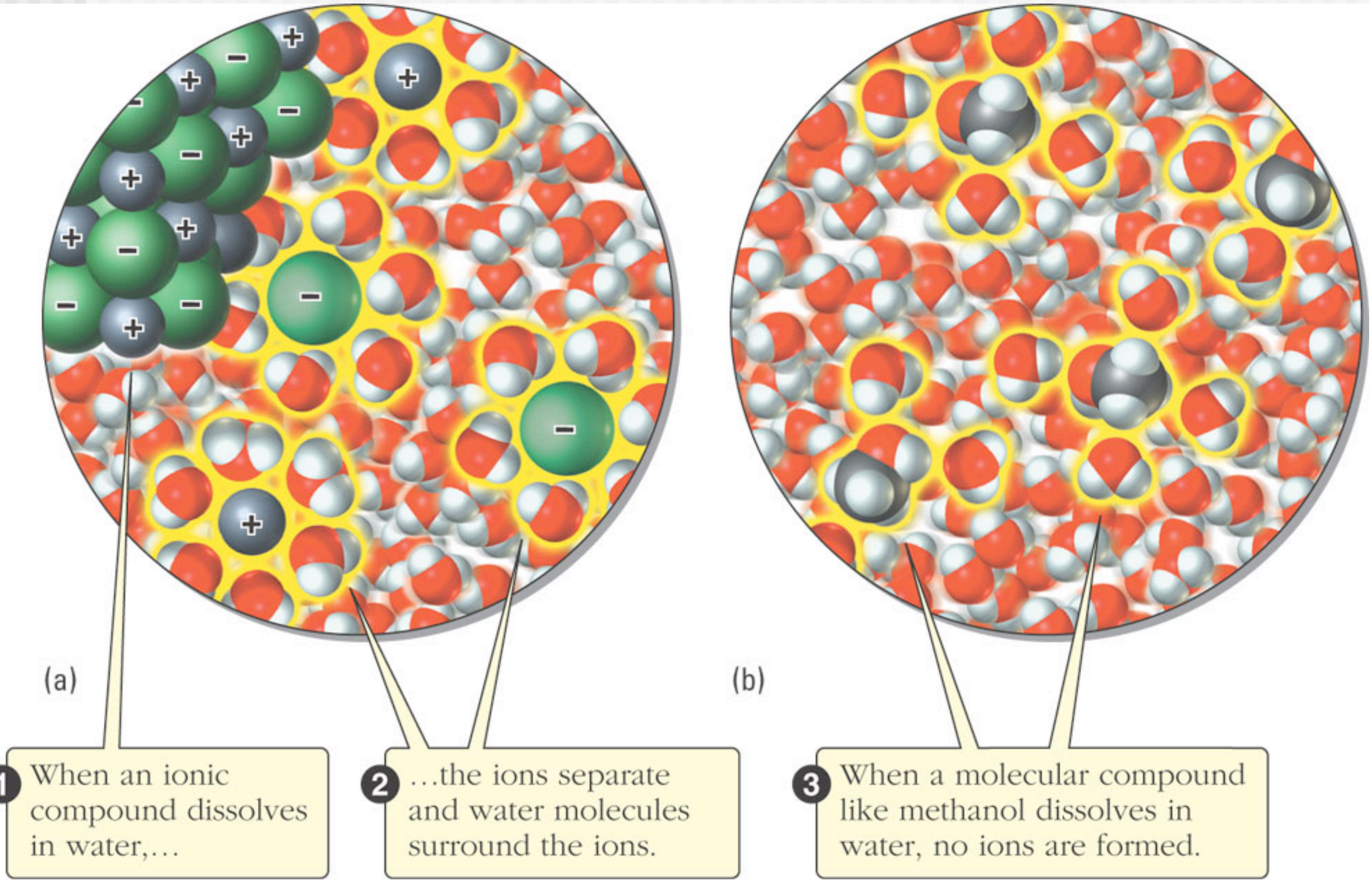
Aqueous Reactions & Sol'n Stoichiometry

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 $NaCl_{(s)} \rightarrow Na^{+}_{(aq)} + Cl^{-}_{(aq)}$
  - weak - dissociate only partly $CH_3COOH_{(s)} \leftrightarrow H^{+}_{(aq)} + CH_3COO^{-}_{(aq)}$


+
−
(a)
(b)
1 When an ionic compound dissolves in water,…
2 …the ions separate and water molecules surround the ions.
3 When a molecular compound like methanol dissolves in water, no ions are formed.

Precipitation Reactions

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

$$Pb(NO_3)_{2\,(aq)} + 2\,KI_{(aq)} \rightarrow PbI_{2\,(s)} + 2\,KNO_{3\,(aq)}$$

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

$$AX + BY \rightarrow AY + BX$$

$$AgNO_3\ (aq) + KCl\ (aq) \rightarrow AgCl\ (s) + KNO_3\ (aq)$$

Example 1

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

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

yes, AlCl (s)

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

yes, PbI_2 (s)

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

yes, $BaSO_4$ (s)

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

yes, $Ba(OH)_2$ (s)

Ionic Equations

molecular equation:

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

complete ionic equation:

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

spectator ions

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?

$$Na_2CO_3\ (aq) + CaCl_2\ (aq) \rightarrow CaCO_3\ (s) + 2\ NaCl\ (aq)$$

$$2\ Na^+ + CO_3^{2-} + Ca^{2+} + 2\ Cl^- \rightarrow CaCO_3 + 2\ Na^+ + 2\ Cl^-$$

$$Ca^{2+}\ (aq) + CO_3^{2-}\ (aq) \rightarrow CaCO_3\ (s)$$

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 → salt + water)
  $HCl (aq) + NaOH (aq) \rightarrow NaCl (aq) + H_2O (\ell)$
  $H^+ (aq) + OH^- (aq) \rightarrow H_2O (\ell)$ net ionic equation
- acid + carbonate (or HCO_3) → salt + water + CO_2 gas
  $2 HCl (aq) + Na_2CO_3 (aq) \rightarrow 2 NaCl (aq) + H_2O (\ell) + CO_2 (g)$
- acid + metal oxide → salt + water
  $2 HNO_3 (aq) + MgO (s) \rightarrow Mg(NO_3)_2 (aq) + H_2O (\ell)$
- acid + metal → salt + H_2 gas
  $2 HCl (aq) + Mg (s) \rightarrow MgCl_2 (aq) + H_2 (g)$

Reactions of Bases

- base + ammonium salt → salt + water + NH_3 gas

  $NaOH\ (aq) + NH_4Cl\ (aq) \rightarrow NaCl\ (aq) + H_2O\ (\ell) + NH_3\ (g)$

- base + non-metal oxide → salt + water

  $2\ NaOH(aq) + N_2O_5\ (g) \rightarrow 2\ NaNO_3\ (aq) + H_2O\ (\ell)$

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)

$$4\ Fe_{(s)} + 3\ O_{2\ (aq)} \rightarrow 2\ Fe_2O_{3\ (s)}$$

Oxidation-Reduction Reactions

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

- loses e-
- oxidized
- reducing agent

- gains e-
- reduced
- oxidizing agent

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 III 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	Na = +1, Cl = -1
(b)	ClO^-	Cl = +1, O = -2
(c)	$Fe_2(SO_4)_3$	Fe = +3, S = +6, O = -2
(d)	SO_2	S = +4, O = -2
(e)	I_2	I = 0
(f)	$KMnO_4$	K = +1, Mn = +7, O = -2
(g)	CaH_2	Ca = +2, H = -1

Redox Reactions

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

+1 0

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

0 +2

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 <u>will not</u> be oxidized by acids or metal salt. How do we determine which will??

Redox Reactions and Activity Series

TABLE 5.5 Activity Series of Metals

Displace H_2 from $H_2O(\ell)$, steam, or acid	Li K Ba Sr Ca Na	↑ Ease of oxidation increases
Displace H_2 from steam, or acid	Mg Al Mn Zn Cr	
Displace H_2 from acid	Fe Ni Sn Pb	
	H_2	
Do not displace H_2 from $H_2O(\ell)$, steam, or acid	Sb Cu Hg Ag Pd Pt Au	

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

$$Cu\ (s) + 2\ Ag^+\ (aq) \rightarrow Cu^{2+}\ (aq) + 2\ Ag\ (s)$$

BUT

$$2\ Ag\ (s) + Cu^{2+}\ (aq) \not\rightarrow 2\ Ag^+\ (aq) + Cu\ (s)$$

Example 4

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

Zn & Fe can be oxidized by Pb^{2+} since they are both above Pb in the activity series table.

$$Zn_{(s)} + Pb^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Pb_{(s)}$$

$$Fe_{(s)} + Pb^{2+}_{(aq)} \rightarrow Fe^{2+}_{(aq)} + Pb_{(s)}$$

TABLE 5.5 Activity Series of Metals

Displace H_2 from $H_2O(\ell)$, steam, or acid	Li K Ba Sr Ca Na
Displace H_2 from steam, or acid	Mg Al Mn Zn Cr
Displace H_2 from acid	Fe Ni Sn Pb
	H_2
Do not displace H_2 from $H_2O(\ell)$, steam, or acid	Sb Cu Hg Ag Pd Pt Au

↑ Ease of oxidation increases

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

dissolve 0.25 mol NaCl in 0.500 L sol’n:

Molarity = 0.25 mol / 0.500 L = 0.50 M

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.

$$\text{mol of } AgNO_3 = (10.0\text{ g})\left(\frac{1\text{ mol } AgNO_3}{169.8731\text{ g}}\right) = 0.05887\text{ mol}$$

$$\text{molarity} = \left(\frac{0.05887\text{ mol}}{0.2500\text{ L}}\right) = \boxed{0.235\text{ M}}$$

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?

$$M_i V_i = M_f V_f$$

$$V_f = \left(\frac{(3.05\ \text{M})(0.625\ \text{L})}{15.8\ \text{M}}\right) \boxed{= 0.121\ \text{L}}$$

Example 7

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

3.05 M $Ca(NO_3)_2$

2 NO_3^- for every 1 $Ca(NO_3)_2$

$$\text{molarity} = \left(3.05\ \text{M}\ Ca(NO_3)_2\right)\left(\frac{2\ \text{mol}\ NO_3^-}{1\ \text{mol}\ Ca(NO_3)_2}\right) = 6.10\ \text{M}\ NO_3^-$$

Example 8

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

$M_i V_i = M_f V_f$

$(4.5\text{ M})\ V_i = (0.75\text{ M})(200\text{ mL})$

$$V_i = \frac{(0.75\text{ M})(200\text{ mL})}{4.5\text{ M}} = \boxed{33\text{ mL}}$$

Example 9

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

$K_2Cr_2O_7$

$$\text{mol} = (0.500\ \text{L})\left(\frac{0.0250\ \text{mol}}{\text{L}}\right) = 0.0125\ \text{mol}$$

$$\text{mass} = (0.0125\ \text{mol})\left(\frac{294.1846\ \text{g}}{1\ \text{mol}}\right) = 3.68\ \text{g}$$

Weigh out 3.68 g of $K_2Cr_2O_7$ and dissolve in small amount of water. Dilute to 500 mL.

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.

$M_iV_i = M_fV_f$

$$V_f = \frac{(0.0250\ \text{M})(0.500\ \text{L})}{0.0140\ \text{M}} = 0.893\ \text{L}$$

Dilute solution in (a) to 893 mL.

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.

$$\text{mol } K_2Cr_2O_7 = (6.20\text{ g})\left(\frac{1\text{ mol}}{294.1846\text{ g}}\right) = 0.021075\text{ mol } K_2Cr_2O_7$$

$$\text{mol HCl} = (0.1000\text{ L})\left(\frac{13.0\text{ mol}}{1\text{ L}}\right) = 1.30\text{ mol HCl}$$

$$\text{mol } Cl_2 \text{ from } K_2Cr_2O_7 = (0.021075\text{ mol } K_2Cr_2O_7)\left(\frac{3\text{ mol } Cl_2}{1\text{ mol } K_2Cr_2O_7}\right) = \boxed{0.0632\text{ mol } Cl_2}$$

$$\text{mol } Cl_2 \text{ from HCl} = (1.30\text{ mol HCl})\left(\frac{3\text{ mol } Cl_2}{14\text{ mol HCl}}\right) = 0.279\text{ mol } Cl_2$$

Example 10 (cont'd)

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

$$\text{mol } K_2Cr_2O_7 = (6.20\text{ g})\left(\frac{1\text{ mol}}{294.1846\text{ g}}\right) = 0.021075\text{ mol } K_2Cr_2O_7$$

$$\text{mol } Cr^{3+} \text{ from } K_2Cr_2O_7 = (0.021075\text{ mol } K_2Cr_2O_7)\left(\frac{2\text{ mol } Cr^{3+}}{1\text{ mol } K_2Cr_2O_7}\right) = 0.0422\text{ mol } Cr^{3+}$$

$$\text{molarity of } Cr^{3+} = \frac{0.0422\text{ mol } Cr^{3+}}{0.100\text{ L}} = 0.422\text{ M}$$

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 $KHC_8H_4O_4$?

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

$$\text{mol } KHC_8H_4O_4 = (0.5333 \text{ g})\left(\frac{1 \text{ mol}}{204.2234 \text{ g}}\right) = 0.0026114 \text{ mol } KHC_8H_4O_4$$

$$\text{mol NaOH} = (0.0026114 \text{ mol } KHC_8H_4O_4)\left(\frac{1 \text{ mol NaOH}}{1 \text{ mol } KHC_8H_4O_4}\right) = 0.0026114 \text{ mol NaOH}$$

$$\text{molarity of NaOH} = \frac{0.0026114 \text{ mol}}{0.02397 \text{ L}} = 0.1089 \text{ M}$$

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.

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

$$\text{mol HCl} = (0.02248\ \text{L})\left(\frac{0.8367\ \text{mol}}{1\ \text{L}}\right) = 0.018809\ \text{mol HCl}$$

$$\text{mol NaOH @ endpoint} = (0.018809\ \text{mol HCl})\left(\frac{1\ \text{mol NaOH}}{1\ \text{mol HCl}}\right) = 0.018809\ \text{mol NaOH}$$

$$\text{molarity of NaOH} = \frac{0.018809\ \text{mol}}{0.02500\ \text{L}} = 0.7524\ \text{M}$$