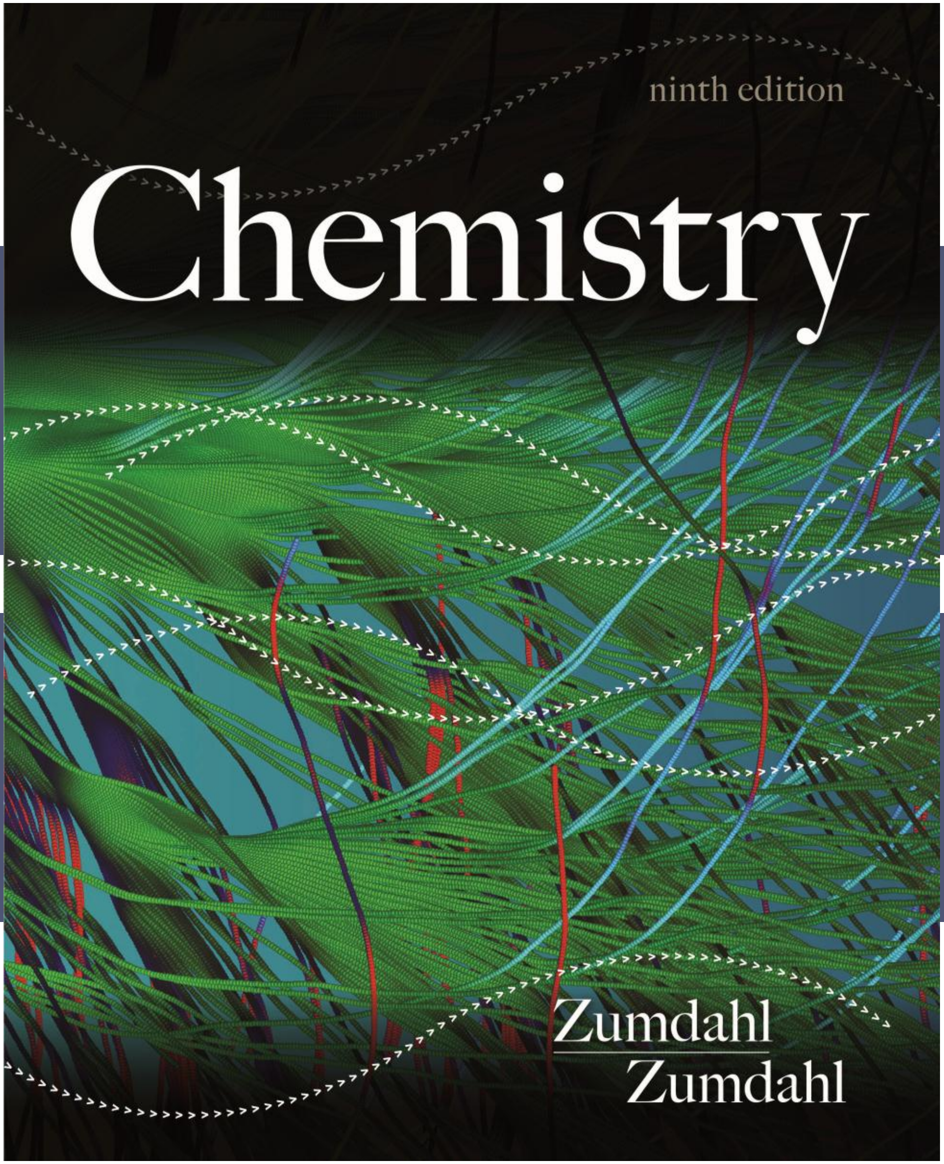

Chapter 4

Types of Chemical Reactions and Solution Stoichiometry

Chapter 4
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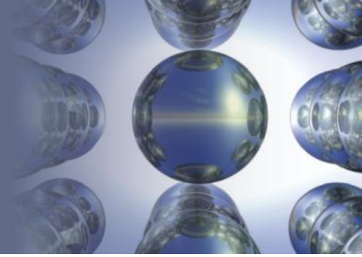

Chapter 4

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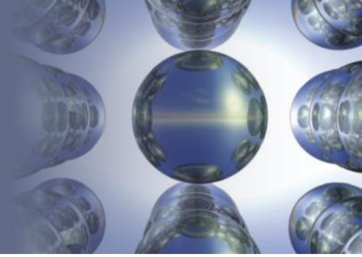


Water

- Possesses the ability to dissolve many substances
- Liquid water consists of a collection of H_2O molecules
    - Each molecule is V-shaped with an H—O—H angle of approximately 105°
    - O—H bonds are covalent in nature
        - Formed by electron sharing between the atoms
        - Oxygen has greater attraction for electrons, and this helps it gain a slight excess of negative charge

Polarity

- Water is a polar molecule
    - **Polar molecule**: Contains an unequal distribution of charge
    - Polarity facilitates water’s ability to dissolve compounds

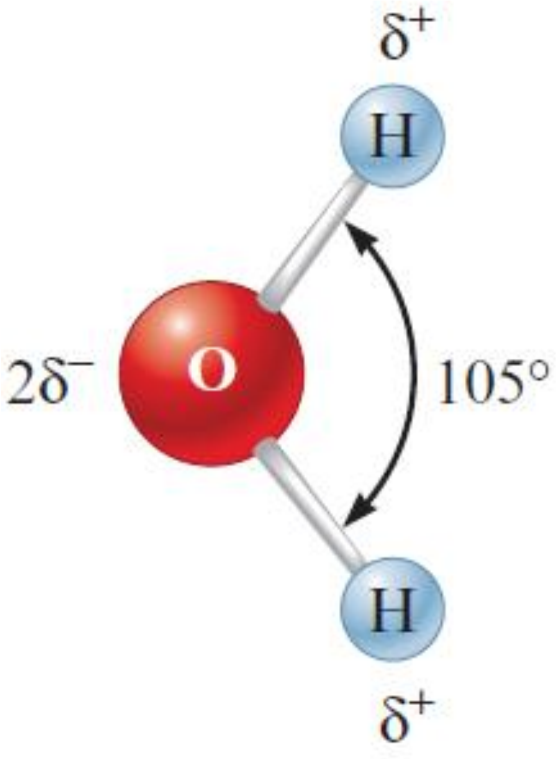
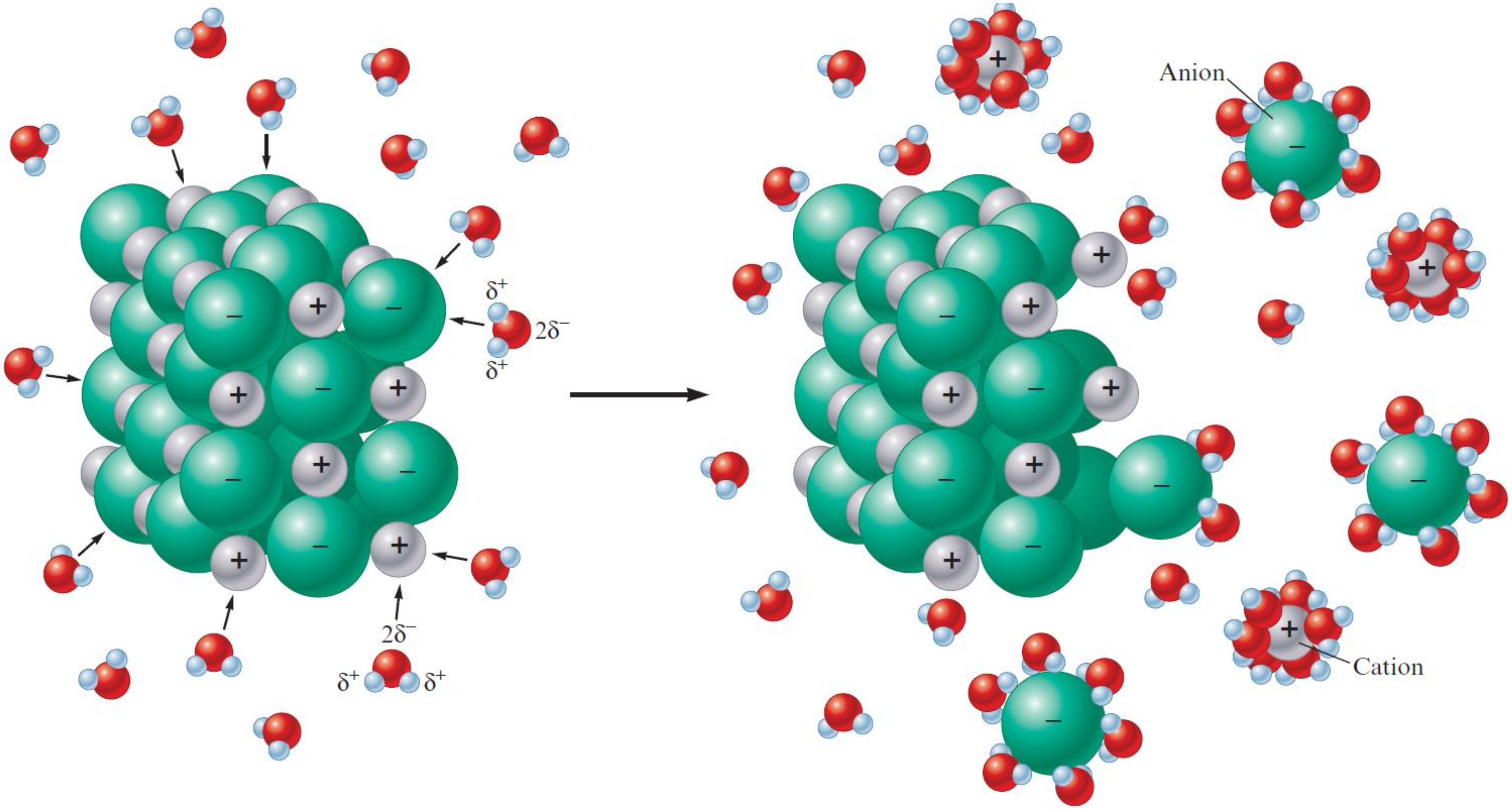


Figure 4.2 - Schematic of an Ionic Solid Dissolving in Water



Hydration

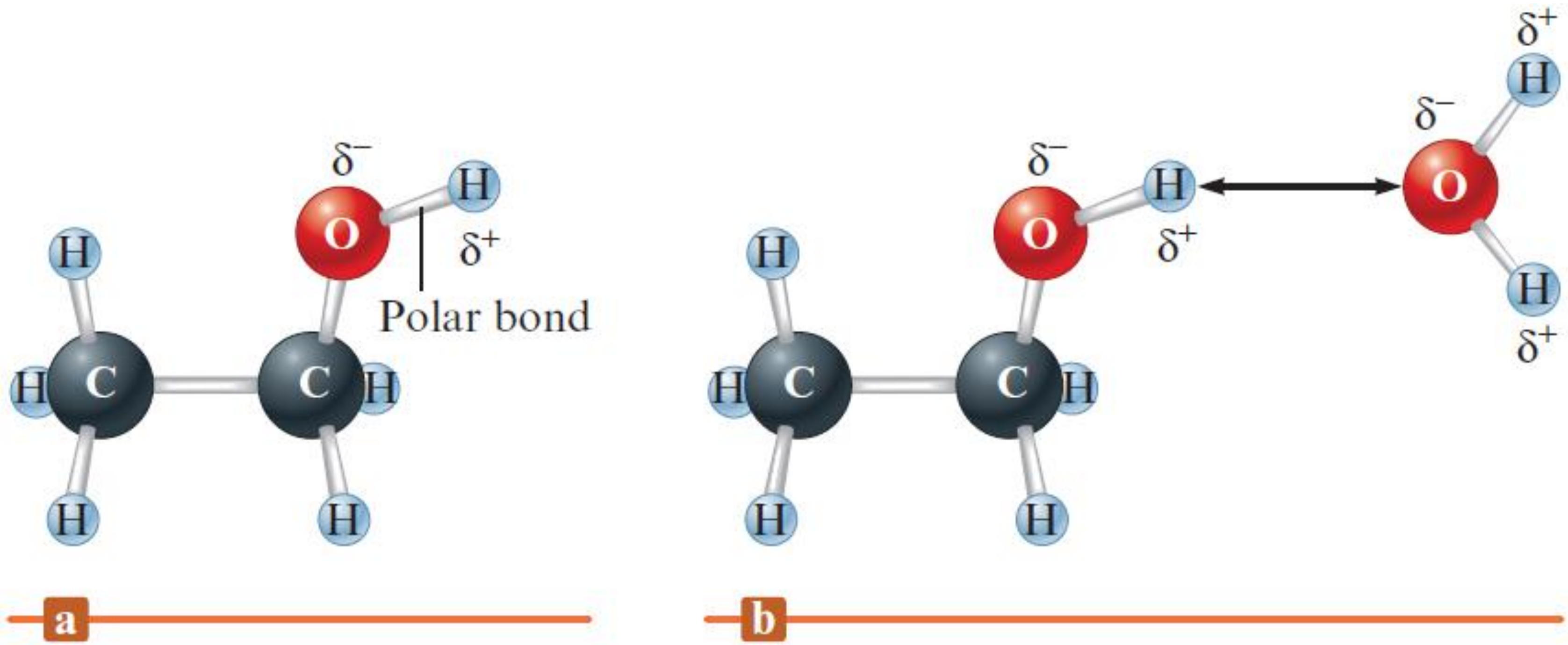
- Process by which positive ends of H_2O molecules are attached to negatively charged ions and vice versa
- Causes salt to split when dissolved in water
  - When ionic salts dissolve in water, they break into individual cations and anions

$$NH_4NO_3(s) \xrightarrow{H_2O(l)} NH_4^+(aq) + NO_3^-(aq)$$

Concept of Solubility

- Solubility of ionic substances in water varies depending on:
  - The attraction among ions
  - The attraction of ions for water molecules
- Polar and ionic substances are expected to be more soluble in water than nonpolar substances
- Nonionic substances such as ethanol are soluble

Figure 4.3 - Solubility of Ethanol in Water



The ethanol molecule contains a polar O—H bond similar to those in the water molecule

The polar water molecule interacts strongly with the polar O—H bond in ethanol

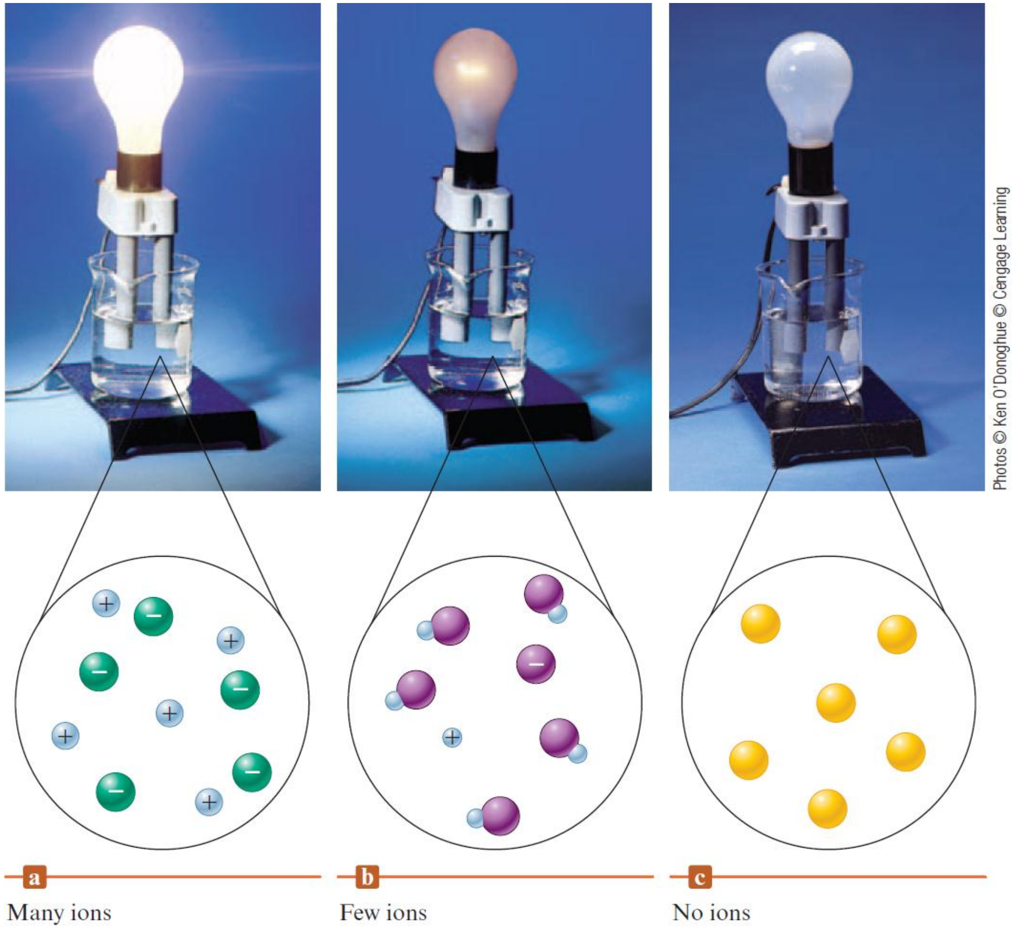
Critical Thinking

- What if no ionic solids were soluble in water?
  - How would this affect the way reactions occur in aqueous solutions?

Electrical Conductivity

- Ability of a solution to conduct electric current
- **Solute**: Substance being dissolved
- **Solvent**: The dissolving medium
  - Example - Water
- Electrolyte
  - Substance that dissolves in water to produce a solution that can conduct electricity

Figure 4.4 - Electrical Conductivity of Aqueous Solutions



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Electrolytes

- **Strong electrolytes**: Highly efficient conductors of current in aqueous solutions
  - Example - NaCl
- **Weak electrolytes**: Conduct small current in aqueous solutions
  - Example - Acetic acid
- **Nonelectrolytes**: Do not conduct current in aqueous solutions
  - Example - Sugar

Svante Arrhenius

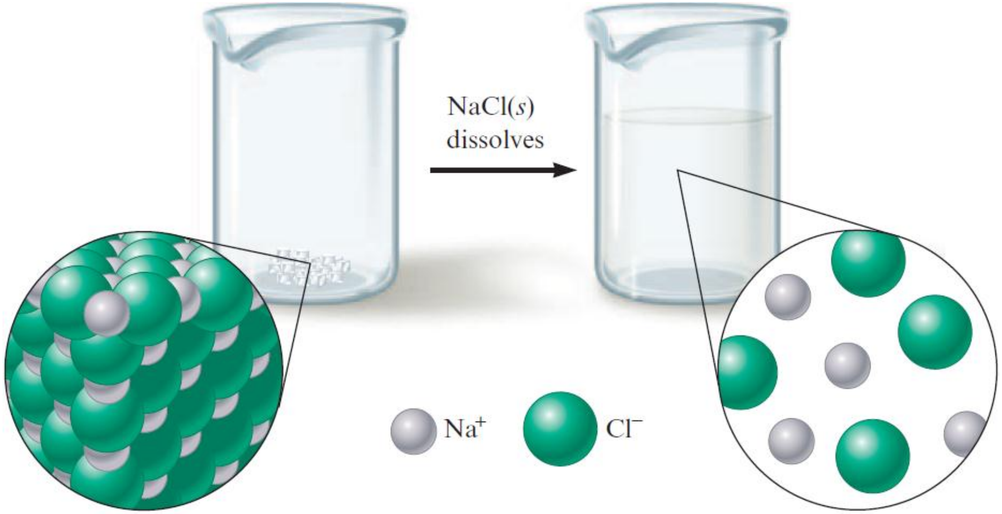
- Identified the basis for the conductivity properties of solutions
- Postulated that the extent to which a solution can conduct an electric current directly depends on the number of ions present
  - Idea was accepted when atoms were found to contain charged particles

Strong Electrolytes

- Completely ionized in water
- Classes
  - Soluble salts
  - Strong acids
  - Strong bases

Soluble Salts

- Salts such as NaCl contain an array of cations and anions
  - Disintegrate and undergo hydration when the salt dissolves



Nature of Acids

- When dissolved in water, acids act as strong electrolytes

$$HCl \xrightarrow{H_2O} H^+(aq) + Cl^-(aq)$$

$$HNO_3 \xrightarrow{H_2O} H^+(aq) + NO_3^-(aq)$$

$$H_2SO_4 \xrightarrow{H_2O} H^+(aq) + HSO_4^-(aq)$$

  - **Acid**: Substance that produces H^+ ions when it is dissolved in water

Nature of Acids (Continued)

- Polarity of water helps produce H^+ ions
  - Ionization of an acid can be represented as follows:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightarrow \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq)$$

- **Strong acids**: Every molecule is completely ionized when dissolved in water
  - Examples - HCl, HNO_3, and H_2SO_4

Strong Bases

- Soluble ionic compounds that contain the OH^- (hydroxide) ion
- When dissolved in water, cations and OH^- ions separate and move independently
- Example
    - Dissolving potassium hydroxide in water

$$\mathrm{KOH}(s) \rightarrow \mathrm{K}^+(aq) + \mathrm{OH}^-(aq)$$

Weak Electrolytes

- Exhibit a small degree of ionization in water
- Include weak acids and weak bases
- Formulas of acids
  - Atom that produces the H^+ ion (acidic hydrogen atom) in the solution is written first
  - Nonacidic hydrogen atoms are written later (if present)

Weak Electrolytes (Continued 1)

- **Weak acids**: Dissociate only to a slight extent in aqueous solutions
  - Example - Dissociation reaction of acetic acid in water

$$HC_2H_3O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_2H_3O_2^-(aq)$$

    - Double arrow indicates that the reaction can occur in either direction

Weak Electrolytes (Continued 2)

- **Weak bases**: Resulting solution will be a weak electrolyte
  - Example - Dissolution of ammonia in water

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

    - The solution is basic due to the production of OH^- ions

Nonelectrolytes

- Substances that dissolve in water but do not produce any ions
    - Leads to absence of electrical conductivity
- Examples
    - Ethanol (C_2H_5OH)
    - Table sugar (sucrose, $C_{12}H_{22}O_{11}$)

Chemical Reactions of Solutions

- Occur when two solutions are mixed
- To perform stoichiometric calculations, one must know:
  - The nature of the reaction
    - Depends on the exact forms taken by the chemicals when dissolved
  - The amounts of chemicals present in the solutions
    - Expressed as concentrations

Molarity (*M*)

- Commonly used expression for concentration
- Expressed as moles of solute per volume of solution in liters

$$M = \text{molarity} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

Exercise

- Calculate the molarity of the solution in which a 184.6 mg sample of $K_2Cr_2O_7$ is dissolved in enough water to make 500.0 mL of solution

$$1.255 \times 10^{-3}\ M$$

Interactive Example 4.2 - Calculation of Molarity II

- Calculate the molarity of a solution prepared by dissolving 1.56 g of gaseous HCl in enough water to make 26.8 mL of solution

Interactive Example 4.2 - Solution

- Where are we going?
  - To find the molarity of HCl solution
- What do we know?
  - 1.56 g HCl
  - 26.8 mL solution
- What information do we need to find molarity?
  - Moles solute

$$\text{molarity} = \frac{\text{mol solute}}{\text{L solution}}$$

Interactive Example 4.2 - Solution (Continued 1)

- How do we get there?
  - What are the moles of HCl (36.46 g/mol)?

$$1.56\ \cancel{\text{g HCl}} \times \frac{1\ \text{mol HCl}}{36.46\ \cancel{\text{g HCl}}} = 4.28 \times 10^{-2}\ \text{mol HCl}$$

  - What is the volume of solution (in liters)?

$$26.8\ \cancel{\text{mL}} \times \frac{1\ \text{L}}{1000\ \cancel{\text{mL}}} = 2.68 \times 10^{-2}\ \text{L}$$

Interactive Example 4.2 - Solution (Continued 2)

- What is the molarity of the solution?

$$\text{Molarity} = \frac{4.28 \times 10^{-2}\ \text{mol HCl}}{2.68 \times 10^{-2}\ \text{L solution}} = 1.60\ M\ \text{HCl}$$

- Reality check
  - The units are correct for molarity

Determining Moles of Solute in a Sample

- Use the definition of molarity

$$\text{Liters of solution} \times \text{molarity} = \cancel{\text{liters of solution}} \times \frac{\text{moles of solute}}{\cancel{\text{liters of solution}}}$$

$$\text{Moles of solute} = \text{Liters of solution} \times \text{molarity}$$

Interactive Example 4.4 - Concentration of Ions II

- Calculate the number of moles of Cl^- ions in 1.75 L of 1.0×10^{-3} *M* $ZnCl_2$

Interactive Example 4.4 - Solution

- Where are we going?
  - To find the moles of Cl^- ion in the solution
- What do we know?
  - 1.0×10^{-3} *M* $ZnCl_2$
  - 1.75 L
- What information is needed to find moles of Cl^-?
  - Balanced equation for dissolving $ZnCl_2$

Interactive Example 4.4 - Solution (Continued 1)

- How do we get there?
  - What is the balanced equation for dissolving the ions?

$$\mathrm{ZnCl_2}(s) \xrightarrow{\mathrm{H_2O}} \mathrm{Zn^{2+}}(aq) + 2\mathrm{Cl^-}(aq)$$

  - What is the molarity of Cl^- ion in the solution?

$$2 \times \left(1.0 \times 10^{-3}\ M\right) = 2.0 \times 10^{-3}\ M\ \mathrm{Cl^-}$$

Interactive Example 4.4 - Solution (Continued 2)

- How many moles of Cl^-?

$$1.75\ \text{L solution} \times 2.0 \times 10^{-3}\ M\ \text{Cl}^-$$

$$= 1.75\ \cancel{\text{L solution}} \times \frac{2.0 \times 10^{-3}\ \text{mol Cl}^-}{\cancel{\text{L solution}}}$$

$$= 3.5 \times 10^{-3}\ \text{mol Cl}^-$$

Interactive Example 4.5 - Concentration and Volume

- Typical blood serum is about 0.14 *M* NaCl
  - What volume of blood contains 1.0 mg of NaCl?

Interactive Example 4.5 - Solution

- Where are we going?
    - To find the volume of blood containing 1.0 mg of NaCl
- What do we know?
    - 0.14 *M* NaCl
    - 1.0 mg NaCl
- What information do we need to find volume of blood containing 1.0 mg of NaCl?
    - Moles of NaCl (in 1.0 mg)

Interactive Example 4.5 - Solution (Continued 1)

- How do we get there?
    - What are the moles of NaCl (58.44 g/mol)?

$$1.0\ \cancel{\text{mg NaCl}} \times \frac{1\ \cancel{\text{g NaCl}}}{1000\ \cancel{\text{mg NaCl}}} \times \frac{1\ \text{mol NaCl}}{58.44\ \cancel{\text{g NaCl}}}$$

$$= 1.7 \times 10^{-5}\ \text{mol NaCl}$$

Interactive Example 4.5 - Solution (Continued 2)

- What volume of 0.14 M NaCl contains 1.0 mg (1.7×10^{-5} mole) of NaCl?
    - There is some volume, call it *V*, that when multiplied by the molarity of this solution will yield 1.7×10^{-5} mole of NaCl

$$V \times \frac{0.14 \text{ mol NaCl}}{\text{L solution}} = 1.7 \times 10^{-5} \text{ mol NaCl}$$

Interactive Example 4.5 - Solution (Continued 3)

- We want to solve for the volume

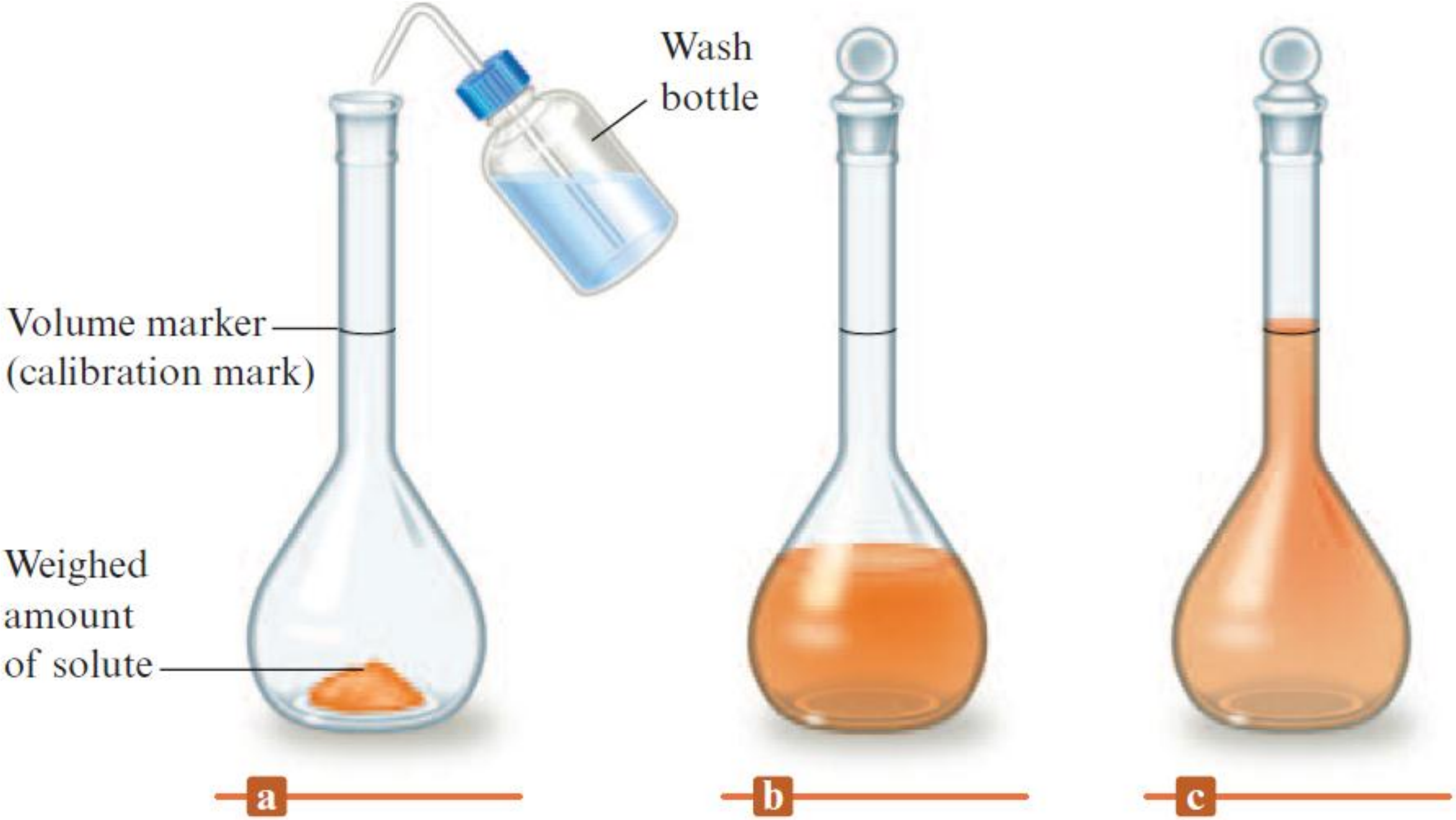
$$V = \frac{1.7 \times 10^{-5}\ \cancel{\text{mol NaCl}}}{\dfrac{0.14\ \cancel{\text{mol NaCl}}}{\text{L solution}}} = 1.2 \times 10^{-4}\ \text{L solution}$$

- Thus, 0.12 mL of blood contains 1.7×10^{-5} mole of NaCl or 1.0 mg of NaCl

Standard Solution

- Solution whose concentration is accurately known
- Process of preparation
  - Place a weighed amount of the solute into a volumetric flask, and add a small amount of water
  - Dissolve the solid by swirling the flask
  - Add more water until the level of the solution reaches the mark etched on the flask
    - Mix the solution by inverting the flask several times

Figure 4.10 - Steps Involved in the Preparation of a Standard Aqueous Solution



Interactive Example 4.6 - Solutions of Known Concentration

- To analyze the alcohol content of a certain wine, a chemist needs 1.00 L of an aqueous 0.200-*M* $K_2Cr_2O_7$ (potassium dichromate) solution
    - How much solid $K_2Cr_2O_7$ must be weighed out to make this solution?

Interactive Example 4.6 - Solution

- Where are we going?
  - To find the mass of $K_2Cr_2O_7$ required for the solution
- What do we know?
  - 1.00 L of 0.200 *M* $K_2Cr_2O_7$ is required
- What information do we need to find the mass of $K_2Cr_2O_7$?
  - Moles of $K_2Cr_2O_7$ in the required solution

Interactive Example 4.6 - Solution (Continued 1)

- How do we get there?
  - What are the moles of $K_2Cr_2O_7$ required?

$$M \times V = \text{mol}$$

$$1.00\ \cancel{\text{L solution}} \times \frac{0.200\ \text{mol}\ K_2Cr_2O_7}{\cancel{\text{L solution}}} = 0.200\ \text{mol}\ K_2Cr_2O_7$$

Interactive Example 4.6 - Solution (Continued 2)

- What mass of $K_2Cr_2O_7$ is required for the solution?

$$0.200 \ \cancel{\text{mol K}_2\text{Cr}_2\text{O}_7} \times \frac{294.20 \text{ g K}_2\text{Cr}_2\text{O}_7}{\cancel{\text{mol K}_2\text{Cr}_2\text{O}_7}} = 58.8 \text{ g K}_2\text{Cr}_2\text{O}_7$$

- To make 1.00 L of 0.200 *M* $K_2Cr_2O_7$, the chemist must:
    - Weigh out 58.8 g $K_2Cr_2O_7$
    - Transfer the weighed solute to a 1.00-L volumetric flask
    - Add distilled water to the mark on the flask

Dilution

- Process of adding water to a concentrated (stock) solution to achieve the molarity desired for a particular solution
- Since only water is added to accomplish dilution:

Moles of solute after dilution = moles of solute before dilution

Glassware Used in Dilution

- Volumetric flask
- Pipet
  - Device used for the accurate measurement and transfer of a given volume of solution
  - Types - Volumetric pipet and measuring pipet

Dilution - Alternate Method

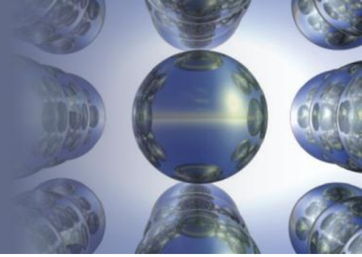
- Central idea behind performing calculations associated with dilution is to ascertain that the moles of solute are not changed by the dilution

$$M_1V_1 = M_2V_2$$

  - M_1 and V_1 - Molarity and volume of original solution
  - M_2 and V_2 - Molarity and volume of the diluted solution

Interactive Example 4.7 - Concentration and Volume

- What volume of 16 *M* sulfuric acid must be used to prepare 1.5 L of a 0.10-*M* H_2SO_4 solution?



Interactive Example 4.7 - Solution

- Where are we going?
  - To find the volume of H_2SO_4 required to prepare the solution
- What do we know?
  - 1.5 L of 0.10 M H_2SO_4 is required
  - We have 16 M H_2SO_4

Interactive Example 4.7 - Solution (Continued 1)

- What information do we need to find the volume of H_2SO_4?
  - Moles of H_2SO_4 in the required solution
- How do we get there?
  - What are the moles of H_2SO_4 required?

$$M \times V = \text{mol}$$

$$1.5\ \cancel{\text{L solution}} \times \frac{0.10\ \text{mol H}_2\text{SO}_4}{\cancel{\text{L solution}}} = 0.15\ \text{mol H}_2\text{SO}_4$$

Interactive Example 4.7 - Solution (Continued 2)

- What volume of 16 *M* H_2SO_4 contains 0.15 mole of H_2SO_4?

$$V \times \frac{16\text{ mol }H_2SO_4}{\text{L solution}} = 0.15\text{ mol }H_2SO_4$$

  - Solving for V gives:

$$V = \frac{0.15\ \cancel{\text{mol }H_2SO_4}}{\frac{16\ \cancel{\text{mol }H_2SO_4}}{\text{L solution}}} = 9.4 \times 10^{-3}\text{ L or }9.4\text{ mL solution}$$

Interactive Example 4.7 - Solution (Continued 3)

- Conclusion
  - To make 1.5 L of 0.10 *M* H_2SO_4 using 16 *M* H_2SO_4, we must take 9.4 mL of the concentrated acid and dilute it with water to 1.5 L
  - The correct way to do this is to add the 9.4 mL of acid to about 1 L of distilled water and then dilute to 1.5 L by adding more water

Exercise

- Describe how you would prepare 2.00 L of each of the following solutions:
  a. 0.250 *M* NaOH from 1.00 *M* NaOH stock solution

     Add 500 mL of the 1.00 *M* NaOH stock solution to a 2-L volumetric flask; fill to the mark with water

  b. 0.100 *M* K_2CrO_4 from 1.75 *M* K_2CrO_4 stock solution

     Add 114 mL of the 1.75 *M* K_2CrO_4 stock solution to a 2-L volumetric flask; fill to the mark with water

Types of Solution Reactions

Precipitation reactions

Acid–base reactions

Oxidation–reduction reactions

Precipitation Reaction

- When two solutions are mixed, a precipitate separates from the solution
  - **Precipitate**: Insoluble solid that is formed in a precipitation reaction
- Example
  - When yellow aqueous solution potassium chromate is added to a colorless aqueous solution of barium nitrate, yellow barium chromate precipitates

Figure 4.15 - The Reaction of Aqueous Potassium Chromate and Barium Nitrate

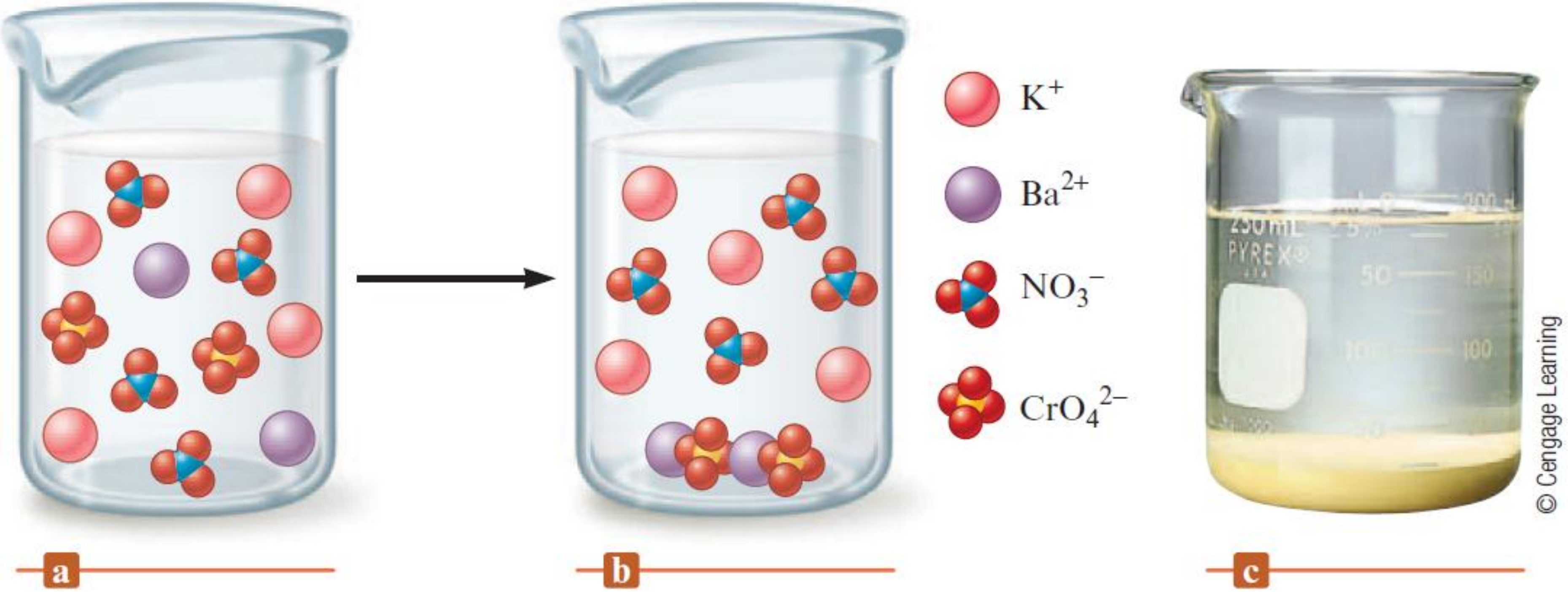


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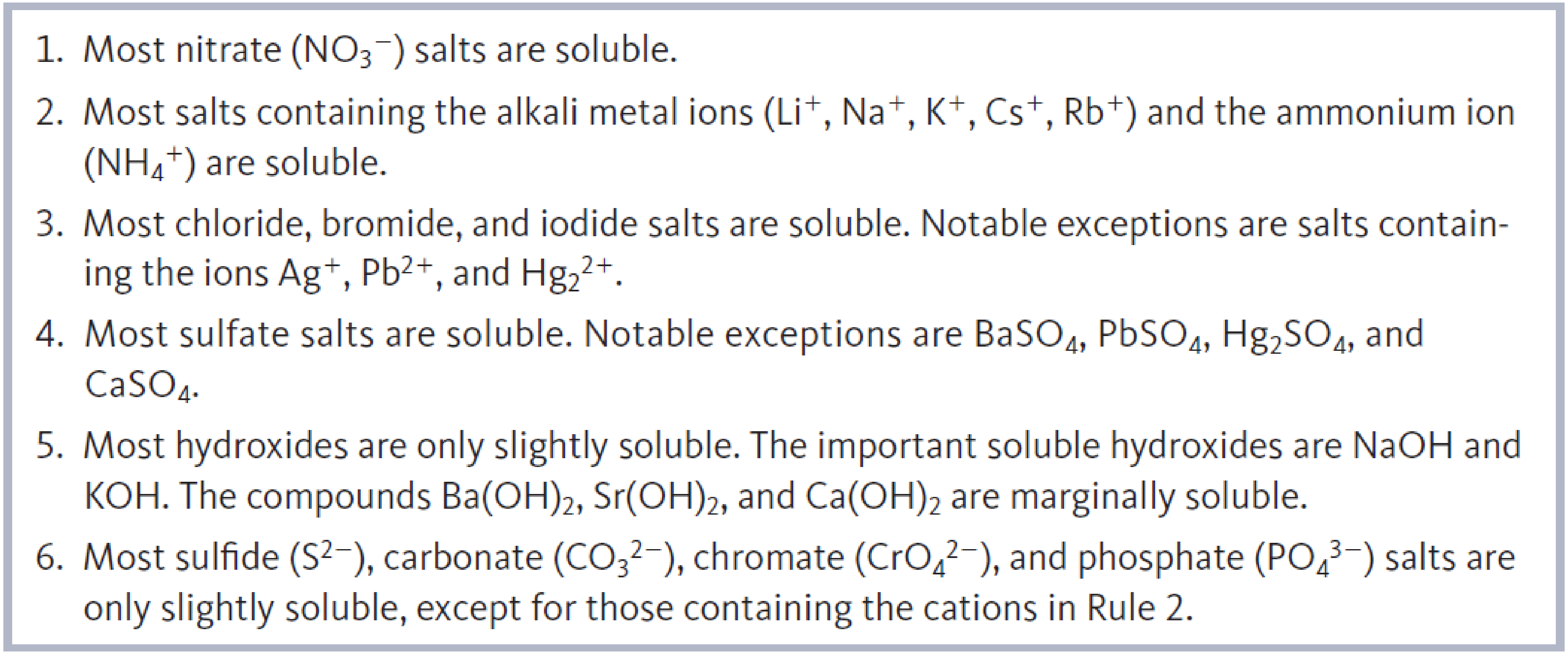
Table 4.1 - Simple Rules for the Solubility of Salts in Water



1. Most nitrate (NO_3^-) salts are soluble.
2. Most salts containing the alkali metal ions (Li^+, Na^+, K^+, Cs^+, Rb^+) and the ammonium ion (NH_4^+) are soluble.
3. Most chloride, bromide, and iodide salts are soluble. Notable exceptions are salts containing the ions Ag^+, Pb^{2+}, and Hg_2^{2+}.
4. Most sulfate salts are soluble. Notable exceptions are $BaSO_4$, $PbSO_4$, Hg_2SO_4, and $CaSO_4$.
5. Most hydroxides are only slightly soluble. The important soluble hydroxides are NaOH and KOH. The compounds $Ba(OH)_2$, $Sr(OH)_2$, and $Ca(OH)_2$ are marginally soluble.
6. Most sulfide (S^{2-}), carbonate (CO_3^{2-}), chromate (CrO_4^{2-}), and phosphate (PO_4^{3-}) salts are only slightly soluble, except for those containing the cations in Rule 2.

Interactive Example 4.8 - Predicting Reaction Products

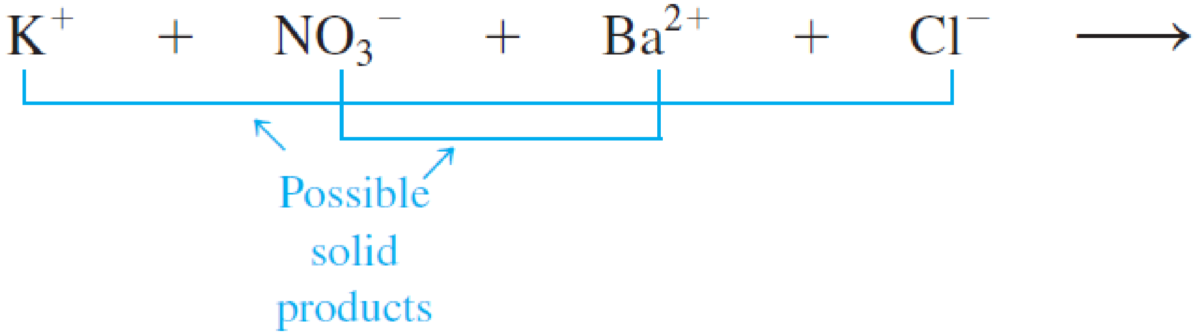
- Using the solubility rules in Table 4.1, predict what will happen when the following two solutions are mixed:
    - KNO_3(*aq*) and $BaCl_2$(*aq*)

Interactive Example 4.8 - Solution

- The formula $KNO_3(aq)$ represents an aqueous solution obtained by dissolving solid KNO_3 in water to form a solution containing the hydrated ions $K^+(aq)$ and $NO_3^-(aq)$
  - Likewise, $BaCl_2(aq)$ represents a solution formed by dissolving solid $BaCl_2$ in water to produce $Ba^{2+}(aq)$ and $Cl^-(aq)$

Interactive Example 4.8 - Solution (Continued 1)

  - When these two solutions are mixed, the resulting solution contains the ions K^+, NO_3^-, Ba^{2+}, and Cl^-
  - All ions are hydrated, but the (*aq*) is omitted for simplicity
- To look for possible solid products, combine the cation from one reactant with the anion from the other



$$K^+ + NO_3^- + Ba^{2+} + Cl^- \longrightarrow$$

Interactive Example 4.8 - Solution (Continued 2)

- Note from Table 4.1 that the rules predict that both KCl and $Ba(NO_3)_2$ are soluble in water
  - Thus, no precipitate forms when KNO_3(*aq*) and $BaCl_2$(*aq*) are mixed
    - All the ions remain dissolved in solution and no chemical reaction occurs

Types of Equations Used to Represent Reactions in Solution

- **Formula equation**: Describes the overall reaction stoichiometry
  - Does not provide correct information regarding the actual forms of the reactants and products
- **Complete ionic equation**: All reactants and products that are strong electrolytes are represented as ions

Types of Equations Used to Describe Reactions in Solution (Continued)

- **Net ionic equation**: Includes those solution components that undergo change
  - Do not include spectator ions
    - **Spectator ions**: Ions that do not directly participate in a reaction

Interactive Example 4.9 - Writing Equations for Reactions

- For the following reaction, write the formula equation, the complete ionic equation, and the net ionic equation
  - Aqueous potassium hydroxide is mixed with aqueous iron(III) nitrate to form a precipitate of iron(III) hydroxide and aqueous potassium nitrate

Interactive Example 4.9 - Solution

- Formula equation

$$3\text{KOH}(aq) + \text{Fe(NO}_3)_3(aq) \rightarrow \text{Fe(OH)}_3(s) + 3\text{KNO}_3(aq)$$

- Complete ionic equation

$$3\text{K}^+(aq) + 3\text{OH}^-(aq) + \text{Fe}^{3+}(aq) + 3\text{NO}_3^-(aq) \rightarrow$$
$$\text{Fe(OH)}_3(s) + 3\text{K}^+(aq) + 3\text{NO}_3^-(aq)$$

Interactive Example 4.9 - Solution (Continued)

- Net ionic equation

$$3\text{OH}^{-}(aq) + \text{Fe}^{3+}(aq) \rightarrow \text{Fe(OH)}_3(s)$$

Problem-Solving Strategy - Solving Stoichiometry Problems for Reactions in Solution

1. Identify the species present in the combined solution
   - Determine what reaction occurs
2. Write the balanced net ionic equation for the reaction
3. Calculate the moles of reactants

Problem-Solving Strategy - Solving Stoichiometry Problems for Reactions in Solution (Continued)

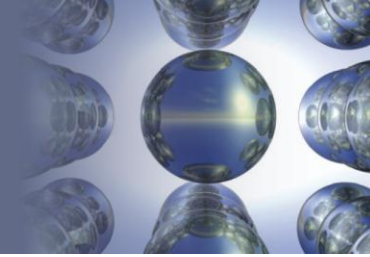
4. Determine the limiting reactant
5. Calculate the moles of product(s), as required
6. Convert to grams or other units, as required

Critical Thinking

- What if all ionic solids were soluble in water?
    - How would this affect stoichiometry calculations for reactions in aqueous solution?

Interactive Example 4.11 - Determining the Mass of Product Formed II

- When aqueous solutions of Na_2SO_4 and $Pb(NO_3)_2$ are mixed, $PbSO_4$ precipitates
  - Calculate the mass of $PbSO_4$ formed when 1.25 L of 0.0500 *M* $Pb(NO_3)_2$ and 2.00 L of 0.0250 *M* Na_2SO_4 are mixed



Interactive Example 4.11 - Solution

- Where are we going?
  - To find the mass of solid $PbSO_4$ formed
- What do we know?
  - 1.25 L of 0.0500 *M* $Pb(NO_3)_2$ and 2.00 L of 0.0250 *M* Na_2SO_4
  - Chemical reaction - $\mathrm{Pb}^{2+}(aq)+\mathrm{SO}_4^{2-}(aq)\rightarrow \mathrm{PbSO}_4(s)$
- What information do we need?
  - The limiting reactant

Interactive Example 4.11 - Solution (Continued 1)

- How do we get there?
  - What are the ions present in the combined solution?

    Na^+ SO_4^{2-} Pb^{2+} NO_3^-

    - Reaction - Since $NaNO_3$ is soluble and $PbSO_4$ is insoluble, solid $PbSO_4$ will form
  - What is the balanced net ionic equation for the reaction?

$$\mathrm{Pb}^{2+}(aq) + \mathrm{SO}_4^{2-}(aq) \rightarrow \mathrm{PbSO}_4(s)$$

Interactive Example 4.11 - Solution (Continued 2)

- What are the moles of reactants present in the solution?

$$1.25\ \cancel{\text{L}} \times \frac{0.0500\ \text{mol Pb}^{2+}}{\cancel{\text{L}}} = 0.0625\ \text{mol Pb}^{2+}$$

$$2.00\ \cancel{\text{L}} \times \frac{0.0250\ \text{mol SO}_4^{2-}}{\cancel{\text{L}}} = 0.0500\ \text{mol SO}_4^{2-}$$

Interactive Example 4.11 - Solution (Continued 3)

- Which reactant is limiting?
  - Since Pb^{2+} and SO_4^{2-} react in a 1:1 ratio, the amount of SO_4^{2-} will be limiting (0.0500 mol SO_4^{2-} is less than 0.0625 mole of Pb^{2+})
- What number of moles of $PbSO_4$ will be formed?
  - Since SO_4^{2-} is limiting, only 0.0500 mole of solid $PbSO_4$ will be formed

Interactive Example 4.11 - Solution (Continued 4)

- What mass of $PbSO_4$ will be formed?

$$0.0500\ \cancel{\text{mol } PbSO_4} \times \frac{303.3\text{ g } PbSO_4}{1\ \cancel{\text{mol } PbSO_4}} = 15.2\text{ g } PbSO_4$$

Definitions - Acid, Base, and Neutralization Reaction

- Brønsted–Lowry definitions for acids and bases
    - **Acid**: Proton donor
    - **Base**: Proton acceptor
- **Neutralization reaction**: General name given to acid–base reactions
    - An acid is neutralized when enough base reacts exactly with it in a solution

Problem-Solving Strategy - Performing Calculations for Acid–Base Reactions

1. List the species present in the combined solution before any reaction occurs
   - Decide what reaction will occur
2. Write the balanced net ionic equation for the reaction
3. Calculate moles of reactants
   - For reactions in solution, use the volumes of the original solutions and their molarities

Problem-Solving Strategy - Performing Calculations for Acid–Base Reactions (Continued)

4. Determine the limiting reactant where appropriate
5. Calculate the moles of the required reactant or product
6. Convert to grams or volume (of solution), as required

Interactive Example 4.13 - Neutralization Reactions II

- In a certain experiment, 28.0 mL of 0.250 *M* HNO_3 and 53.0 mL of 0.320 *M* KOH are mixed
    - What is the concentration of H^+ or OH^- ions in excess after the reaction goes to completion?

Interactive Example 4.13 - Solution

- Where are we going?
  - To find the concentration of H^+ or OH^- in excess after the reaction is complete
- What do we know?
  - 28.0 mL of 0.250 *M* HNO_3
  - 53.0 mL of 0.320 *M* KOH
  - Chemical reaction

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

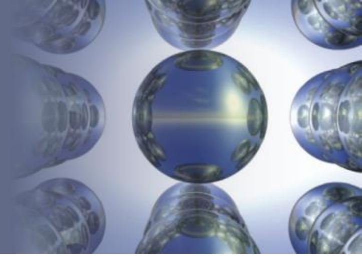
Interactive Example 4.13 - Solution (Continued 1)

- How do we get there?
  - What are the ions present in the combined solution?

H^+ NO_3^- K^+ OH^-

  - What is the balanced net ionic equation for the reaction?

$$\mathrm{H}^+(aq) + \mathrm{OH}^-(aq) \rightarrow \mathrm{H}_2\mathrm{O}(l)$$



Interactive Example 4.13 - Solution (Continued 2)

- What are the moles of reactant present in the solution?

$$28.0\ \cancel{\text{mL HNO}_3} \times \frac{1\ \cancel{\text{L}}}{1000\ \cancel{\text{mL}}} \times \frac{0.250\ \text{mol H}^+}{\cancel{\text{L HNO}_3}} = 7.00 \times 10^{-3}\ \text{mol H}^+$$

$$53.0\ \cancel{\text{mL KOH}} \times \frac{1\ \cancel{\text{L}}}{1000\ \cancel{\text{mL}}} \times \frac{0.320\ \text{mol OH}^-}{\cancel{\text{L KOH}}} = 1.70 \times 10^{-2}\ \text{mol OH}^-$$

Interactive Example 4.13 - Solution (Continued 3)

- Which reactant is limiting?
    - Since H^+ and OH^- ions react in a 1:1 ratio, the limiting reactant is H^+
- What amount of OH^- will react?
    - 7.00×10^{-3} mole of OH^- is required to neutralize the H^+ ions present
    - To determine the excess of OH^- ions, consider the following difference:

$$\text{Original amount} - \text{amount consumed} = \text{amount in excess}$$

Interactive Example 4.13 - Solution (Continued 4)

- Excess OH^- is:

$$1.70 \times 10^{-2} \text{ mol OH}^- - 7.00 \times 10^{-3} \text{ mol OH}^- = 1.00 \times 10^{-2} \text{ mol OH}^-$$

- The volume of the combined solution is the sum of the individual volumes

$$\text{Original volume of HNO}_3 + \text{original volume of KOH} = \text{total volume}$$

$$28.0 \text{ mL} + 53.0 \text{ mL} = 81.0 \text{ mL} = 8.10 \times 10^{-2} \text{ L}$$

Interactive Example 4.13 - Solution (Continued 5)

- What is the molarity of the OH^- ions in excess?

$$\frac{\text{mol OH}^-}{\text{L solution}} = \frac{1.00 \times 10^{-2} \text{ mol OH}^-}{8.10 \times 10^{-2} \text{ L}} = 0.123\ M \text{ OH}^-$$

- Reality check
  - This calculated molarity is less than the initial molarity, as it should be

Volumetric Analysis

- Technique used for ascertaining the amount of a certain substance by doing a titration
  - **Titration**: Delivery of a titrant into an analyte
    - Titrant - Solution of known concentration
    - Analyte - Solution containing the substance being analyzed

Acid–Base Titrations

- **Equivalence (stoichiometric) point**: Marks the point in titration where enough titrant has been added to react exactly with the analyte
  - **Indictor**: Substance added at the beginning of the titration
    - Changes color at the equivalence point
    - **Endpoint**: Point where the indicator actually changes color

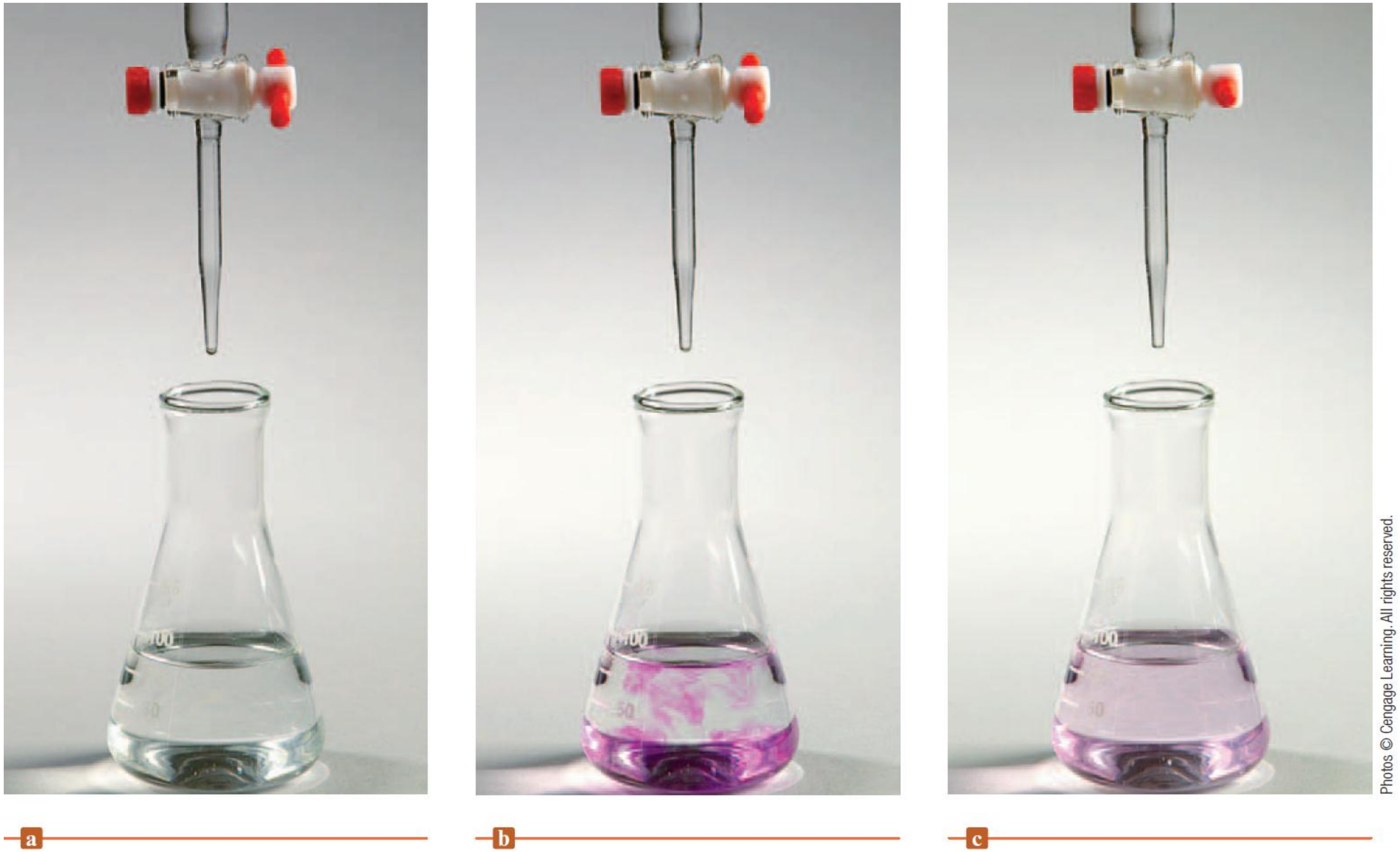
Requirements for a Successful Titration

- Exact reaction between titrant and analyte must be known and must be rapid
- Equivalence point must be accurately marked
- Volume of titrant that is needed to reach the equivalence point must be accurately known

Indicator Used in Acid–Base Titrations

- Phenolphthalein
  - Colorless in an acidic solution
  - Pink in a basic solution
  - When an acid is titrated with a base, the indicator remains colorless until after the acid is consumed and the first drop of excess base is added

Figure 4.18 - Titration of an Acid with a Base



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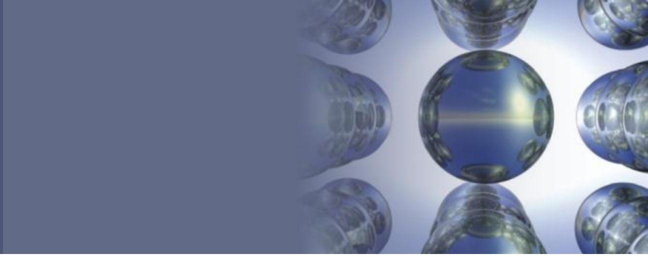
Interactive Example 4.14 - Neutralization Titration

- A student carries out an experiment to standardize (determine the exact concentration of) a sodium hydroxide solution
  - To do this, the student weighs out a 1.3009-g sample of potassium hydrogen phthalate ($KHC_8H_4O_4$, often abbreviated KHP)
    - KHP (molar mass 204.22 g/mol) has one acidic hydrogen

Interactive Example 4.14 - Neutralization Titration

(Continued)

- The student dissolves the KHP in distilled water, adds phenolphthalein as an indicator, and titrates the resulting solution with the sodium hydroxide solution to the phenolphthalein endpoint
  - The difference between the final and initial buret readings indicates that 41.20 mL of the sodium hydroxide solution is required to react exactly with the 1.3009 g KHP
  - Calculate the concentration of the sodium hydroxide solution



Interactive Example 4.14 - Solution

- Where are we going?
  - To find the concentration of NaOH solution
- What do we know?
  - 1.3009 g $KHC_8H_4O_4$ (KHP), molar mass (204.22 g/mol)
  - 41.20 mL NaOH solution to neutralize KHP
  - The chemical reaction

$$HC_8H_4O_4^-(aq) + OH^-(aq) \rightarrow H_2O(l) + C_8H_4O_4^{2-}(aq)$$

Interactive Example 4.14 - Solution (Continued 1)

- How do we get there?
  - What are the ions present in the combined solution?

    K^+ $HC_8H_4O_4^-$ Na^+ OH^-

  - What is the balanced net ionic equation for the reaction?

$$HC_8H_4O_4^-(aq) + OH^-(aq) \rightarrow H_2O(l) + C_8H_4O_4^{2-}(aq)$$

Interactive Example 4.14 - Solution (Continued 2)

- What are the moles of KHP?

$$1.3009\,\cancel{\text{g KHC}_8\text{H}_4\text{O}_4} \times \frac{1\text{ mol KHC}_8\text{H}_4\text{O}_4}{204.22\,\cancel{\text{g KHC}_8\text{H}_4\text{O}_4}}$$

$$= 6.3701 \times 10^{-3}\text{ mol KHC}_8\text{H}_4\text{O}_4$$

- Which reactant is limiting?
  - This problem requires the addition of just enough OH^- ions to react exactly with the KHP present
  - We do not need to be concerned with limiting reactant here

Interactive Example 4.14 - Solution (Continued 3)

- What moles of OH^- are required?
  - 6.3701×10^{-3} mole of OH^- is required to neutralize the KHP present
- What is the molarity of the NaOH solution?

$$\text{Molarity of NaOH} = \frac{\text{mol NaOH}}{\text{L solution}} = \frac{6.3701 \times 10^{-3}\ \text{mol NaOH}}{4.120 \times 10^{-2}\ \text{L}}$$

$$= 0.1546\ M$$

Critical Thinking

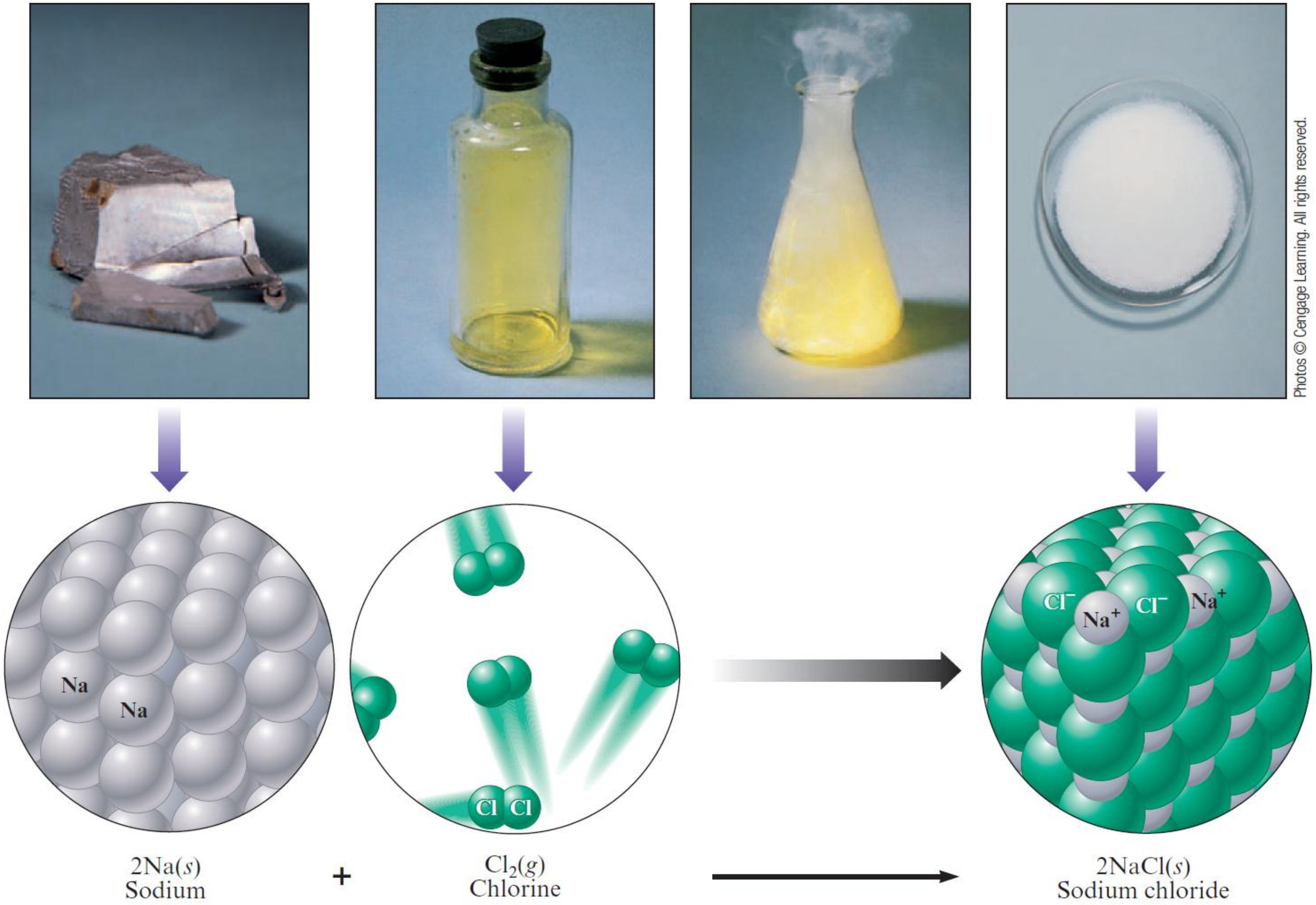
- In Example 4.14 you determined the concentration of an aqueous solution of NaOH using phenolphthalein as an indicator
  - What if you used an indicator for which the endpoint of the titration occurs after the equivalence point?
    - How would this affect your calculated concentration of NaOH?

Oxidation–Reduction (Redox) Reactions

- Involve the transfer of one or more electrons
- Example
    - Formation of sodium chloride from elemental sodium and chlorine

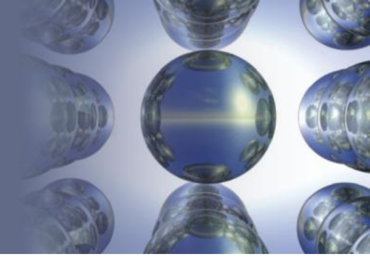
$$2\mathrm{Na}(s) + \mathrm{Cl}_2(g) \rightarrow 2\mathrm{NaCl}(s)$$

Figure 4.19 - Reaction of Solid Sodium and Gaseous Chlorine to Form Solid Sodium Chloride



Oxidation States (Oxidation Numbers)

- For atoms in covalent compounds, the oxidation state refers to imaginary charges that atoms would have if:
  - Shared electrons were equally divided between identical atoms bonded to each other
  - In different atoms, the shared electrons were all assigned to the atom in each bond that has greater electron affinity



Oxidation States (Oxidation Numbers) (Continued)

- In ionic compounds that contain monatomic ions, the oxidation states of the ions are equal to the ion charges
- For electrically neutral compounds, the sum of oxidation states must be zero
- Written as $+n$ or $-n$

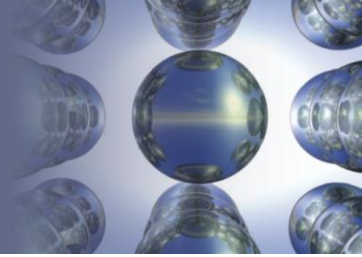
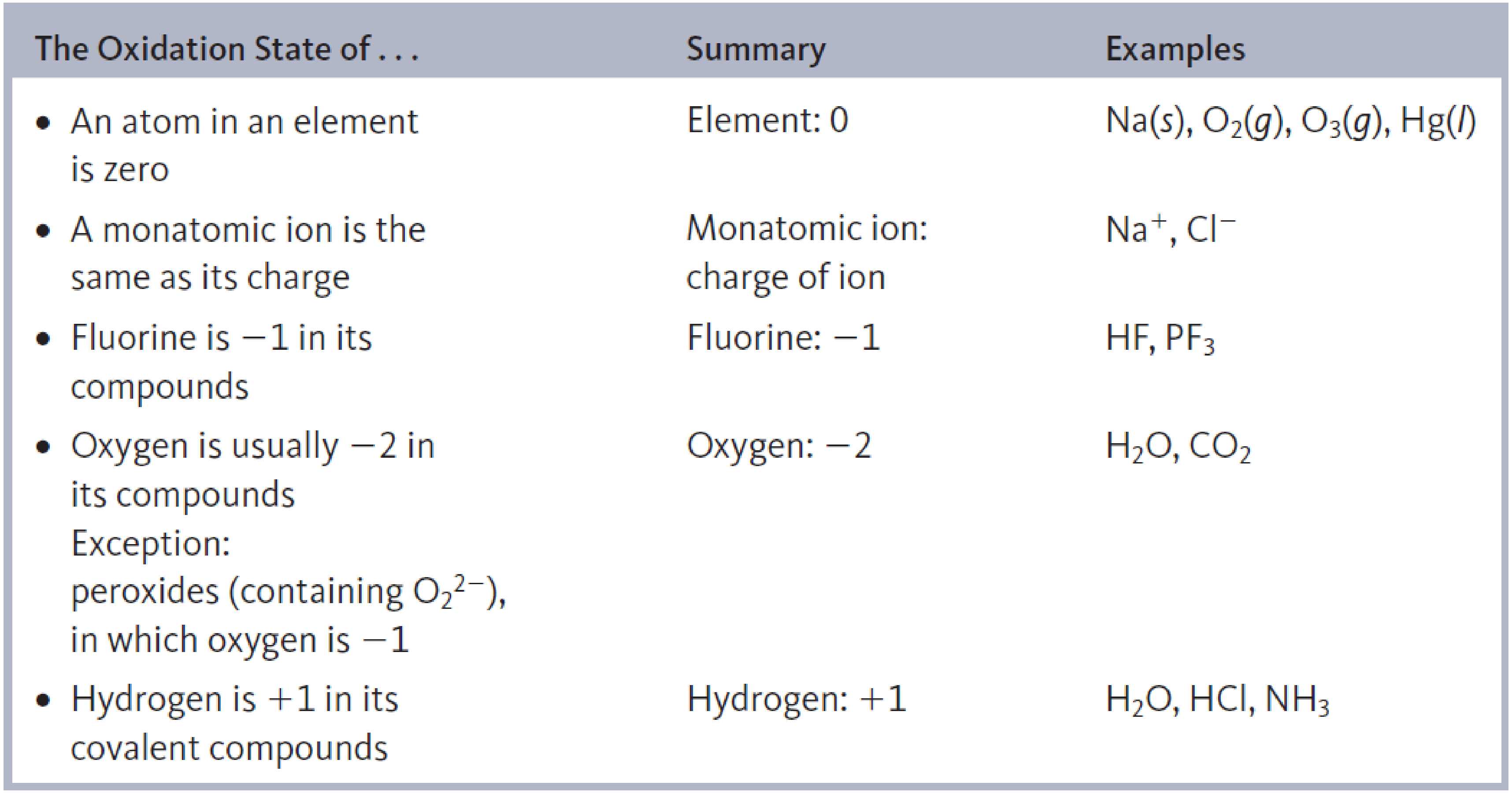
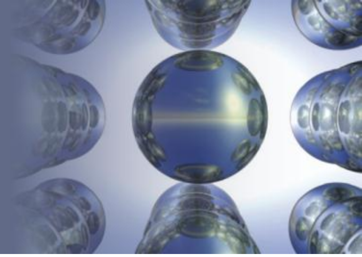


Table 4.2 - Rules for Assigning Oxidation States



The Oxidation State of . . .	Summary	Examples
• An atom in an element is zero	Element: 0	Na(*s*), $O_2(g)$, $O_3(g)$, Hg(*l*)
• A monatomic ion is the same as its charge	Monatomic ion: charge of ion	Na^+, Cl^-
• Fluorine is −1 in its compounds	Fluorine: −1	HF, PF_3
• Oxygen is usually −2 in its compounds Exception: peroxides (containing O_2^{2-}), in which oxygen is −1	Oxygen: −2	H_2O, CO_2
• Hydrogen is +1 in its covalent compounds	Hydrogen: +1	H_2O, HCl, NH_3



Critical Thinking

- What if the oxidation state for oxygen was defined as –1 instead of –2?
  - What effect, if any, would it have on the oxidation state of hydrogen?

Interactive Example 4.16 - Assigning Oxidation States

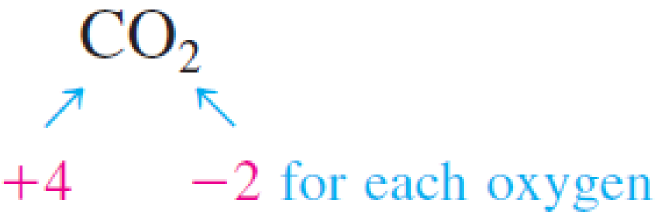
- Assign oxidation states to all atoms in the following:
  a. CO_2
  b. NO_3^-

Interactive Example 4.16 - Solution (a)

- Since we have a specific rule for the oxidation state of oxygen, we will assign its value first
  - The oxidation state of oxygen is –2
- The oxidation state of the carbon atom can be determined by recognizing that since CO_2 has no charge, the sum of the oxidation states for oxygen and carbon must be zero

Interactive Example 4.16 - Solution (a) (Continued)

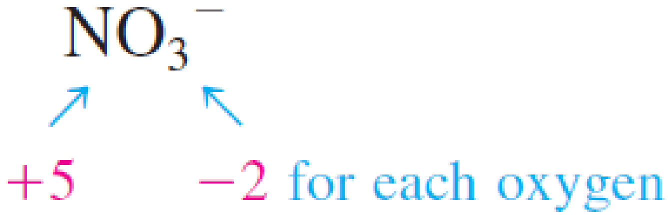
- Since each oxygen is –2 and there are two oxygen atoms, the carbon atom must be assigned an oxidation state of +4



- Reality check
  - 1(+4) + 2(–2) = 0

Interactive Example 4.16 - Solution (b)

- Oxygen has an oxidation state of –2
    - Since the sum of the oxidation states of the three oxygens is –6 and the net charge on the NO_3^- ion is 1–, the nitrogen must have an oxidation state of +5



- Reality check
    - +5 + 3(–2) = –1

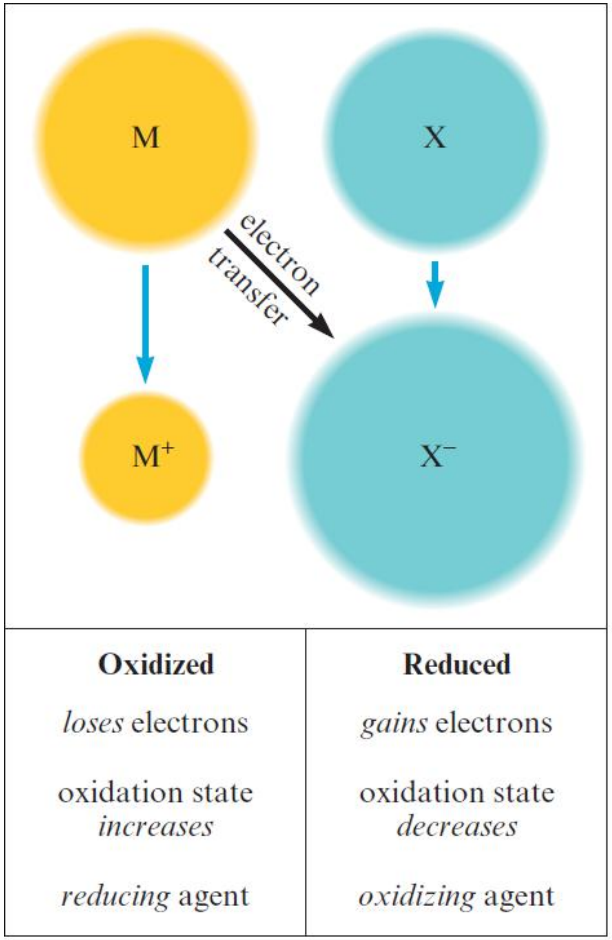
Exercise

- Assign oxidation states for all atoms in each of the following compounds:
  a. $KMnO_4$ **K = +1; O = –2; Mn = +7**
  b. $Na_4Fe(OH)_6$ **Na = +1; Fe = +2; O = –2; H = +1**
  c. $(NH_4)_2HPO_4$ **H = +1; O = –2; N = –3; P = +5**
  d. $C_6H_{12}O_6$ **C = 0; H = +1; O = –2**

Terminologies

- **Oxidation**: Increase in oxidation state
    - Characterized by electron loss
- **Reduction**: Decrease in oxidation state
    - Characterized by electron gain
- **Reducing agent**: Electron donor
- **Oxidizing agent**: Electron acceptor

Figure 4.20 - Summary of an Oxidation–Reduction Process



Oxidized	**Reduced**
loses electrons	*gains* electrons
oxidation state *increases*	oxidation state *decreases*
reducing agent	*oxidizing* agent

Interactive Example 4.17 - Oxidation–Reduction Reactions

- Metallurgy, the process of producing a metal from its ore, always involves oxidation–reduction reactions
    - In the metallurgy of galena (PbS), the principal lead-containing ore, the first step is the conversion of lead sulfide to its oxide (a process called roasting):

$$2\mathrm{PbS}(s) + 3\mathrm{O}_2(g) \rightarrow 2\mathrm{PbO}(s) + 2\mathrm{SO}_2(g)$$

Interactive Example 4.17 - Oxidation–Reduction Reactions (Continued)

  - The oxide is then treated with carbon monoxide to produce the free metal:

$$\mathrm{PbO}(s) + \mathrm{CO}(g) \rightarrow \mathrm{Pb}(s) + \mathrm{CO_2}(g)$$

- For each reaction, identify the atoms that are oxidized and reduced, and specify the oxidizing and reducing agents

Interactive Example 4.17 - Solution

- For the first reaction, we can assign the following oxidation states:

$$2\underset{\substack{\uparrow\\+2}}{\mathrm{Pb}}\underset{\substack{\uparrow\\-2}}{\mathrm{S}}(s) + 3\underset{\substack{\uparrow\\0}}{\mathrm{O}_2}(g) \rightarrow 2\underset{\substack{\uparrow\\+2}}{\mathrm{Pb}}\underset{\substack{\uparrow\\-2}}{\mathrm{O}}(s) + 2\underset{\substack{\uparrow\\+4}}{\mathrm{S}}\underset{\substack{\uparrow\\-2\\\text{(each O)}}}{\mathrm{O}_2}(g)$$

  - The oxidation state for the sulfur atom increases from –2 to +4
    - Thus, sulfur is oxidized

Interactive Example 4.17 - Solution (Continued 1)

- The oxidation state for each oxygen atom decreases from 0 to –2
    - Oxygen is reduced
- The oxidizing agent is O_2, and the reducing agent is PbS
- For the second reaction we have

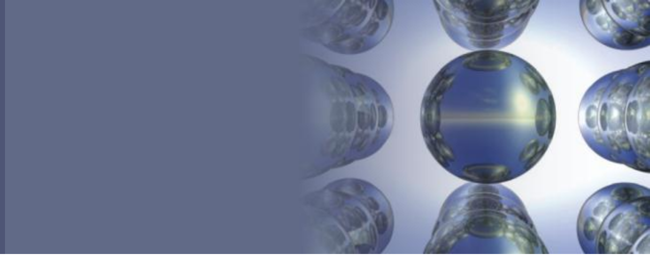
$$\underset{\substack{\uparrow\\+2}}{\mathrm{Pb}}\underset{\substack{\nwarrow\\-2}}{\mathrm{O}}(s)+\underset{\substack{\uparrow\\+2}}{\mathrm{C}}\underset{\substack{\nwarrow\\-2}}{\mathrm{O}}(g)\rightarrow\underset{\substack{\uparrow\\0}}{\mathrm{Pb}}(s)+\underset{\substack{\uparrow\\+4}}{\mathrm{C}}\underset{\substack{\nwarrow\\-2\\\text{(each O)}}}{\mathrm{O}_2}(g)$$

Interactive Example 4.17 - Solution (Continued 2)

- Lead is reduced (its oxidation state decreases from +2 to 0), and carbon is oxidized (its oxidation state increases from +2 to +4)
- PbO is the oxidizing agent, and CO is the reducing agent

Critical Thinking

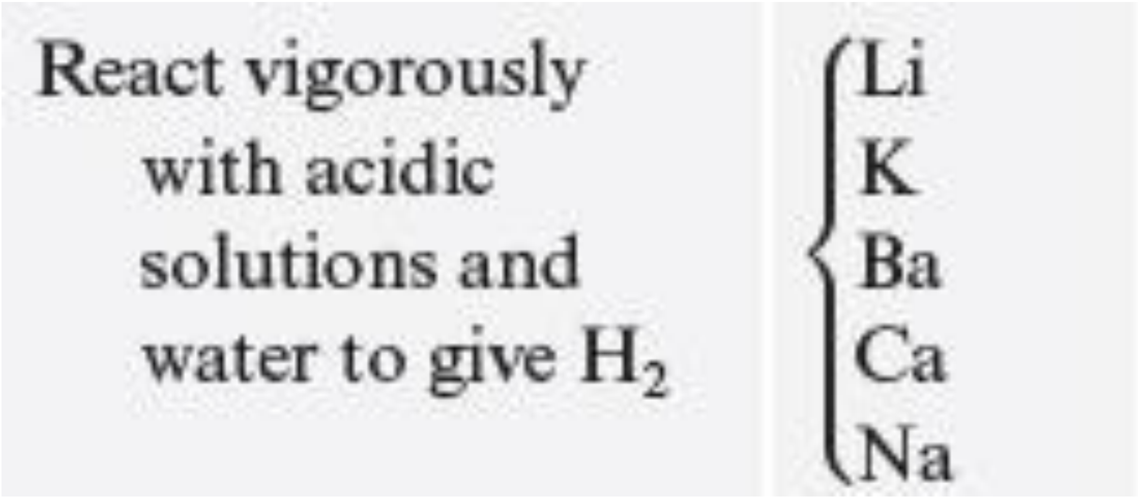
- Dalton believed that atoms were indivisible
  - Thomson and Rutherford helped to show that this was not true
  - What if atoms were indivisible?
    - How would this affect the types of reactions you have learned about in this chapter?



Problem-Solving Strategy - Balancing Oxidation–Reduction Reactions by Oxidation States

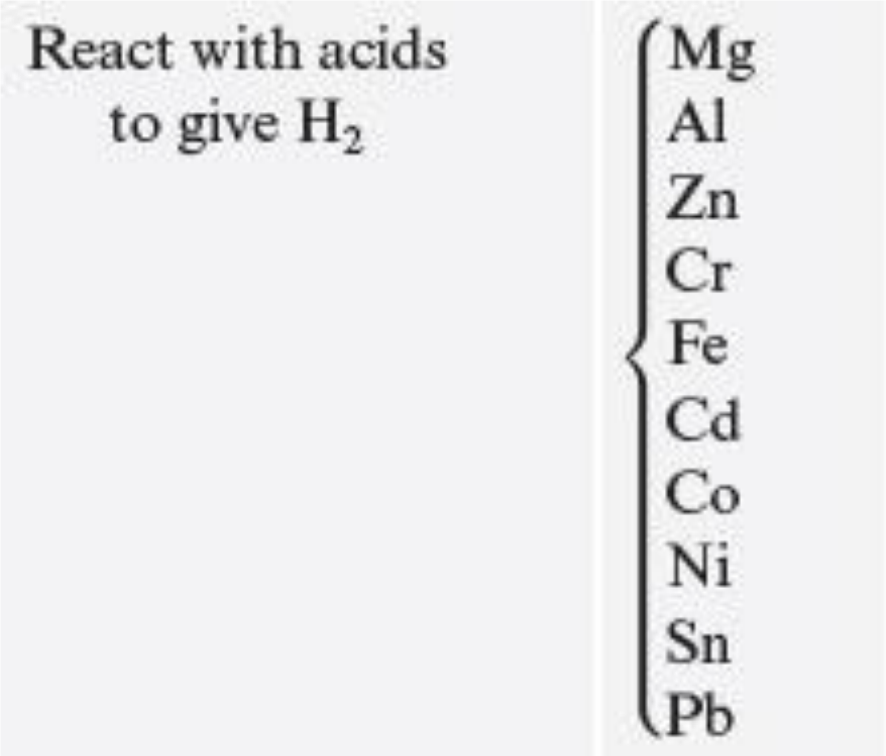
- Write the unbalanced equation
- Determine the oxidation states of all atoms in the reactants and products
- Show electrons gained and lost using tie lines
- Use coefficients to equalize the electrons gained and lost
- Balance the rest of the equation by inspection
- Add appropriate states

Activity Series of Elements



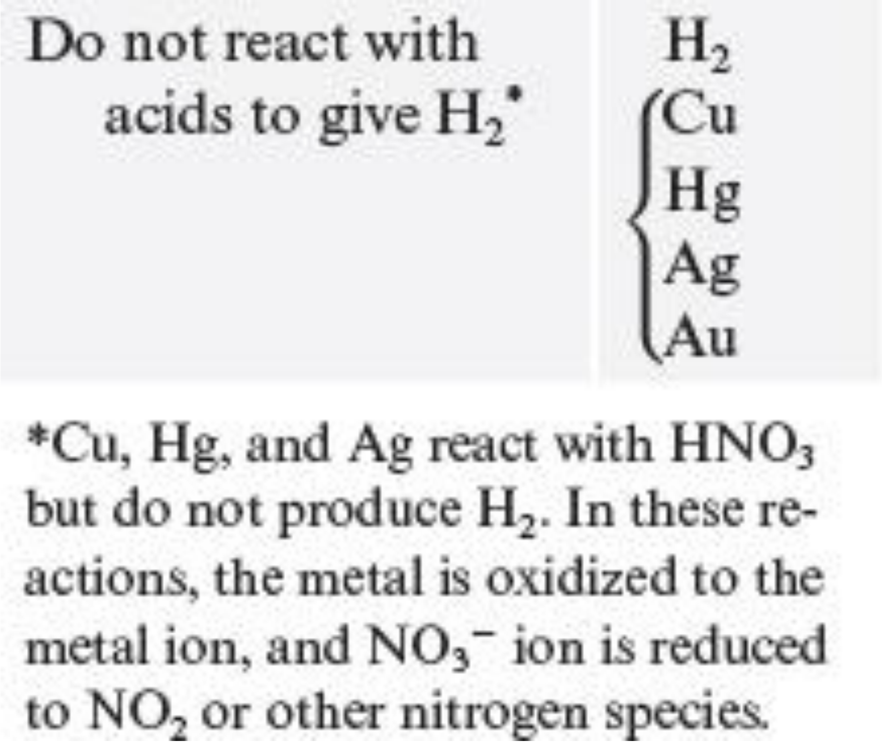
React vigorously with acidic solutions and water to give H_2	Li K Ba Ca Na

Activity Series of Elements (Continued 1)



React with acids to give H_2	Mg Al Zn Cr Fe Cd Co Ni Sn Pb

Activity Series of Elements (Continued 2)



	H_2
Do not react with acids to give H_2*	Cu Hg Ag Au

*Cu, Hg, and Ag react with HNO_3 but do not produce H_2. In these reactions, the metal is oxidized to the metal ion, and NO_3^- ion is reduced to NO_2 or other nitrogen species.

Example 4.18 - Balancing Oxidation–Reduction Reactions

- Balance the reaction between solid lead(II) oxide and ammonia gas to produce nitrogen gas, liquid water, and solid lead

Example 4.18 - Solution

- What is the unbalanced equation?

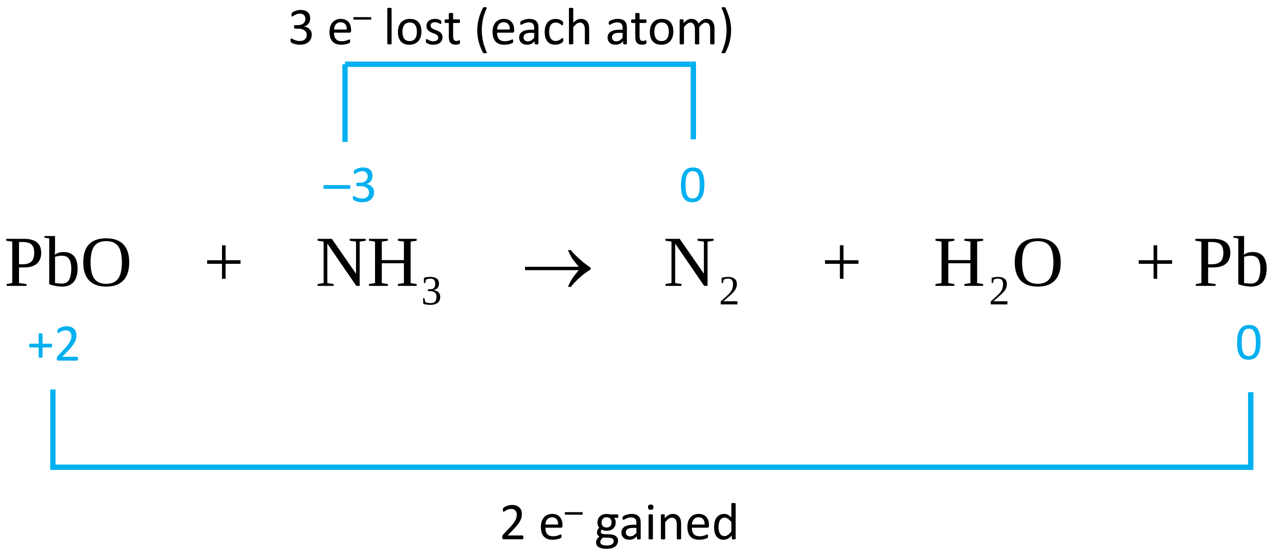
$$\mathrm{PbO}(s) + \mathrm{NH_3}(g) \rightarrow \mathrm{N_2}(g) + \mathrm{H_2O}(l) + \mathrm{Pb}(s)$$

- What are the oxidation states for each atom?

$$\underset{+2}{\mathrm{Pb}}\overset{-2}{\mathrm{O}} + \overset{-3}{\mathrm{N}}\underset{+1}{\mathrm{H}}_3 \rightarrow \overset{0}{\mathrm{N}}_2 + \underset{+1}{\mathrm{H}}_2\overset{-2}{\mathrm{O}} + \underset{0}{\mathrm{Pb}}$$

Example 4.18 - Solution (Continued 1)

- How are electrons gained and lost?



3 e^- lost (each atom)

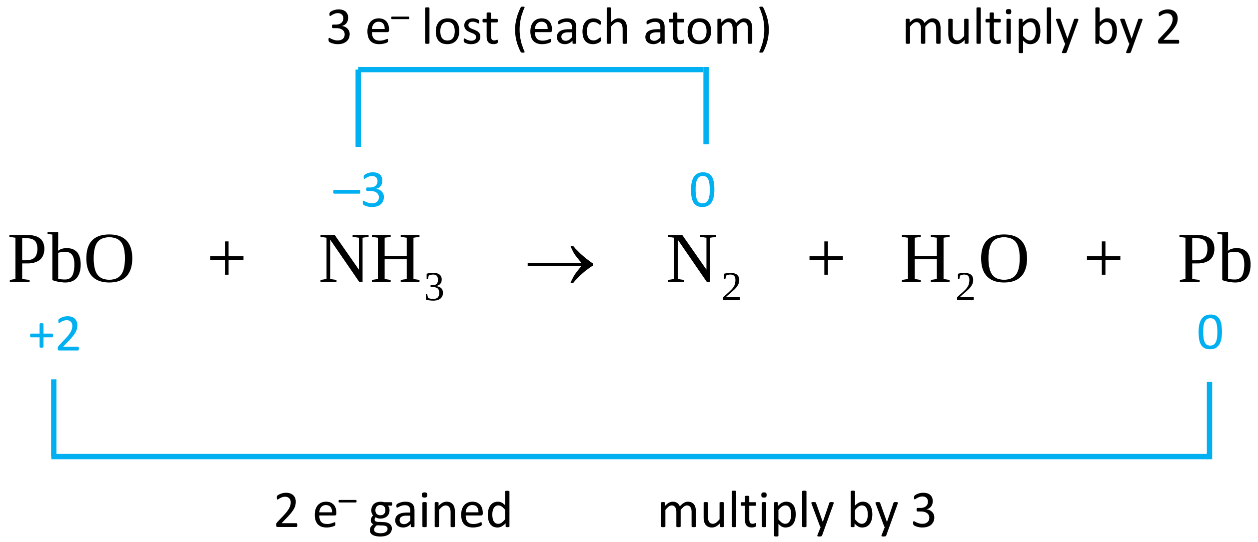
$$\underset{+2}{PbO} + \overset{-3}{NH_3} \rightarrow \overset{0}{N_2} + H_2O + \underset{0}{Pb}$$

2 e^- gained

  - The oxidation states of all other atoms are unchanged

Example 4.18 - Solution (Continued 2)

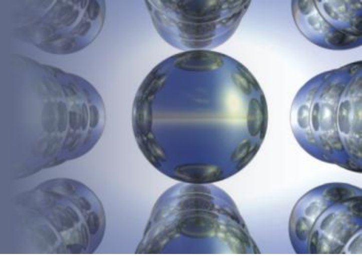
- What coefficients are needed to equalize the electrons gained and lost?



3 e^- lost (each atom) multiply by 2

$$\underset{+2}{\mathrm{PbO}} + \overset{-3}{\mathrm{NH_3}} \rightarrow \overset{0}{\mathrm{N_2}} + \mathrm{H_2O} + \underset{0}{\mathrm{Pb}}$$

2 e^- gained multiply by 3



Example 4.18 - Solution (Continued 3)

$$3PbO + 2NH_3 \rightarrow N_2 + H_2O + 3Pb$$

- What coefficients are needed to balance the remaining elements?
    - Balance O

$$3PbO + 2NH_3 \rightarrow N_2 + 3H_2O + 3Pb$$

Example 4.18 - Solution (Continued 4)

- All the elements are now balanced
  - The balanced equation with states is:

$$3\mathrm{PbO}(s) + 2\mathrm{NH}_3(g) \rightarrow \mathrm{N}_2(g) + 3\mathrm{H}_2\mathrm{O}(l) + 3\mathrm{Pb}(s)$$