CHEMISTRY

an atoms-focused approach

Gilbert
Kirss
Foster

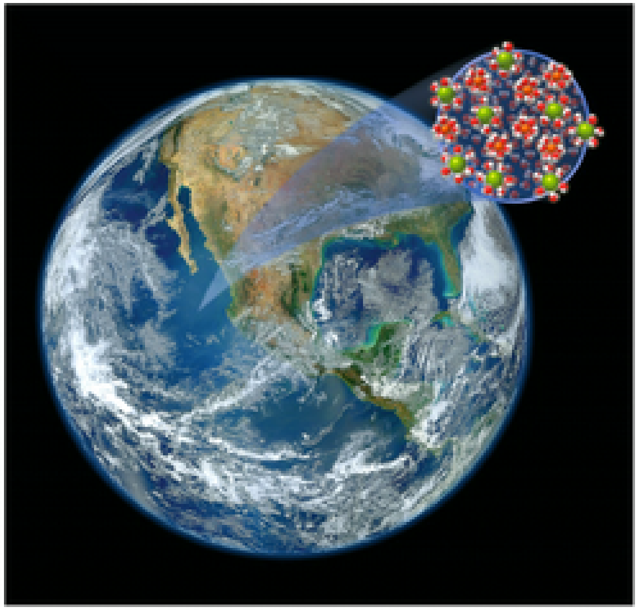
Chapter 8

Aqueous Solutions

Chemistry of the Hydrosphere

Chapter Outline

- 8.1 Solutions and Their Concentrations
- 8.2 Dilutions
- 8.3 Electrolytes and Non-Electrolytes
- 8.4 Acids, Bases, and Neutralization Reactions
- 8.5 Precipitation Reactions
- 8.6 Oxidation-Reduction Reactions
- 8.7 Titrations
- 8.8 Ion Exchange



The Blue Planet: Seawater

- Earth – “the water planet”
  - Covered ~70% by water
  - Depressions in Earth’s crust filled with 1.5×10^{21} L of $H_2O(\ell)$
- Properties of water responsible for life on Earth, and many geographical features
- All natural waters have ionic and molecular compounds dissolved in them

Solutions

- Solutions:
  - Homogeneous mixtures of two or more substances
    - **Solvent:** Component of a solution that is present in the greatest amount
    - **Solute:** Any component in a solution *other than* the solvent (i.e., the other ingredients in the mixture)
- Aqueous solutions → water solvent

Solution Concentration

- Define the amount of solute in a solution:

$$\frac{\text{amount of solute}}{\text{amount of solvent}} \quad \text{or} \quad \frac{\text{amount of solute}}{\text{amount of solution}}$$

- Most common concentration units based on:
  - Mass of solute
  - Moles of solute

Concentration Units

- Parts per million (*ppm*):

$$\text{ppb} = \left(\frac{\text{grams of solute}}{10^9\,\text{grams of solution}}\right) = \left(\frac{1\,\mu\text{g of solute}}{1\,\text{kg of solution}}\right)$$

- Parts per billion (*ppb*):

$$\text{ppb} = \left(\frac{\text{grams of solute}}{10^9\,\text{grams of solution}}\right) = \left(\frac{1\,\mu\text{g of solute}}{1\,\text{kg of solution}}\right)$$

- Useful for very small amounts of solute

Concentration Units

- Molarity (*M*)

$$\text{Mass of solute} = (\text{volume} \times \text{molarity}) \times \mathcal{M}$$

$$\text{g} = \left(\text{L} \times \frac{\text{mol}}{\text{L}}\right) \times \frac{\text{g}}{\text{mol}}$$

- As a conversion factor → g of solute

$$\text{Mass of solute} = (\text{volume} \times \text{molarity}) \times \mathcal{M}$$

$$\text{g} = \left(\text{L} \times \frac{\text{mol}}{\text{L}}\right) \times \frac{\text{g}}{\text{mol}}$$

- Small concentrations: *mM* (10^{-3} *M*), *μM* (10^{-6} *M*)

TABLE 8.1 **Average Concentrations of 11 Major Constituents of Seawater and Human Serum**

Constituent	SEAWATER		HUMAN SERUM
	mmol/kg	m*M*	m*M*
Na^+	468.96	480.57	135–145
K^+	10.21	10.46	3.5–5.0
Mg^{2+}	52.83	54.14	0.08–0.12
Ca^{2+}	10.28	10.53	0.2–0.3
Sr^{2+}	0.0906	0.0928	$<3 \times 10^{-4}$
Cl^-	545.88	559.40	98–108
SO_4^{2-}	28.23	28.93	0.3
HCO_3^-	2.06	2.11	22–30
Br^-	0.844	0.865	0.04–0.06
$B(OH)_3$	0.416	0.426	$<8 \times 10^{-4}$
F^-	0.068	0.070	5–6

Practice: Calculating Molarity

What is the molarity of an aqueous solution prepared by adding 36.5 g of barium chloride to enough water to make 750.0 mL of solution?

- Collect and Organize:
- Analyze:
- Solve:
- Think about It:

Practice: Mass of Solute

How many grams of aluminum nitrate are required to make 500.0 mL of a 0.0525 M aqueous solution?

- Collect and Organize:
- Analyze:
- Solve:
- Think about It:

Practice: Molarity from Density

If the density of ocean water at a depth of 10,000 m is 1.071 g/mL, and if 25.0 g of water at that depth contains 190 mg of KCl, what is the molarity of KCl?

- Collect and Organize:
- Analyze:
- Solve:
- Think about It:

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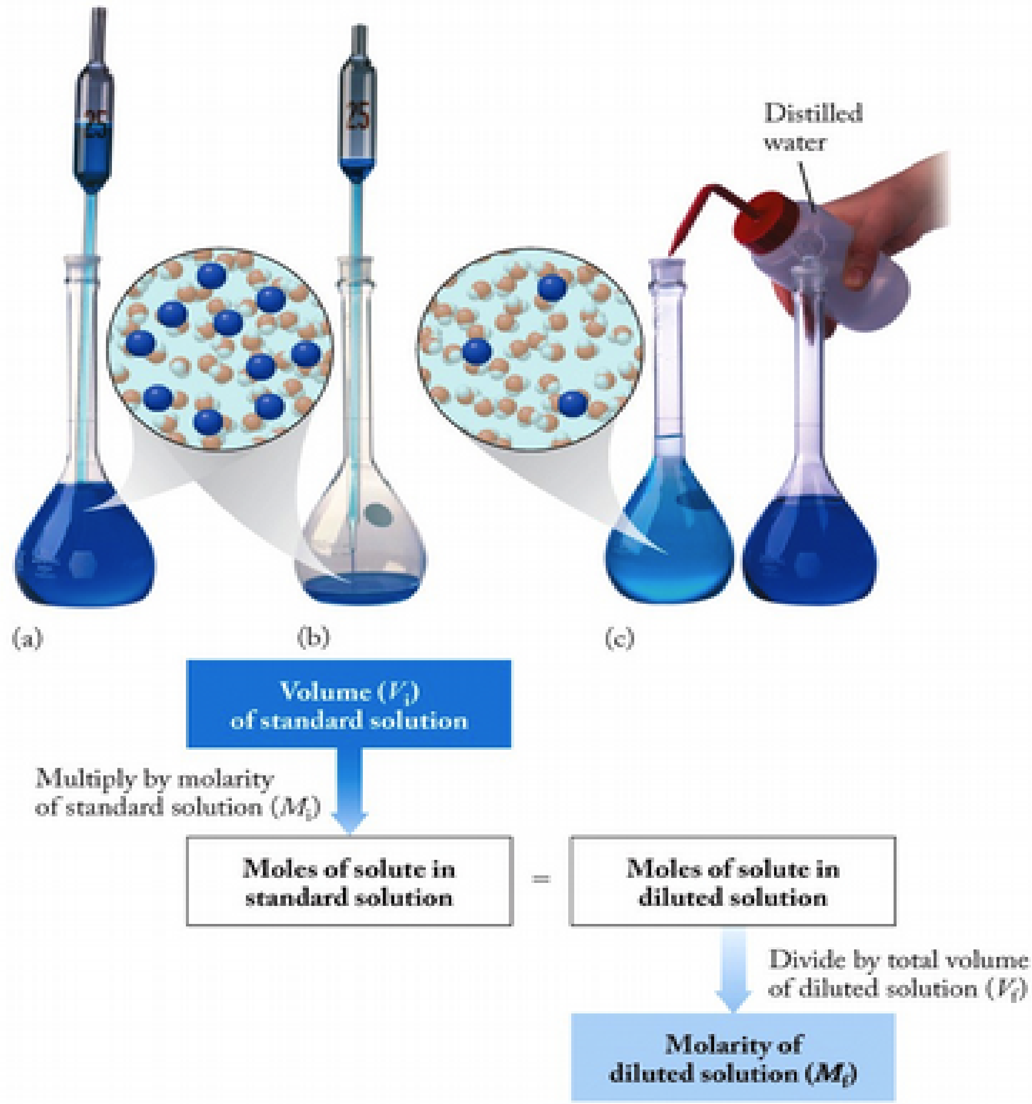
Dilutions

- **Stock solution:** A **concentrated** solution of a substance used to prepare solutions of lower concentration
- **Standard solution:** A solution whose concentration is fairly precisely known
- **Dilution:** Process of lowering the concentration of a solution by adding more solvent

$$(\text{\# moles solute})_{\text{stock}} = (\text{\# moles solute})_{\text{dilute}}$$

$$V_{\text{initial}} \times M_{\text{initial}} = V_{\text{dilute}} \times M_{\text{dilute}}$$

Dilution



Distilled water
(a)
(b)
(c)
Volume (V_i) of standard solution
Multiply by molarity of standard solution (M_i)
Moles of solute in standard solution
=
Moles of solute in diluted solution
Divide by total volume of diluted solution (V_f)
Molarity of diluted solution (M_f)

Practice: Diluting Stock Solutions

Hydrochloric acid is obtained in 12.0 M stock solution. What volume of stock solution is required to make 500.0 mL of a 0.145 M dilute solution?

- Collect and Organize:
- Analyze:
- Solve:
- Think about It:

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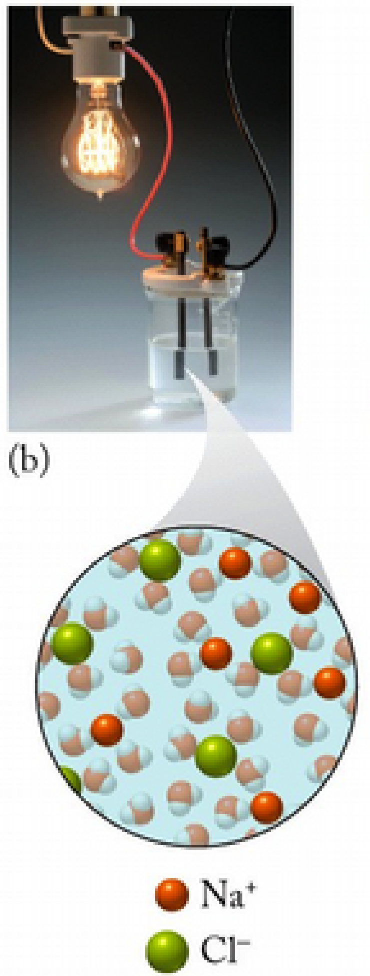
Electrolytes

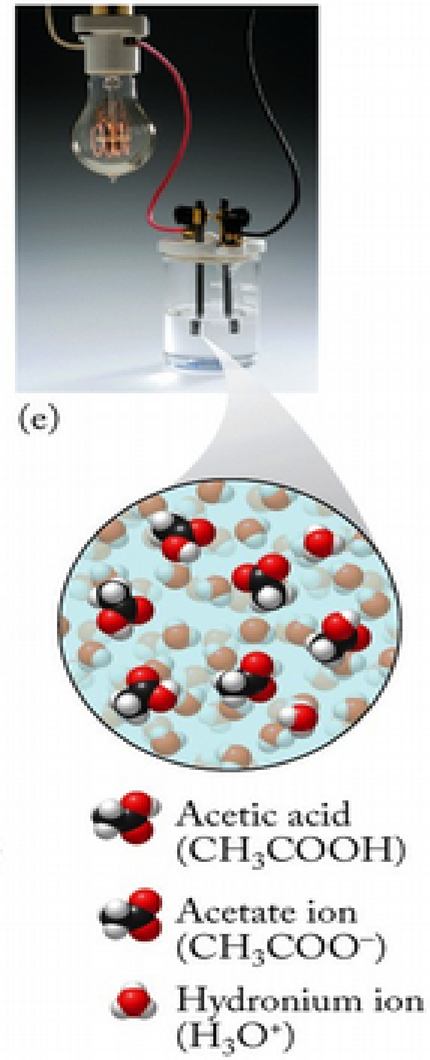
- Strong Electrolytes:
  - Nearly 100% dissociated into ions
  - Conduct current efficiently
- Examples: solutions of NaCl, HNO_3, HCl
  - NaCl → $Na^+(aq)$ + $Cl^-(aq)$



Electrolytes

- Weak Electrolytes:
  - Only partially dissociate into ions
  - Slightly conductive
- Examples: Vinegar (aq. solution of acetic acid); tap water.

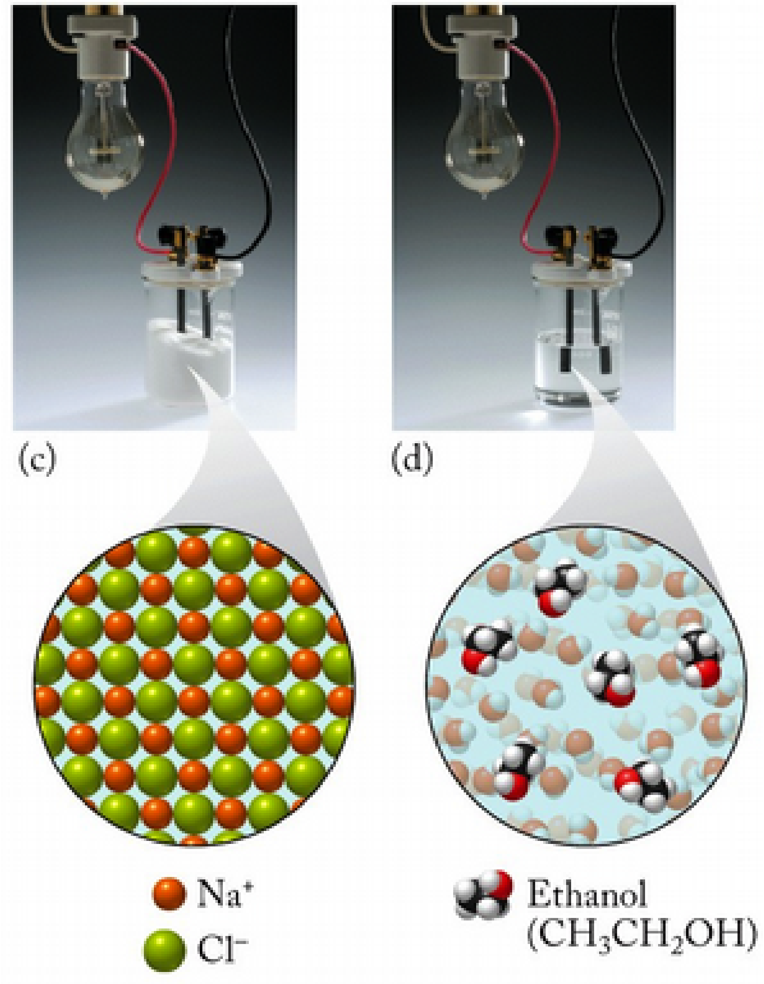
$$CH_3CO_2H \rightleftharpoons CH_3CO_2^-(aq) + H^+(aq)$$



Nonelectrolytes

Substances in which no ionization occurs; no conduction of electrical current

Examples: Aqueous solutions of sugar, ethanol, ethylene glycol; solid NaCl



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Acid–Base Reactions

- Arrhenius Definitions:
  - Acids: Produce H_3O^+ in solution
  - Bases: Produce OH^- in solution
  - $HCl\ (aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + Cl^-(aq)$
- H_3O^+ simplified by leaving out water, often written as just H^+

Acid–Base Reactions

- Brønsted–Lowry definitions:
  - Acids: Proton (H^+) donors
  - Bases: Proton acceptors
  - $HCl\,(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + Cl^-(aq)$

    HCl: proton donor (acid)

    H_2O: proton acceptor (base)
- H^+ ions strongly associated with water molecules → hydronium ions (H_3O^+)

Strong and Weak Acids

- Strong Acids/Bases:
  - Dissociate completely in aqueous solution (i.e., strong electrolytes)
- Strong Acids:
  - HCl, HBr, HI, H_2SO_4, HNO_3, $HClO_4$
- Examples:

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

$$HNO_2(aq) \rightleftharpoons H^+(aq) + NO_2^-(aq)$$

Strong and Weak Bases

- Strong Bases:
  - 1A, 2A hydroxides

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

- Weak Bases:

$$NH_3(aq) + H_2O(\ell) \rightleftharpoons NH_4^{+}(aq) + OH^{-}(aq)$$

Water: Acid or Base?

- Water as Base:
  - $HCl(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + Cl^-(aq)$

    Proton donor (acid) — Proton acceptor (base)
- Water as Acid:
  - $NH_3(aq) + H_2O(\ell) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

    Proton acceptor (base) — Proton donor (acid)
- **Amphiprotic:** Acts as acid or base

Acid-Base Reactions

- Neutralization: Reaction that takes place when an acid reacts with a base, producing a solution of a salt in water
- Salt:
  - Product of a neutralization reaction
  - Made up of the cation of the base plus the anion of the acid
- Example: $HCl + NaOH \rightarrow NaCl + H_2O$

Types of Equations

- **Molecular Equation:**
  - Reactants/products written as undissociated molecules

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(\ell)$$

- **Overall Ionic Equation:**
  - Distinguishes between molecular and ionic substances
  - Ionic species represented as dissolved ions.

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

Types of Equations

- **Net Ionic Equation:**
  - Equation where **spectator** ions (ions present in same form on both reactants and products side of chemical equation) are removed from ionic equation

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

Net Ionic Equation: $H^+(aq) + OH^-(aq) \longrightarrow H_2O(\ell)$

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Precipitation Reactions

- Precipitate: Solid product formed from a reaction in solution

  $AgNO_3(aq) + NaCl(aq) \rightarrow NaNO_3(aq) + AgCl(s)$

- Can predict formation of precipitates based on solubility "rules"
  - Precipitation reactions can be written using net ionic equations

Solubility Rules

- Soluble Cations:
  - Group I ions (alkali metals) and NH_4^+
- Soluble Anions:
  - NO_3^- and CH_3COO^- (acetate)
  - Halides (Group 17): Except Ag^+, Cu^+, Pb^{2+}, Hg_2^{2+}
  - Sulfates (SO_4^{2-}): Except Pb^{2+}, Hg_2^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}
- Combining anions/cations not listed above results in formation of an insoluble compound.

Insoluble Compounds

- All hydroxides (OH^-) except:
  - Group IA (e.g., NaOH) and IIA (e.g., $Ca(OH)_2$, $Sr(OH)_2$, and $Ba(OH)_2$)
- All sulfides (S^{2-}) except:
  - Group IA andNH_4^+; and CaS, SrS, BaS
- All carbonates (CO_3^{2-}) except IA, NH_4^+
- All phosphates (PO_4^{3-}) except IA, NH_4^+

Solubility Rules

TABLE 8.3 Solubility Rules for Ionic Compounds

All compounds containing the following ions are soluble in water: • Cations: group 1 ions (alkali metals) and NH_4^+ • Anions: NO_3^- and CH_3COO^- (acetate)
Compounds containing the following anions are soluble except as noted: • Group 17 ions (halides), except the halides of Ag^+, Cu^+, Hg_2^{2+}, and Pb^{2+} • SO_4^{2-}, except the sulfates of Ba^{2+}, Ca^{2+}, Hg_2^{2+}, Pb^{2+}, and Sr^{2+}
Compounds that are only slightly soluble include these: • All hydroxides except those of group 1 cations[a] • All sulfides except those of group 1 cations and NH_4^+[a] • All carbonates except those of group 1 cations and NH_4^+ • All phosphates except those of group 1 cations and NH_4^+
[a]The solubilities of the group 2 hydroxides and sulfides increase with increasing atomic number. MgS decomposes in water, forming H_2S and $Mg(OH)_2$.

Precipitation

Combining nonsoluble cation with nonsoluble anion → ppt!

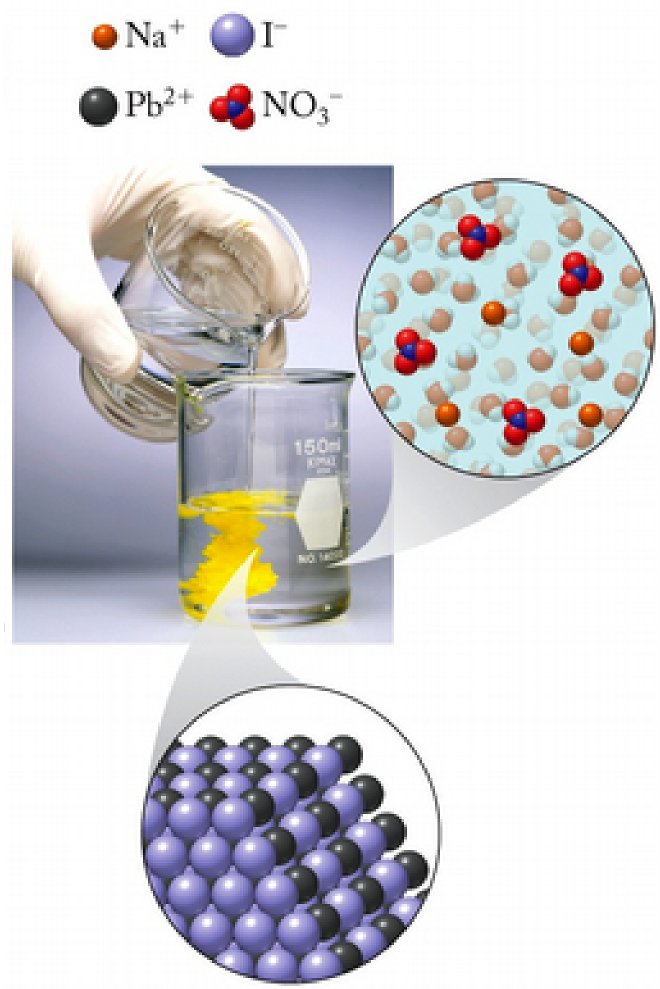
Example: $PbNO_{3}(aq)$ + $NaI(aq)$

Cations: Pb^{2+} ~~Na^{+}~~

Anions: ~~NO_{3}^{-}~~ I^{-}

Soluble Not soluble

Precipitate: $PbI_{2}(s)$



Net Ionic Equation

- Soluble ionic compounds
  - Strong electrolytes!

$Pb(NO_3)_2(aq) + 2NaI(aq) \rightarrow 2NaNO_3(aq) + PbI_2(s)$

- Overall Ionic Equation:

$Pb^{2+}(aq) + 2NO_3^-(aq) + 2Na^+(aq) + 2I^-(aq)$

$\rightarrow PbI_2(s) + 2Na^+(aq) + 2NO_3(aq)$

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

Practice: Will a Precipitate Form?

Does a precipitate form when sodium chloride is mixed with silver nitrate? If so, write the net ionic equation for the formation of the precipitate?

$$NaCl \rightarrow Na^+ + Cl^-$$

$$AgNO_3 \rightarrow Ag^+ + NO_3^-$$

- Collect and Organize:
- Analyze:
- Solve:
- Think about It:

Practice: Calculating Mass of Precipitate

What mass of barium sulfate is produced when 100.0 mL of a 0.100 *M* solution of barium chloride is mixed with 100.0 mL of a 0.100 *M* solution of iron (III) sulfate?

- Collect and Organize:
- Analyze:
- Solve:
- Think about It:

Types of Solutions

- **Saturated solution:** A solution that contains the maximum concentration of a solute possible at a given temperature
- **Supersaturated solution:** Contains more than the maximum quantity of solute predicted to be soluble in a given volume of solution at a given temperature

Supersaturated Solution

(a) (b) (c)

Sodium acetate precipitates from a supersaturated solution.

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Oxidation-Reduction Reactions

- **Oxidation:** Reaction that increases oxygen content of a substance (loss of electrons)
  - e.g., $4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$
- **Reduction:** Reaction involving loss of O_2 (gain of electrons)

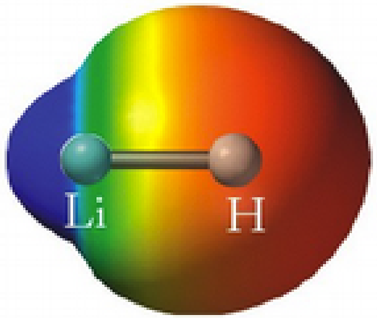
$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$$

- Redox reactions: Transfer of electrons

Oxidation Numbers (O.N.)

TABLE 8.4 Oxidation Number (O.N.) Assignment Rules

1. O.N. = 0 for atoms in pure elements.
2. O.N. = the charge of monatomic ions.
3. O.N. of fluorine = −1 in all of its compounds.
4. O.N. of oxygen = −2 in *nearly* all its compounds. Exceptions occur when O is bonded to fluorine (for example, OF_2), where its O.N. = +2, or when O is bonded to another O atom in a peroxide (for example, H_2O_2, where its O.N. = −1), or in a superoxide (for example, KO_2, where its O.N. = $-\frac{1}{2}$).
5. O.N. of hydrogen = +1 in *nearly* all its compounds. The exception is hydrogen in metal hydrides (for example, LiH), where H is the more electronegative element and its O.N. = −1.



6. O.N. values of the atoms in a neutral molecule sum to zero.
7. O.N. values of the atoms in a polyatomic ion sum to the charge on the ion.

Practice: Assigning Oxidation Numbers

Assign oxidation numbers to each element in the following compounds. (The first two are provided as examples.)

SO_2 Oxygen is -2 and Sulfur is +4.

CrO_4^{2-} Oxygen is -2 and Chromium is +6.

NH_3

ClO_3^-

SF_6

Cl_2

- Collect and Organize:
- Analyze:
- Solve:
- Think about It:

Redox Reactions: Electron Transfer

- Change in oxidation states results from gain or loss of electrons:

  +2 e^-

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

  - 2 e^-

- Zn: O.N. = 0 to +2; loss of 2 electrons; oxidation; reducing agent
- Cu: O.N. = +2 to 0; gain of 2 electrons; reduction, oxidizing agent

Balancing Redox Reactions

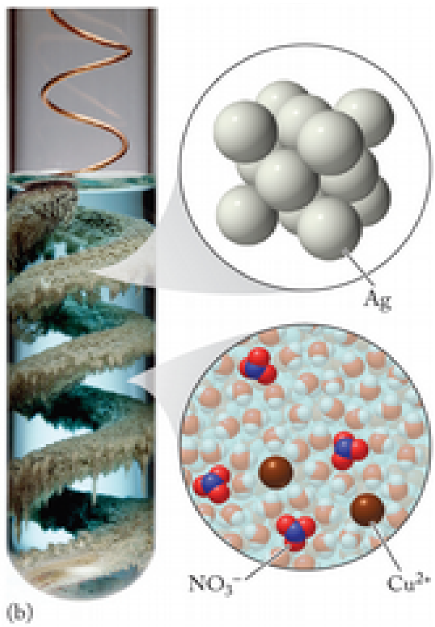
- Copper wire immersed in silver nitrate solution:

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

Can divide overall redox reaction into half-reactions:

Ox.: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$

Red.: $Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$



Half-Reaction Method

1. Write separate reduction, oxidation ½-reactions.
2. Balance number of particles in each ½-reaction.
3. Balance charge by adding electrons to the appropriate side.
4. Multiply ½-reactions by appropriate whole number to balance electrons.
5. Add ½-reactions to generate redox equation.

Practice: Balancing Redox Reactions

A nail made of Fe(s) that is placed in a solution of a soluble Pd^{2+} salt gradually disappears as the iron enters the solution as Fe^{3+}. Balance the redox reaction.

- Collect and Organize:
- Analyze:
- Solve:
- Think about It:

Redox in Nature

- Soil color influenced by mineral content
  - Iron(III): Red/orange minerals (yellow/orange in solution)
  - Iron(II): Blue/gray minerals (pale green in solution)
- Analysis of iron in minerals → redox rxn.
  - $Fe^{2+}(aq) + MnO_4^-(aq) \rightarrow Fe^{3+}(aq) + Mn^{2+}(aq)$

    (colorless) (deep purple) (yellow-orange) (pink)

Redox in Nature

- Balancing by ½-reaction method:
- Oxidation: $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + 1e^-$
- Reduction: $MnO_4^-(aq) \rightarrow Mn^{2+}(aq)$
  - Balance particles by adding H_2O, H^+:
  - $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(\ell)$
  - Balance e^-: multiply Fe ½-reaction × 5, add:

$$8H^+ + MnO_4^- + 5Fe^{2+} \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

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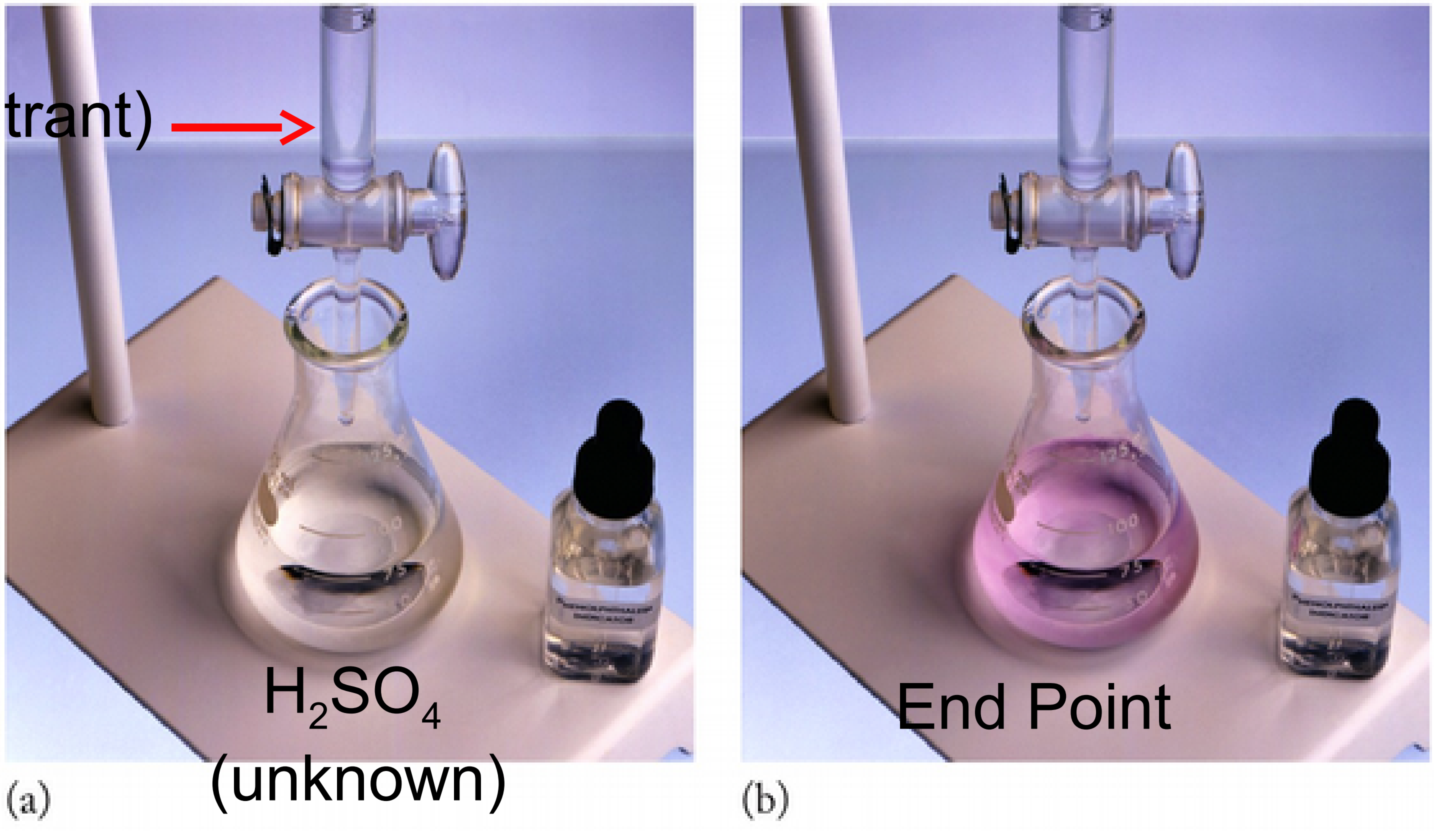
Key Titration Terms

- **Titration:** Analytical method to determine the concentration of a solute in a sample by reacting it with a standard solution
- **Standard Solution:** A solution of known concentration (also called the **titrant**)
- **Equivalence Point:** When moles of titrant is stoichiometrically equivalent to moles of the substance being analyzed
- **End Point:** When the indicator changes color

Titration Example

$$H_2SO_4 + 2\ NaOH \rightarrow Na_2SO_4 + 2\ H_2O$$



Stoichiometry Calculations

$$H_2SO_4 + 2\ NaOH \rightarrow Na_2SO_4 + 2\ H_2O$$

At the equivalence point:

$$\#\text{ moles } H_2SO_4 = (\#\text{ moles NaOH})/2$$

$$M_{acid} \cdot V_{acid} = (M_{base} \cdot V_{base})/(2)$$

Rearrange to find M_{acid}:

$$M_{acid} = (M_{base} \cdot V_{base})/(2)(V_{acid})$$

Practice: Acid–Base Titration

- What is the concentration of sulfuric acid if 15.00 mL of it reacts with 18.45 mL of a 0.0973 M NaOH solution?

  - Collect and Organize:
  - Analyze:
  - Solve:
  - Think about It:

Practice: Titration #2

If 30.34 mL of a 0.135 M solution of hydrochloric acid (HCl) were required to neutralize 25.00 mL of a sodium hydroxide (NaOH) solution, what is the molarity of the sodium hydroxide solution?

- Collect and Organize:
- Analyze:
- Solve:
- Think about It:

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Ion Exchange

- **Ion Exchange:** Process by which one ion is displaced by another
  - Important in purification/softening of water
- "Soft" metal ions (Na^+) exchanged for metals that contribute to "hard" water (Ca^{2+}, Mg^{2+})
  - Uses ion exchange resin or zeolites:

$$2(R\text{-}COO^- Na^+) + Ca^{2+} \rightarrow (RCOO^-)_2 Ca^{2+} + 2Na^+$$

Exchange resin

Zeolites: Natural Ion Exchangers

Zeolites

Natural crystalline minerals or synthetic materials consisting of a 3-D network of channels containing Na^+ or other +1 ion

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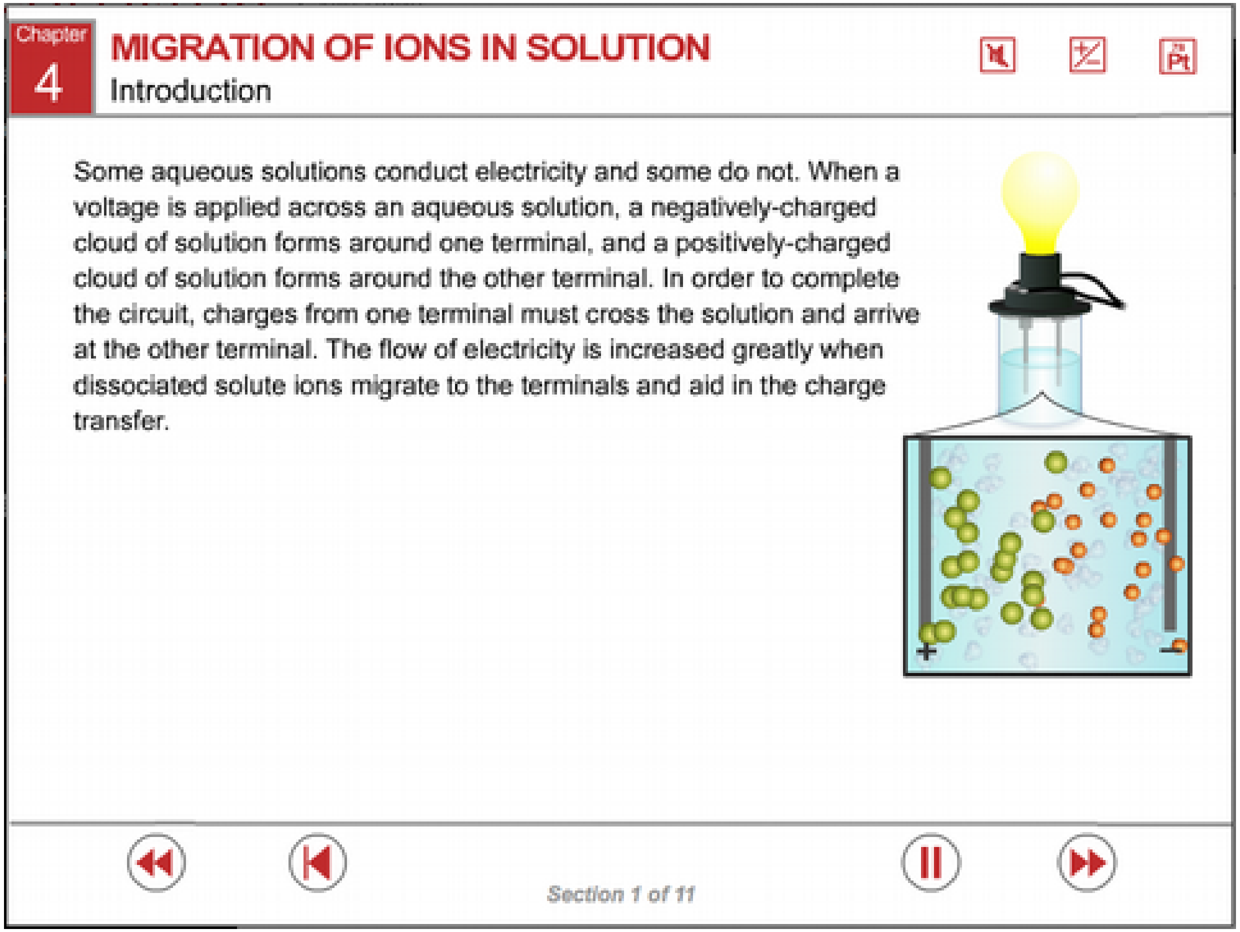

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