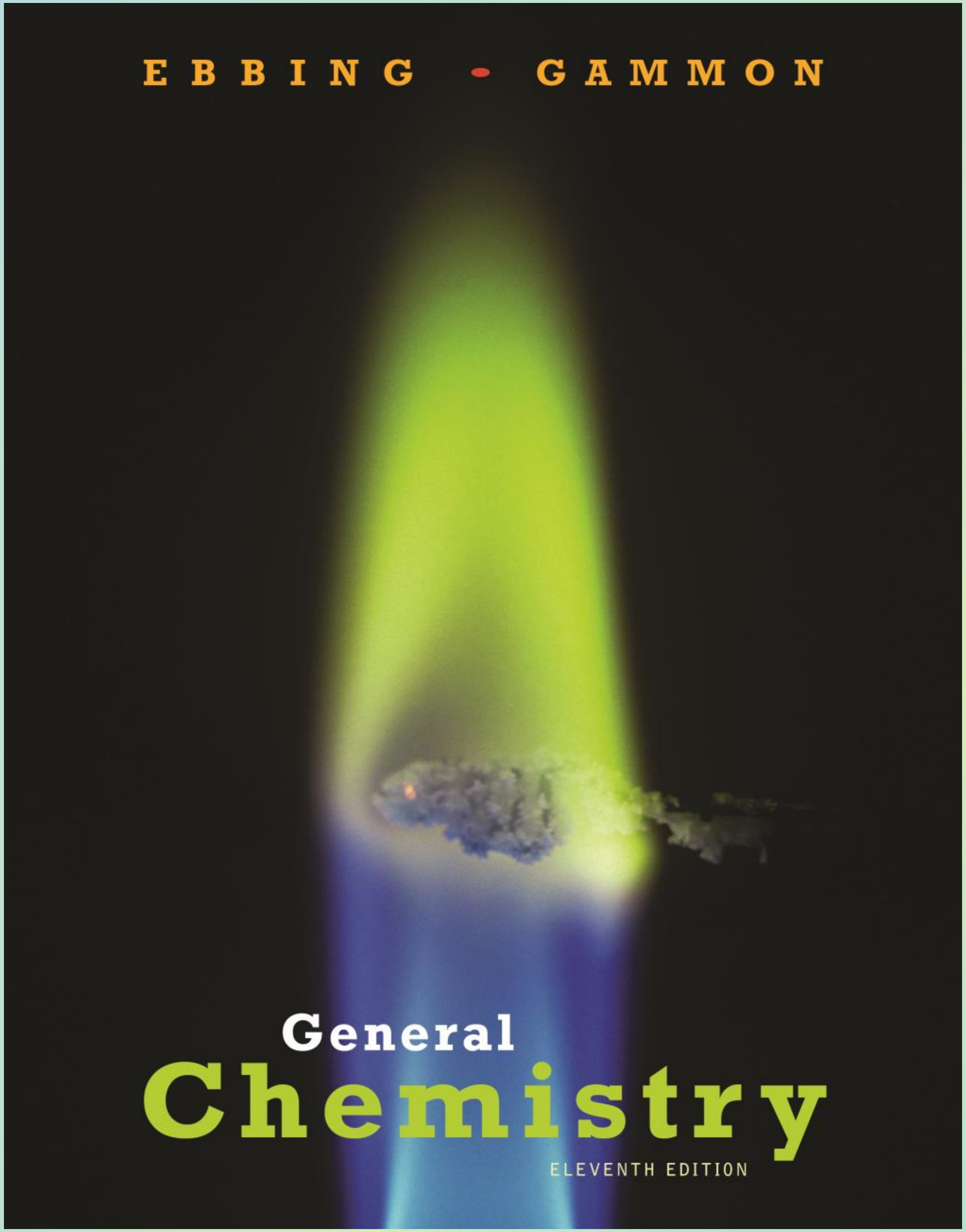


Chemical Reactions

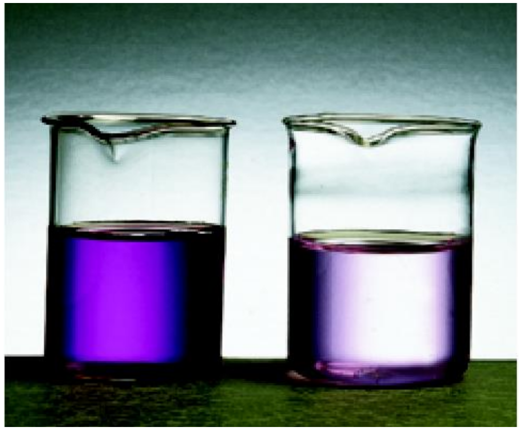
➢ Ions in Aqueous Solution

A ***solution*** is a homogenous mixture of 2 or more substances.

The ***solute*** is (are) the substance(s) present in the smaller amount(s).

The ***solvent*** is the substance present in the larger amount.

Solution	Solvent	Solute
Soft drink (*l*)	H_2O	Sugar, CO_2
Air (*g*)	N_2	O_2, Ar, CH_4
Soft solder (*s*)	Pb	Sn



aqueous solutions of $KMnO_4$

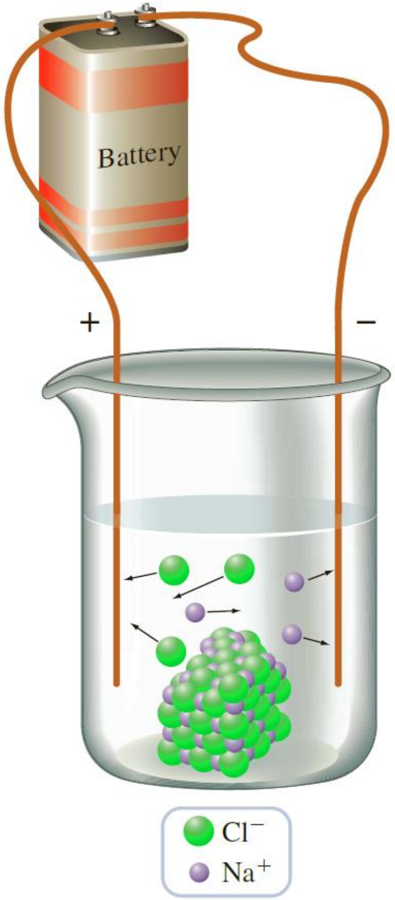
4.1 Ionic Theory of Solutions and Solubility Rules

- ✓ Arrhenius proposed the *ionic theory of solutions* to account for the conductivity of water solutions.

“Certain substances produce freely moving ions when they dissolve in water, and these ions conduct an electric current”

- ✓ Pure H_2O doesn’t contain ions → not conductive
- ✓ An aqueous solution of ions (aq) is conductive

- ➢ Electrolytes and Nonelectrolytes:



- ✓ An **electrolyte** is *a substance that dissolves in water to give an electrically conducting solution.*
- ✓ *ionic solids that dissolve in water are electrolytes.*
- ✓ Not all electrolytes are ionic substances
- ✓ molecular substances that dissolve in water **to form ions** *are electrolytes*

Electrolytes in Aqueous Solution

- Ionic compounds conduct electricity
- Molecular compounds don’t conduct electricity. Why**?**

Bright light

Ions present

Michael Watson

(*a*)

$CuSO_4$ and water

Michael Watson

(*b*)

Sugar and water

No light

Molecular

Ionic Compounds (Salts) in Water

- Water molecules arrange themselves around ions and remove them from lattice.

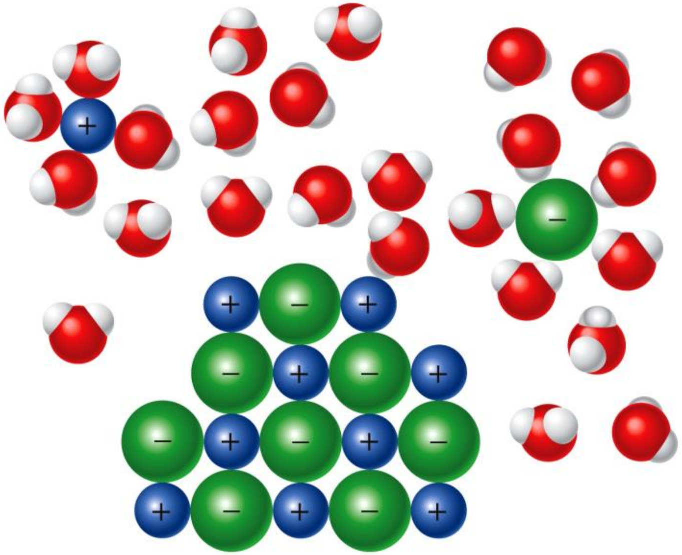
Dissociation

- Salts break apart into ions when entering solution

Separated ions

- **Hydrated**
- Conduct electricity

- **Note:** Polyatomic ions remain intact
  - **e.g.,** $KIO_3 \rightarrow K^+ + IO_3^-$



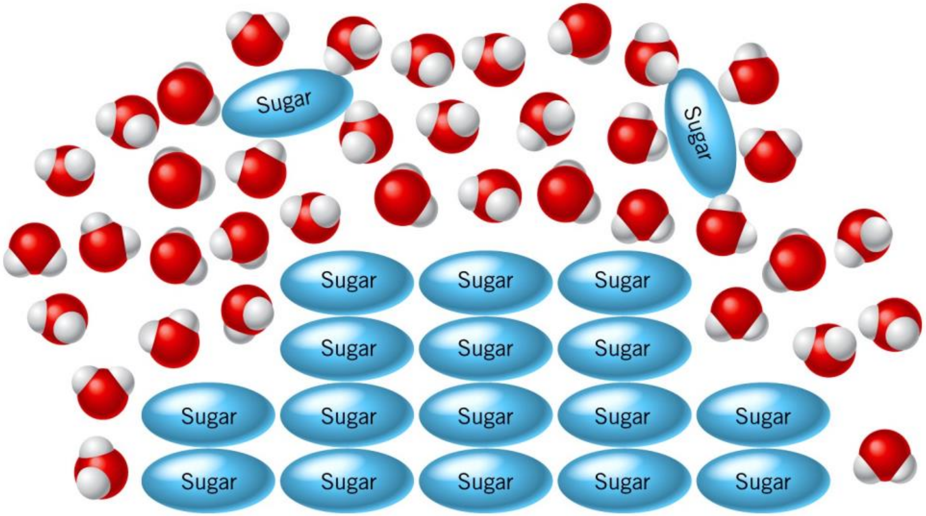
$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$

(Q)How many ions form on the dissociation of Na_3PO_4?

(Q)How many ions form on the dissociation of $Al_2(SO_4)_3$?

Molecular Compounds In Water

- When molecules dissolve in water
  - Solute particles are surrounded by water
  - Molecules do not dissociate



Electrical Conductivity

Electrolyte

–Solutes that yield electrically conducting solutions

–Separate into ions when enter into solution

Strong electrolyte

–Electrolyte that dissociates 100% in water

–Yields aqueous solution that conducts electricity

–Ionic compounds, **e.g.,** NaCl, KNO_3

–Strong acids and bases, **e.g.,** $HClO_4$, HCl

Non-electrolyte

–Aqueous solution that doesn't conduct electricity

–Molecules remain intact in solution **e.g.,** Sugar (glucose, sucrose), Alcohol(Methanol, ethanol), Urea

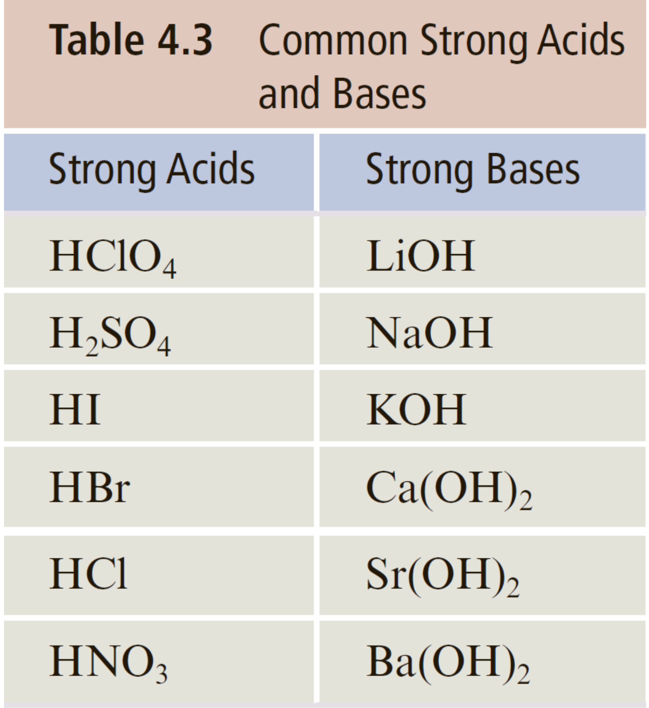


Table 4.3 Common Strong Acids and Bases

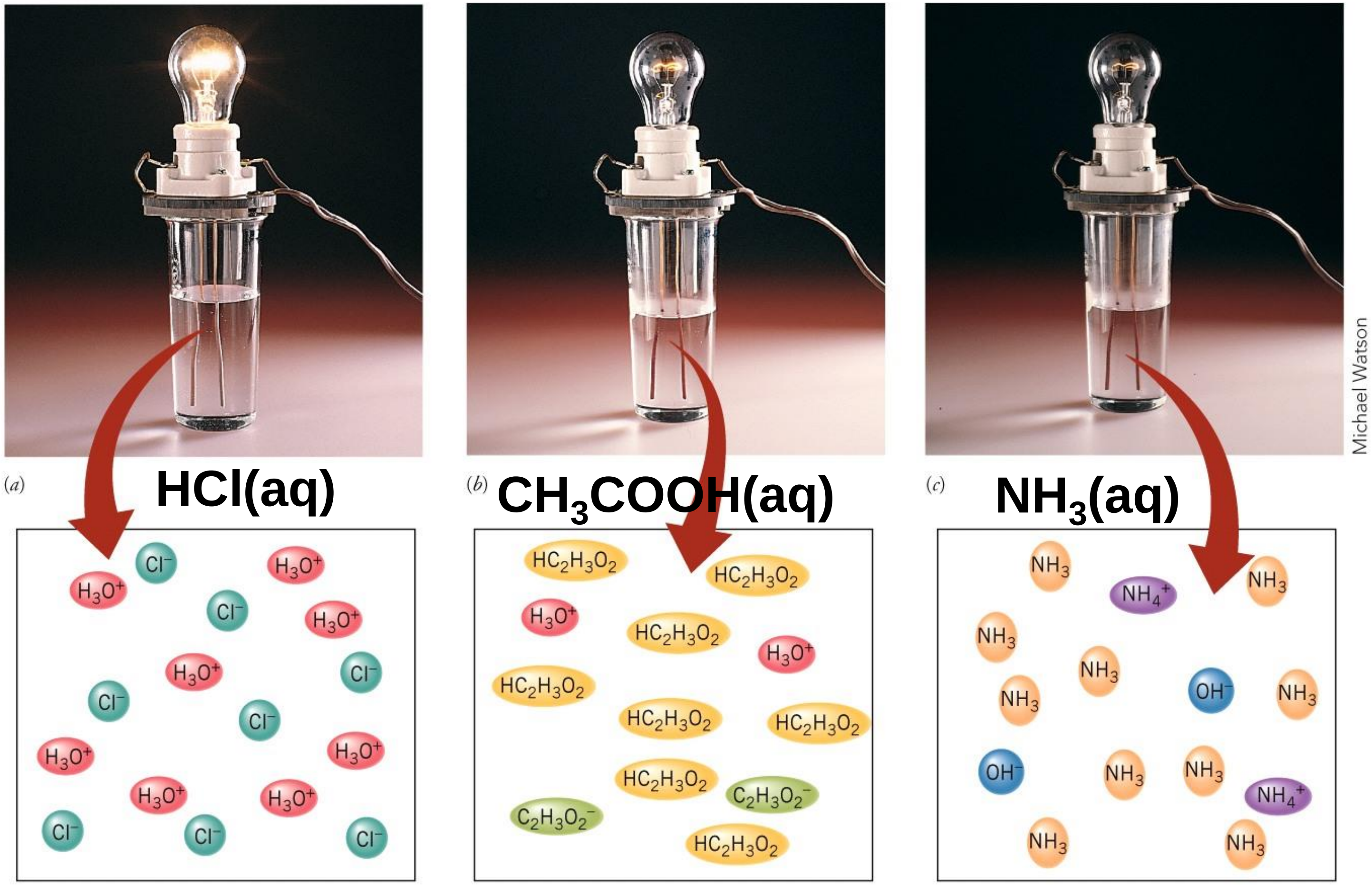
Strong Acids	Strong Bases
$HClO_4$	LiOH
H_2SO_4	NaOH
HI	KOH
HBr	$Ca(OH)_2$
HCl	$Sr(OH)_2$
HNO_3	$Ba(OH)_2$

Weak electrolyte

- When dissolved in water a small percentage of molecules ionize
- Common examples are **weak acids and bases**
- Solutions weakly conduct electricity
- **e.g.,** Acetic acid (CH_3COOH), ammonia (NH_3)

$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$

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



$HCl(aq)$

$CH_3COOH(aq)$

$NH_3(aq)$

Solubility Rules

- ✓ Soluble: NaCl, CH_3CH_2OH, CH_3OH
- ✓ Insoluble: benzene (C_6H_6), hexane (C_6H_{14})

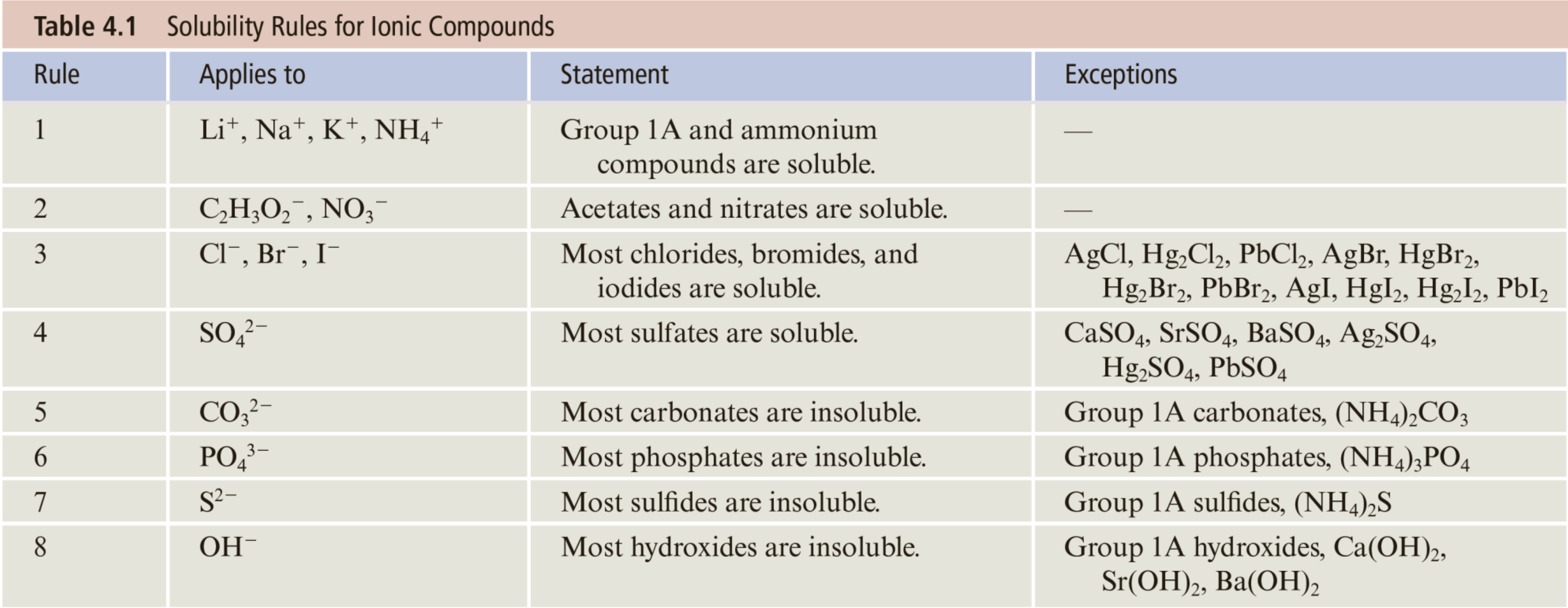


Table 4.1 Solubility Rules for Ionic Compounds

Rule	Applies to	Statement	Exceptions
1	Li^+, Na^+, K^+, NH_4^+	Group 1A and ammonium compounds are soluble.	—
2	$C_2H_3O_2^-$, NO_3^-	Acetates and nitrates are soluble.	—
3	Cl^-, Br^-, I^-	Most chlorides, bromides, and iodides are soluble.	AgCl, Hg_2Cl_2, $PbCl_2$, AgBr, $HgBr_2$, Hg_2Br_2, $PbBr_2$, AgI, HgI_2, Hg_2I_2, PbI_2
4	SO_4^{2-}	Most sulfates are soluble.	$CaSO_4$, $SrSO_4$, $BaSO_4$, Ag_2SO_4, Hg_2SO_4, $PbSO_4$
5	CO_3^{2-}	Most carbonates are insoluble.	Group 1A carbonates, $(NH_4)_2CO_3$
6	PO_4^{3-}	Most phosphates are insoluble.	Group 1A phosphates, $(NH_4)_3PO_4$
7	S^{2-}	Most sulfides are insoluble.	Group 1A sulfides, $(NH_4)_2S$
8	OH^-	Most hydroxides are insoluble.	Group 1A hydroxides, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$

(Q)Which of the following would you expect to be strong electrolyte when placed in water?

NH_4Cl, $MgBr_2$, H_2O, HCl, $Ca_3(PO_4)_2$, CH_3OH

Example 4.1 Determine whether the following compounds are soluble or insoluble in water.

a. Hg_2Cl_2 b. KI c. lead(II) nitrate

Which of the following compounds are expected to be soluble in water? a. $Ca(C_2H_3O_2)_2$ b. $FeCO_3$ c. AgCl

a. NaBr b. $Ba(OH)_2$ c. calcium carbonate d. Ag_2SO_4

4.2 Molecular and Ionic Equations

- Molecular Equation:

$$Ca(OH)_2(aq) + Na_2CO_3(aq) \longrightarrow CaCO_3(s) + 2NaOH(aq)$$

- Complete Ionic Equation:

$$Ca^{2+}(aq) + 2OH^-(aq) + 2Na^+(aq) + CO_3^{2-}(aq) \longrightarrow CaCO_3(s) + 2Na^+(aq) + 2OH^-(aq)$$

- Net Ionic Equation:

spectator ions: OH^- and Na^+

$$Ca^{2+}(aq) + \cancel{2OH^-(aq)} + \cancel{2Na^+(aq)} + CO_3^{2-}(aq) \longrightarrow CaCO_3(s) + \cancel{2Na^+(aq)} + \cancel{2OH^-(aq)}$$

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

- Molecular Equation:

$$Ca(NO_3)_2(aq) + K_2CO_3(aq) \longrightarrow CaCO_3(s) + 2KNO_3(aq)$$

- Complete Ionic Equation:

$$Ca^{2+}(aq) + \cancel{2NO_3^-(aq)} + \cancel{2K^+(aq)} + CO_3^{2-}(aq) \longrightarrow CaCO_3(s) + \cancel{2K^+(aq)} + \cancel{2NO_3^-(aq)}$$

- Net Ionic Equation:

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

Example 4.2 Writing Net Ionic Equations

a. $2HClO_4(aq) + Ca(OH)_2(aq) \longrightarrow Ca(ClO_4)_2(aq) + 2H_2O(l)$

$$2H^+(aq) + \cancel{2ClO_4^-(aq)} + \cancel{Ca^{2+}(aq)} + 2OH^-(aq) \longrightarrow \cancel{Ca^{2+}(aq)} + \cancel{2ClO_4^-(aq)} + 2H_2O(l)$$

$$\mathbf{H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)}$$

b. $HC_2H_3O_2(aq) + NaOH(aq) \longrightarrow NaC_2H_3O_2(aq) + H_2O(l)$

$$HC_2H_3O_2(aq) + \cancel{Na^+(aq)} + OH^-(aq) \longrightarrow \cancel{Na^+(aq)} + C_2H_3O_2^-(aq) + H_2O(l)$$

$$\mathbf{HC_2H_3O_2(aq) + OH^-(aq) \longrightarrow C_2H_3O_2^-(aq) + H_2O(l)}$$

c. $NH_3(aq) + HCl(aq) \longrightarrow NH_4Cl(aq)$

Ionic: $NH_3(aq) + H^+(aq) + Cl^-(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$

Net ionic: $NH_3(aq) + H^+(aq) \longrightarrow NH_4^+(aq)$

Write weak electrolytes in “molecular form”

✓ **Many ways to make PbI_2**

1. $Pb(NO_3)_2(aq) + 2KI(aq) \rightarrow PbI_2(s) + 2KNO_3(aq)$
2. $Pb(C_2H_3O_2)_2(aq) + 2NH_4I(aq) \rightarrow PbI_2(s) + 2NH_4C_2H_3O_2(aq)$

Different starting reagents Same net ionic equation

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

Exercise 4.2 Write complete ionic and net ionic equations for each of the following molecular equations.

a. $2HNO_3(aq) + Mg(OH)_2(s) \rightarrow 2H_2O(l) + Mg(NO_3)_2(aq)$

Ionic:

$2H^+(aq) + 2NO_3^-(aq) + Mg(OH)_2(s) \rightarrow 2H_2O(l) + Mg^{2+}(aq) + 2NO_3^-(aq)$

Net Ionic:

$2H^+(aq) + Mg(OH)_2(s) \rightarrow 2H_2O(l) + Mg^{2+}(aq)$

b. $Pb(NO_3)_2(aq) + Na_2SO_4(aq) \rightarrow PbSO_4(s) + 2NaNO_3(aq)$

Ionic:

$Pb^{2+}(aq) + 2NO_3^-(aq) + 2Na^+(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2Na^+(aq) + 2NO_3^-(aq)$

Net Ionic:

$Pb^{2+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s)$

(Q) Write the correct ionic equation for each:

$Pb(NO_3)_2(aq) + 2NH_4IO_3(aq) \rightarrow Pb(IO_3)_2(s) + 2NH_4NO_3(aq)$

$Pb^{2+}(aq) + 2NO_3^{-}(aq) + 2NH_4^{+}(aq) + 2IO_3^{-}(aq) \rightarrow$

$Pb(IO_3)_2(s) + 2NH_4^{+}(aq) + 2NO_3^{-}(aq)$

$2NaCl\ (aq) + Hg_2(NO_3)_2\ (aq) \rightarrow 2NaNO_3\ (aq) + Hg_2Cl_2\ (s)$

$2Na^{+}(aq) + 2Cl^{-}(aq) + Hg_2^{2+}(aq) + 2NO_3^{-}(aq) \rightarrow$

$2Na^{+}(aq) + 2NO_3^{-}(aq) + Hg_2Cl_2(s)$

(Q) Consider the following reaction :

$Na_2SO_4(aq) + BaCl_2(aq) \rightarrow 2NaCl(aq) + BaSO_4(s)$

Write the correct **ionic** equation.

A. $2Na^+(aq) + SO_4^{2-}(aq) + Ba^{2+}(aq) + Cl_2^{2-}(aq) \rightarrow 2Na^+(aq) + 2Cl^-(aq) + BaSO_4(s)$

B. $2Na^+(aq) + SO_4^{2-}(aq) + Ba^{2+}(aq) + 2Cl^-(aq) \rightarrow 2Na^+(aq) + 2Cl^-(aq) + BaSO_4(s)$

C. $2Na^+(aq) + SO_4^{2-}(aq) + Ba^{2+}(aq) + Cl_2^{2-}(aq) \rightarrow 2Na^+(aq)+ 2Cl^-(aq) + Ba^{2+}(s) + SO_4^{2-}(s)$

D. $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$

E. $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow Ba^{2+}(s) + SO_4^{2-}(s)$

Consider the following molecular equation:

$$(NH_4)_2SO_4(aq) + Ba(CH_3CO_2)_2(aq) \rightarrow 2NH_4CH_3CO_2(aq) + BaSO_4(s)$$

Write the correct **net** ionic equation.

A. $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$

B. $2NH_4^+(aq) + 2CH_3CO_2^-(aq) \rightarrow 2NH_4CH_3CO_2(s)$

C. $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(aq)$

D. $2NH_4^+(aq) + Ba^{2+}(aq) + SO_4^{2-}(aq) + 2CH_3CO_2^-(aq) \rightarrow 2NH_4^+(aq) + 2CH_3CO_2^-(aq) + BaSO_4(s)$

E. $2NH_4^+(aq) + 2CH_3CO_2^-(aq) \rightarrow 2NH_4CH_3CO_2(aq)$

What is the net ionic equation for the following reaction?

Molecular equation

$Mg(OH)_2(s) + 2HC_2H_3O_2(aq) \longrightarrow$

$Mg(C_2H_3O_2)_2(aq) + 2H_2O$

Ionic equation

$Mg(OH)_2(s) + 2HC_2H_3O_2(aq) \longrightarrow$

$Mg^{2+}(aq) + 2H_2O + 2C_2H_3O_2^{-}(aq)$

- There are NO spectator ions!
- So net ionic and ionic equations are the ***same***

➢ Types of Chemical Reactions

1. Precipitation reactions. In these reactions, you mix solutions of two ionic substances, and a solid ionic substance (a precipitate) forms.

2. Acid–base reactions. An acid substance reacts with a substance called a base. Such reactions involve the transfer of a proton between reactants.

3. Oxidation–reduction reactions. These involve the transfer of electrons between reactants.

4.3 Precipitation Reactions

- ✓ A precipitation reaction occurs in aqueous solution because one product is insoluble.

$$MgCl_2(aq) + 2AgNO_3(aq) \rightarrow 2AgCl(s) + Mg(NO_3)_2(aq)$$

- ✓ An **exchange (**or **metathesis) reaction** is *a reaction between compounds that, when written as a molecular equation, appears to involve the exchange of parts between the two reactants*

Example 4.3 Deciding Whether a Precipitation Reaction Occurs

For each of the following, decide whether a precipitation reaction occurs. If it does, write the balanced molecular equation and then the net ionic equation. If no reaction occurs, write the compounds followed by an arrow and then *NR* (no reaction).

a. Aqueous solutions of sodium chloride and iron(II) nitrate are mixed.

$NaCl + Fe(NO_3)_2 \rightarrow NaNO_3 + FeCl_2$ (not balanced)

$2NaCl + Fe(NO_3)_2 \rightarrow 2NaNO_3 + FeCl_2$ (balanced)

soluble soluble soluble soluble

$2Na^+ + 2Cl^- + Fe^{2+} + 2NO_3^- \rightarrow 2Na^+ + 2NO_3^- + Fe^{2+} + 2Cl^-$

$\mathbf{NaCl(\mathit{aq}) + Fe(NO_3)_2(\mathit{aq}) \rightarrow NR}$

b. Aqueous solutions of aluminum sulfate and sodium hydroxide are mixed.

$$Al_2(SO_4)_3 + NaOH \rightarrow Al(OH)_3 + Na_2SO_4 \quad \text{(not balanced)}$$

$$Al_2(SO_4)_3 + 6NaOH \rightarrow 2Al(OH)_3 + 3Na_2SO_4 \qquad \text{(balanced)}$$

$$2Al^{3+}(aq) + \cancel{3SO_4^{2-}(aq)} + \cancel{6Na^{+}(aq)} + 6OH^{-}(aq) \longrightarrow 2Al(OH)_3(s) + \cancel{6Na^{+}(aq)} + \cancel{3SO_4^{2-}(aq)}$$

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

4.4 Acid–Base Reactions

- ✓ Acids have sour taste. Bases have bitter taste & soapy feel.
- ✓ An **acid–base indicator** is *a dye used to distinguish between acidic and basic solutions by means of color change*
- ✓ Litmus: in acidic solution = red & in basic solution = blue
- ✓ Phenolphthalein: in acidic solution = colorless & in basic solution = pink

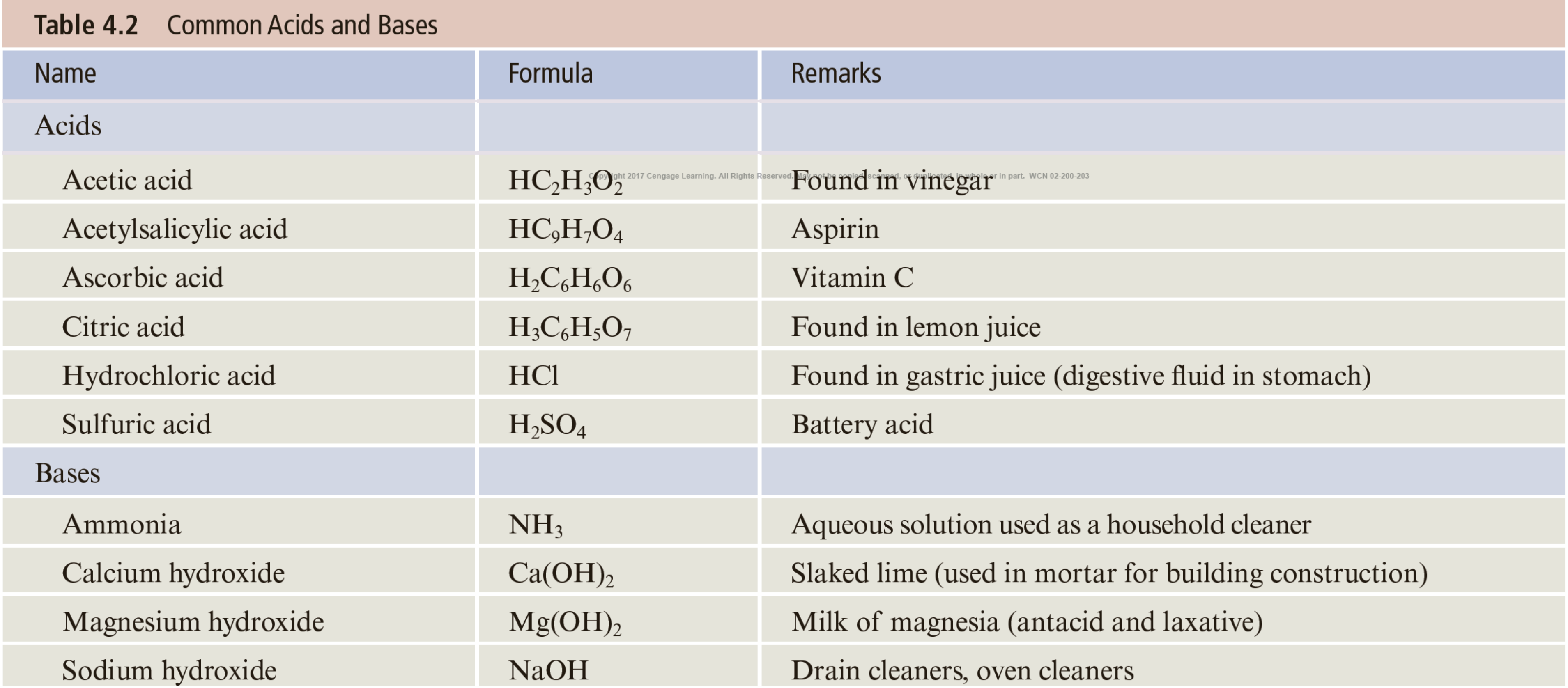


Table 4.2 Common Acids and Bases

Name	Formula	Remarks
Acids		
Acetic acid	$HC_2H_3O_2$	Found in vinegar
Acetylsalicylic acid	$HC_9H_7O_4$	Aspirin
Ascorbic acid	$H_2C_6H_6O_6$	Vitamin C
Citric acid	$H_3C_6H_5O_7$	Found in lemon juice
Hydrochloric acid	HCl	Found in gastric juice (digestive fluid in stomach)
Sulfuric acid	H_2SO_4	Battery acid
Bases		
Ammonia	NH_3	Aqueous solution used as a household cleaner
Calcium hydroxide	$Ca(OH)_2$	Slaked lime (used in mortar for building construction)
Magnesium hydroxide	$Mg(OH)_2$	Milk of magnesia (antacid and laxative)
Sodium hydroxide	$NaOH$	Drain cleaners, oven cleaners

➢ Definitions of Acid and Base

- ✓ Arrhenius **acid**: *a substance that produces hydrogen ions,* H^+, *when it dissolves in water.*

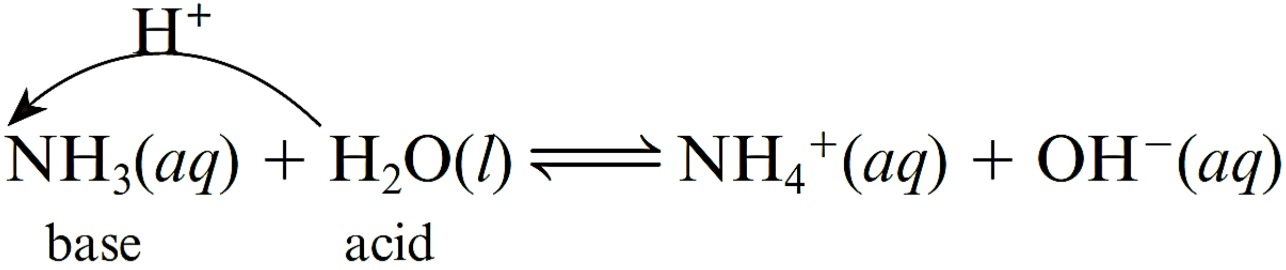
$$HNO_3(aq) \xrightarrow{H_2O} H^+(aq) + NO_3^-(aq)$$

- ✓ Arrhenius **base:** *a substance that produces hydroxide ions,* OH^-, *when it dissolves in water.*

$$NaOH(s) \xrightarrow{H_2O} Na^+(aq) + OH^-(aq)$$

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

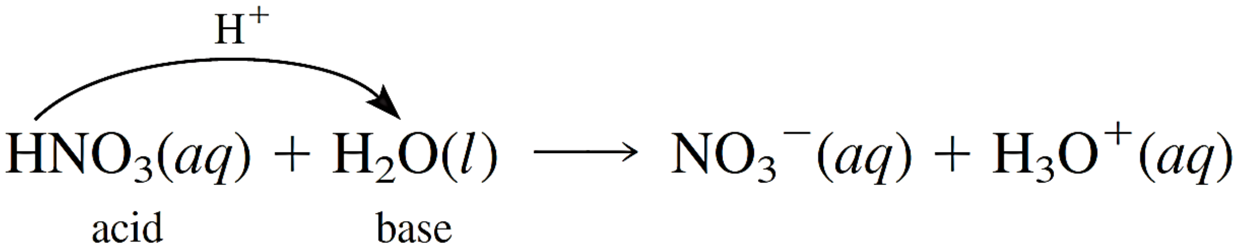
- ✓ Brønsted and Lowry **acid:** *a species (molecule or ion) that donates a* ***proton*** *to another species in a proton-transfer reaction*
- ✓ Brønsted and Lowry **base:** *a species (molecule or ion) that accepts a* ***proton*** *from another species.*



$$\underset{\text{base}}{NH_3(aq)} + \underset{\text{acid}}{H_2O(l)} \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

- ✓ The dissolution of HNO_3 in water is actually a proton-transfer reaction.

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



$$\underset{\text{acid}}{HNO_3(aq)} + \underset{\text{base}}{H_2O(l)} \longrightarrow NO_3^-(aq) + H_3O^+(aq)$$

Hydronium ion

- ✓ The Arrhenius definitions and those of Brønsted and Lowry are essentially equivalent for aqueous solutions

- ✓ NaOH and NH_3 are bases in the Arrhenius view because they increase the percentage of OH^- ion in the aqueous solution.

- ✓ NaOH and NH_3 are bases in the Brønsted–Lowry view because they provide species that can accept protons.

Strong and Weak Acids and Bases

- ✓ A **strong acid or base** *ionizes completely in water.*
- ✓ A **weak acid or base** *only partly ionizes in water.*

$$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$$

$$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$$

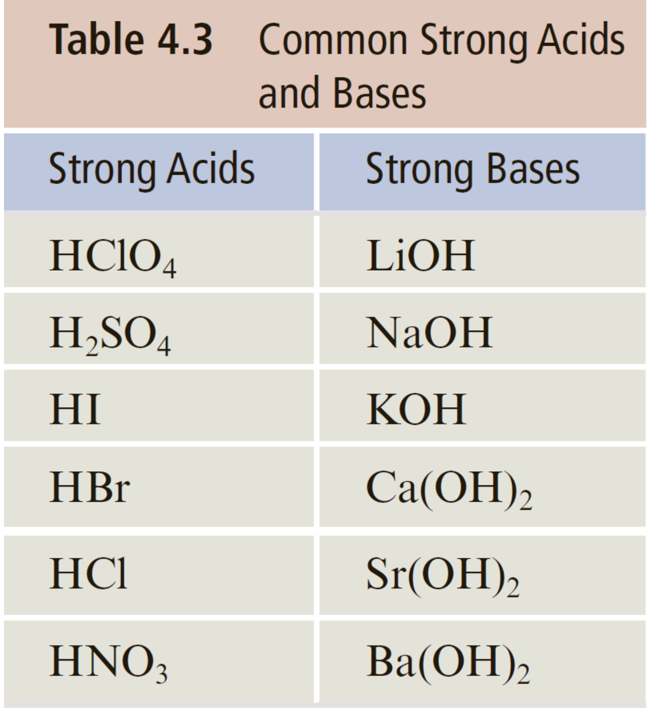


Table 4.3 Common Strong Acids and Bases

Strong Acids	Strong Bases
$HClO_4$	$LiOH$
H_2SO_4	$NaOH$
HI	KOH
HBr	$Ca(OH)_2$
HCl	$Sr(OH)_2$
HNO_3	$Ba(OH)_2$

$$NaOH(s) \xrightarrow{H_2O} Na^+(aq) + OH^-(aq)$$

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

- ✓ The hydroxides of Groups 1A and 2A elements are strong bases. **Except** for beryllium hydroxide ($Be(OH)_2$)
- ✓ Some weak acids: CH_3COOH, HNO_2, $HClO$, H_3PO_4,

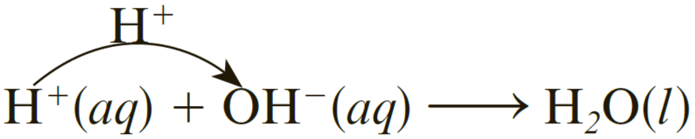
➢ Neutralization Reactions

- ✓ A **neutralization reaction** is *a reaction of an acid and a base that results in an ionic compound (salt) and possibly water.*
- ✓ Most ionic compounds other than hydroxides & oxides are salts

$$\underset{\text{acid}}{2HCl(aq)} + \underset{\text{base}}{Ca(OH)_2(aq)} \longrightarrow \underset{\text{salt}}{CaCl_2(aq)} + 2H_2O(l)$$

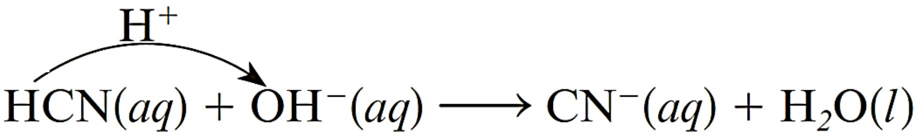
Driving force of reaction

$$2H^+(aq) + \cancel{2Cl^-(aq)} + \cancel{Ca^{2+}(aq)} + 2OH^-(aq) \longrightarrow \cancel{Ca^{2+}(aq)} + \cancel{2Cl^-(aq)} + 2H_2O(l)$$



$$H^+(aq) + OH^-(aq) \xrightarrow{} H_2O(l)$$

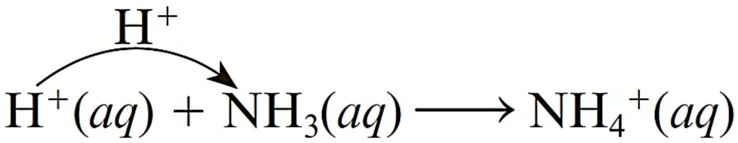
$$\underset{\text{acid}}{HCN(aq)} + \underset{\text{base}}{KOH(aq)} \longrightarrow \underset{\text{salt}}{KCN(aq)} + H_2O(l)$$



$$HCN(aq) + OH^-(aq) \longrightarrow CN^-(aq) + H_2O(l)$$

Reactions with NH_3
Do not produce
H_2O

$$\underset{\text{acid}}{H_2SO_4(aq)} + \underset{\text{base}}{2NH_3(aq)} \longrightarrow \underset{\text{salt}}{(NH_4)_2SO_4(aq)}$$



$$H^+(aq) + NH_3(aq) \longrightarrow NH_4^+(aq)$$

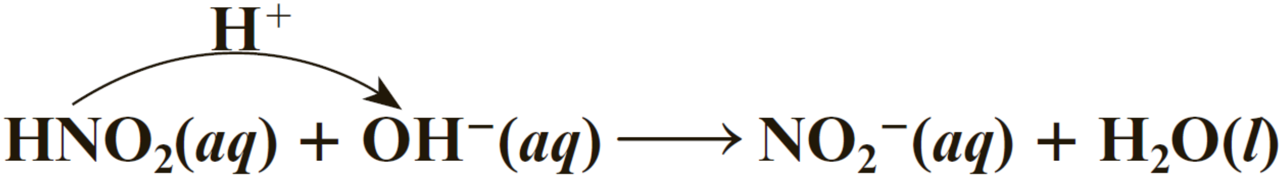
Example 4.5 Writing an Equation for a Neutralization

(Q)Write the molecular equation and then the net ionic equation for the neutralization of nitrous acid by sodium hydroxide, both in aqueous solution.

$$\mathrm{HNO_2}(aq) + \mathrm{NaOH}(aq) \longrightarrow \mathrm{NaNO_2}(aq) + \mathrm{H_2O}(l) \qquad \textbf{(molecular equation)}$$

$$\mathrm{HNO_2}(aq) + \cancel{\mathrm{Na^+}(aq)} + \mathrm{OH^-}(aq) \longrightarrow \cancel{\mathrm{Na^+}(aq)} + \mathrm{NO_2^-}(aq) + \mathrm{H_2O}(l)$$

$$\textbf{(net ionic equation)} \quad \mathrm{HNO_2}(aq) + \mathrm{OH^-}(aq) \longrightarrow \mathrm{NO_2^-}(aq) + \mathrm{H_2O}(l)$$



$$\mathrm{HNO_2}(aq) + \mathrm{OH^-}(aq) \longrightarrow \mathrm{NO_2^-}(aq) + \mathrm{H_2O}(l)$$

Exercise 4.5 Write the molecular equation and the net ionic equation for the neutralization of hydrocyanic acid, HCN, by lithium hydroxide, $LiOH$, both in aqueous solution

Exercise 4.6 Write molecular and net ionic equations for the successive neutralizations of each of the acidic hydrogens of sulfuric acid with potassium hydroxide.

- *monoprotic* acids: one acidic hydrogen; HCl, HNO_3
- *polyprotic* acids: *two or more acidic hydrogens;* H_2SO_4, H_3PO_4
- H_3PO_4 : triprotic acid
- By reacting this acid with different amounts of a base, you can obtain a series of salts:

$$H_3PO_4(aq) + NaOH(aq) \longrightarrow NaH_2PO_4(aq) + H_2O(l)$$

$$H_3PO_4(aq) + 2NaOH(aq) \longrightarrow Na_2HPO_4(aq) + 2H_2O(l)$$

$$H_3PO_4(aq) + 3NaOH(aq) \longrightarrow Na_3PO_4(aq) + 3H_2O(l)$$

- Salts such as NaH_2PO_4 and Na_2HPO_4 that have acidic hydrogen atoms and can undergo neutralization with bases are called ***acid salts***

➢ Acid–Base Reactions with Gas Formation

$$Na_2CO_3(aq) + 2HCl(aq) \longrightarrow 2NaCl(aq) + \underbrace{H_2O(l) + CO_2(g)}_{H_2CO_3(aq)}$$

Net ionic eqn. $$CO_3^{2-}(aq) + 2H^+(aq) \longrightarrow H_2O(l) + CO_2(g)$$

$$\overset{\overset{2H^+}{\curvearrowleft}}{CO_3^{2-}(aq) + 2H_3O+(aq)} \longrightarrow H_2CO_3(aq) + 2H_2O(l) \longrightarrow 3H_2O(l) + CO_2(g)$$

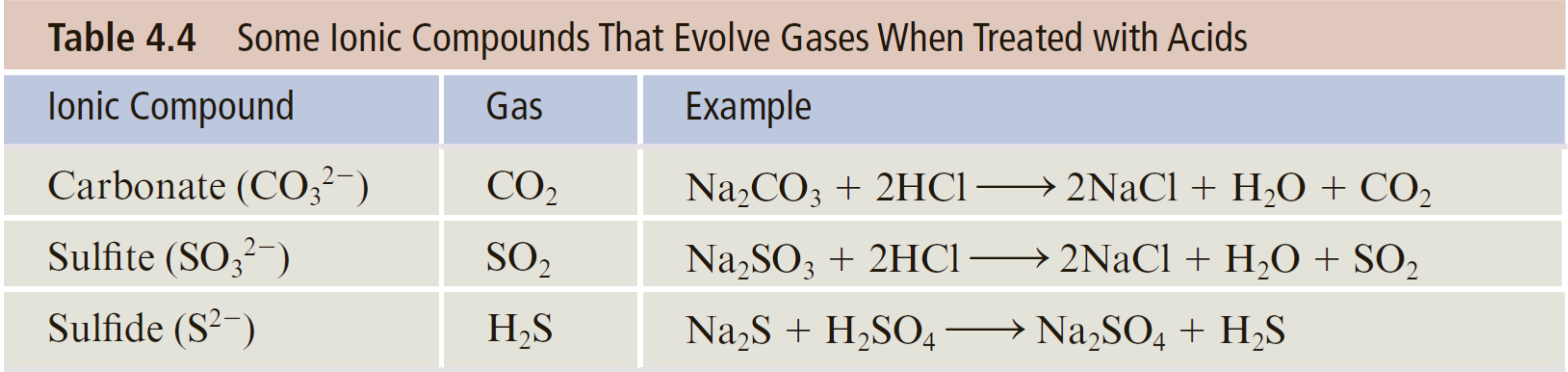


Table 4.4 Some Ionic Compounds That Evolve Gases When Treated with Acids

Ionic Compound	Gas	Example
Carbonate (CO_3^{2-})	CO_2	$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$
Sulfite (SO_3^{2-})	SO_2	$Na_2SO_3 + 2HCl \longrightarrow 2NaCl + H_2O + SO_2$
Sulfide (S^{2-})	H_2S	$Na_2S + H_2SO_4 \longrightarrow Na_2SO_4 + H_2S$

Example 4.6 Writing an Equation for a Reaction with Gas Formation

(Q)Write the molecular equation and the net ionic equation for the reaction of zinc sulfide with hydrochloric acid.

$$\mathbf{ZnS(\mathit{s}) + 2HCl(\mathit{aq}) \longrightarrow ZnCl_2(\mathit{aq}) + H_2S(\mathit{g})}$$

$$ZnS(s) + 2H^+(aq) + \cancel{2Cl^-(aq)} \longrightarrow Zn^{2+}(aq) + \cancel{2Cl^-(aq)} + H_2S(g)$$

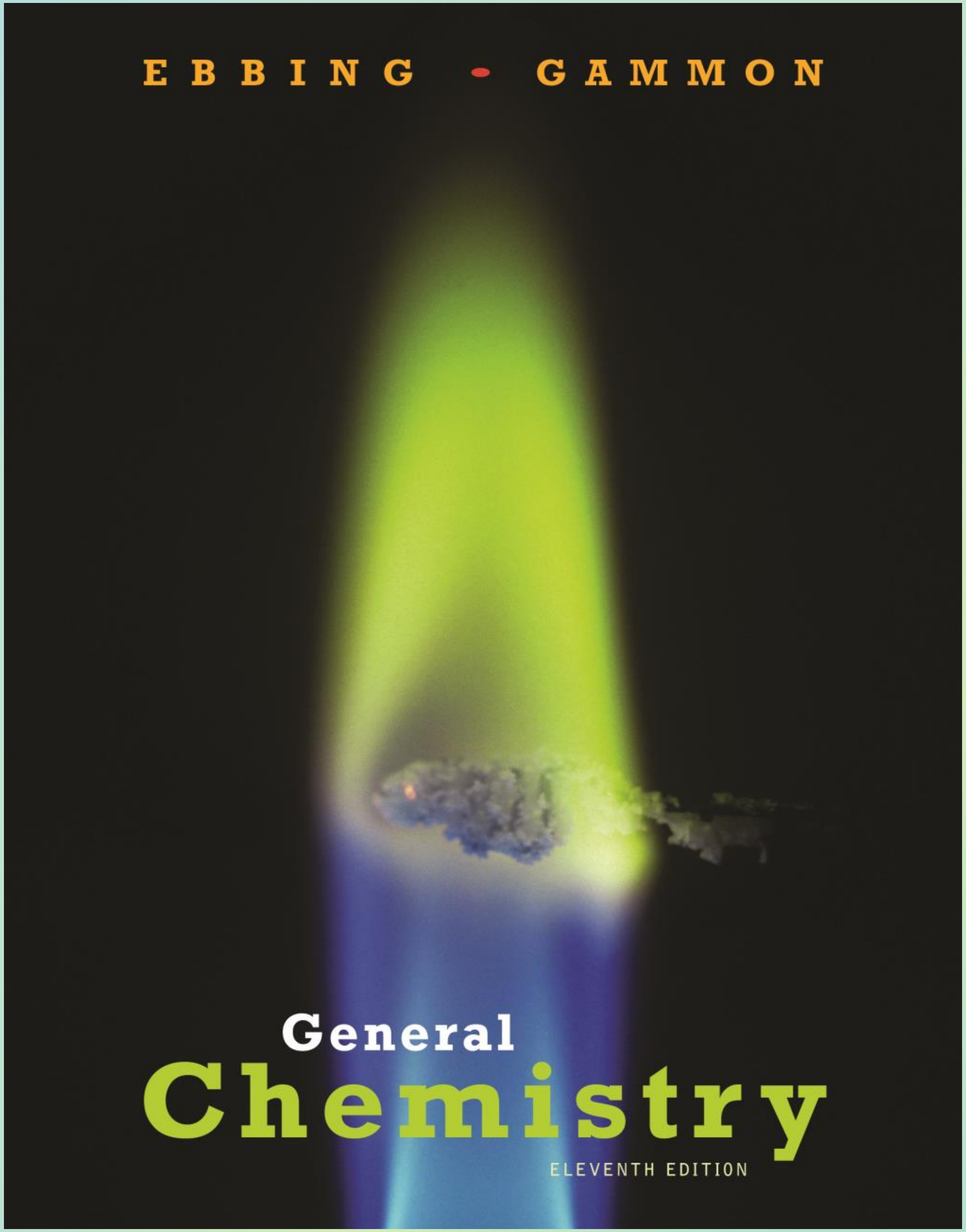
$$\mathbf{ZnS(\mathit{s}) + 2H^+(\mathit{aq}) \longrightarrow Zn^{2+}(\mathit{aq}) + H_2S(\mathit{g})}$$

Exercise 4.7 Write the molecular equation and the net ionic equation for the reaction of calcium carbonate with nitric acid.

$CaCO_3$ (s)+ $2HNO_3$ (aq) → $Ca(NO_3)_2$ (aq)+ H_2CO_3 (aq)

$CaCO_3$(s)+ $2H^+$(aq) +$2NO_3^-$(aq) →
Ca^{2+} + $2NO_3^-$(aq)+ H_2O(l) + CO_2(g)

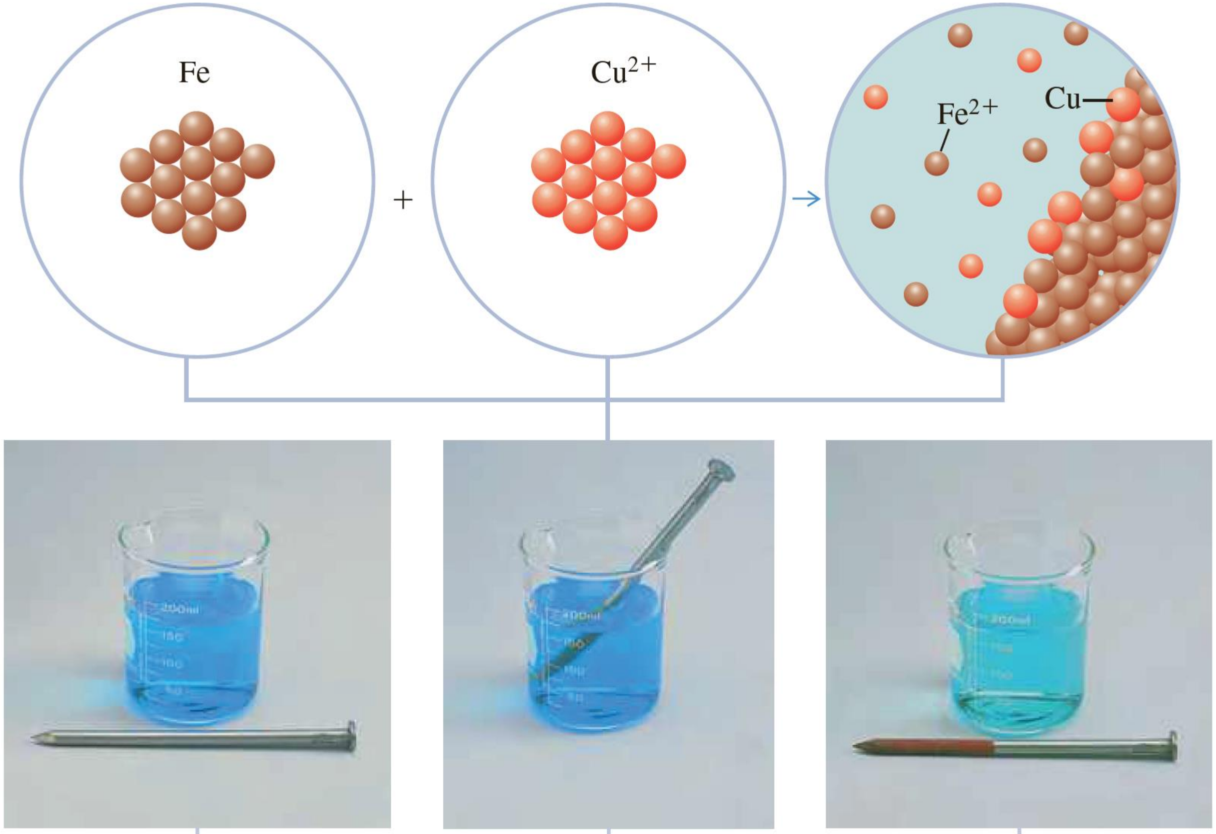
$CaCO_3$(s)+ $2H^+$(aq) → Ca^{2+} + H_2O(l) + CO_2(g)



Chemical Reactions

4.5 Oxidation–Reduction Reactions

$$Fe(s) + CuSO_4(aq) \rightarrow FeSO_4(aq) + Cu(s)$$



Iron nail and copper(II) sulfate solution, which has a blue color.

Fe reacts with $Cu^{2+}(aq)$ to yield $Fe^{2+}(aq)$ and Cu(s). The molecular view above the pictures depicts the net ionic equation; water and the sulfate anion have been omitted.

The copper metal forms a coating on the nail.

$$Fe(s) + CuSO_4(aq) \rightarrow FeSO_4(aq) + Cu(s)$$

The net ionic equation is:

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

- **Oxidation Numbers**

an **oxidation–reduction reaction** (or **redox reaction**) is *a reaction in which electrons are transferred between species or in which atoms change oxidation number.*

Formerly, the term *oxidation* meant “reaction with oxygen.”

$$2Ca(s) + O_2(g) \rightarrow 2CaO(s)$$

$$Ca(s) + Cl_2(g) \rightarrow CaCl_2(s)$$

➢ Oxidation-Number Rules:

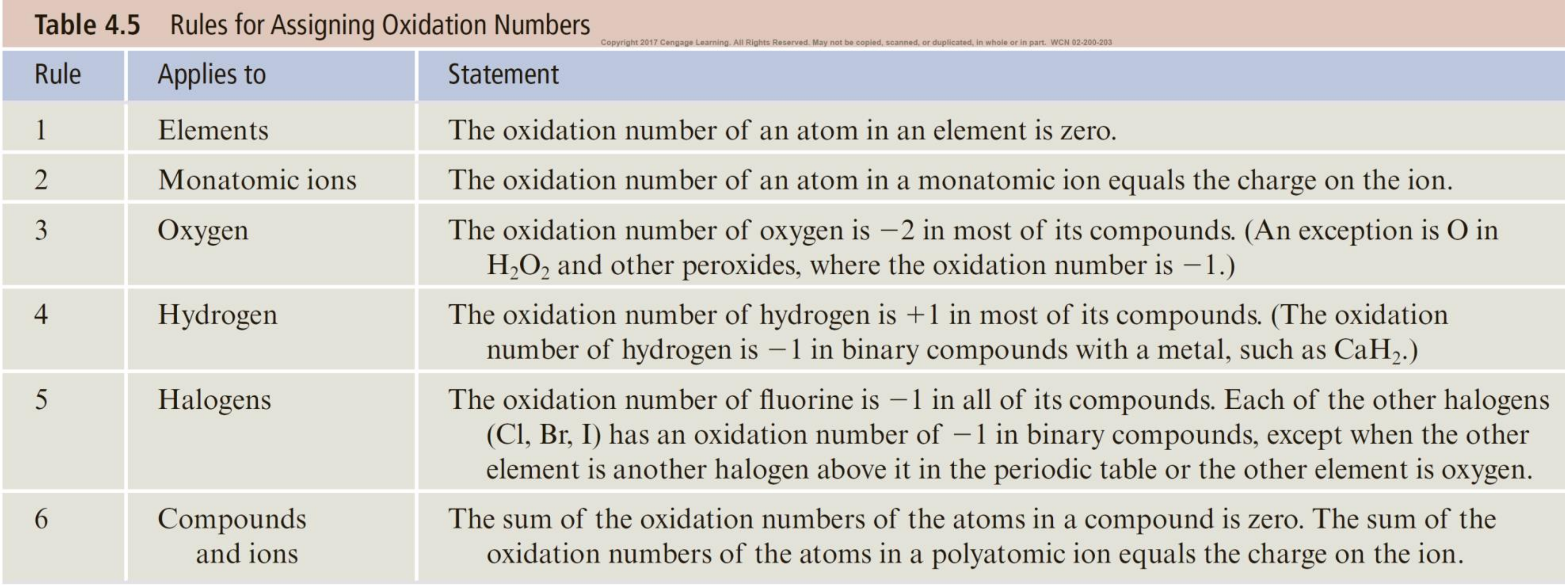


Table 4.5 Rules for Assigning Oxidation Numbers

Rule	Applies to	Statement
1	Elements	The oxidation number of an atom in an element is zero.
2	Monatomic ions	The oxidation number of an atom in a monatomic ion equals the charge on the ion.
3	Oxygen	The oxidation number of oxygen is −2 in most of its compounds. (An exception is O in H_2O_2 and other peroxides, where the oxidation number is −1.)
4	Hydrogen	The oxidation number of hydrogen is +1 in most of its compounds. (The oxidation number of hydrogen is −1 in binary compounds with a metal, such as CaH_2.)
5	Halogens	The oxidation number of fluorine is −1 in all of its compounds. Each of the other halogens (Cl, Br, I) has an oxidation number of −1 in binary compounds, except when the other element is another halogen above it in the periodic table or the other element is oxygen.
6	Compounds and ions	The sum of the oxidation numbers of the atoms in a compound is zero. The sum of the oxidation numbers of the atoms in a polyatomic ion equals the charge on the ion.

Examples:

SO_2:

$HClO_4$:

ClO_3^-:

$K_2Cr_2O_7$:

MnO_4^-:

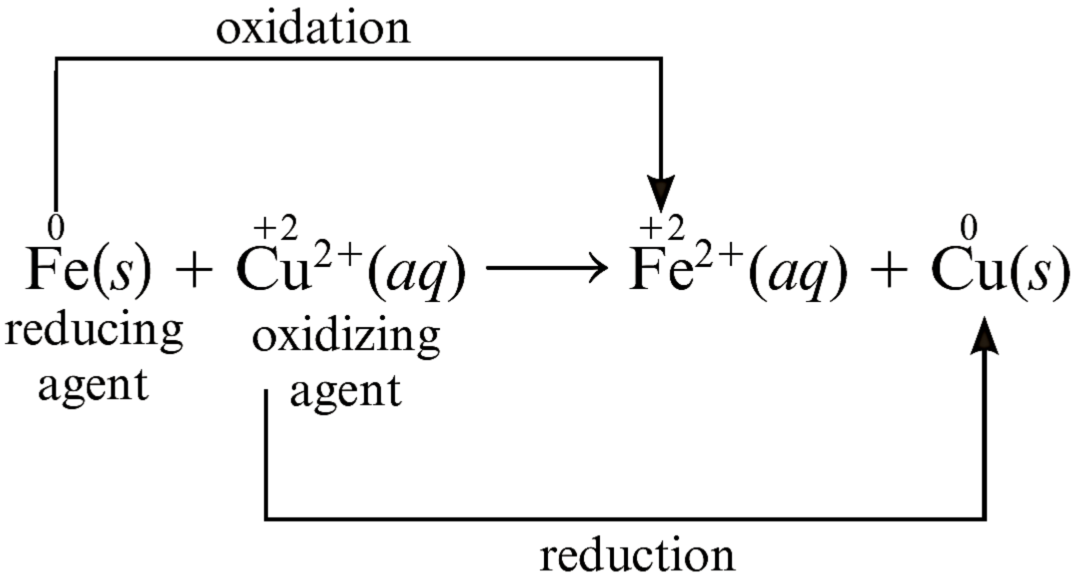
➢ Describing Oxidation–Reduction Reactions

$$\overset{0}{\mathrm{Fe}}(s) + \overset{+2}{\mathrm{Cu}}{}^{2+}(aq) \longrightarrow \overset{+2}{\mathrm{Fe}}{}^{2+}(aq) + \overset{0}{\mathrm{Cu}}(s)$$

We can write this reaction in terms of two half-reactions

$$\overset{0}{\mathrm{Fe}}(s) \longrightarrow \overset{+2}{\mathrm{Fe}}{}^{2+}(aq) + 2e^{-} \qquad \text{(electrons lost by Fe)}$$

$$\overset{+2}{\mathrm{Cu}}{}^{2+}(aq) + 2e^{-} \longrightarrow \overset{0}{\mathrm{Cu}}(s) \qquad \text{(electrons gained by Cu}^{2+}\text{)}$$



oxidation

$$\underset{\substack{\text{reducing}\\\text{agent}}}{\overset{0}{\mathrm{Fe}}(s)} + \underset{\substack{\text{oxidizing}\\\text{agent}}}{\overset{+2}{\mathrm{Cu}}{}^{2+}(aq)} \longrightarrow \overset{+2}{\mathrm{Fe}}{}^{2+}(aq) + \overset{0}{\mathrm{Cu}}(s)$$

reduction

- Some Common Oxidation–Reduction Reactions

1. Combination reaction
2. Decomposition reaction
3. Displacement reaction
4. Combustion reaction

1. **Combination Reactions** is *a reaction in which two substances combine to form a third substance*

$$2Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$$

$$2Sb + 3Cl_2 \longrightarrow 2SbCl_3$$

✓ Not all combination reactions are oxidation- reduction reactions

$$CaO(s) + SO_2(g) \longrightarrow CaSO_3(s)$$

2. **Decomposition Reactions** is *a reaction in which a single compound reacts to give two or more substances*

$$2HgO(s) \xrightarrow{\Delta} 2Hg(l) + O_2(g)$$

$$2KClO_3(s) \xrightarrow[MnO_2]{\Delta} 2KCl(s) + 3O_2(g)$$

✓ Not all decomposition reactions are oxidation-reduction reactions

$$CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)$$

3. **Displacement reaction** (also called a **single-replacement reaction**) is *a reaction in which an element reacts with a compound, displacing another element from it.*

✓ involve an element and one of its compounds →must be oxidation–reduction reactions.

$$Cu(s) + 2AgNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + 2Ag(s)$$

Net ionic rxn. $Cu(s) + 2Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$

$$Zn(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(g)$$

Net ionic rxn.

$$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$

- ✓ metals listed at the top are the strongest reducing agents (they lose electrons easily)
- ✓ A free element reacts with the monatomic ion of another element if the free element is above the other element in the activity series
- ✓ The highlighted elements react slowly with liquid water, but readily with steam, to give H_2

$$2K(s) + 2H^+(aq) \longrightarrow 2K^+(aq) + H_2(g)$$

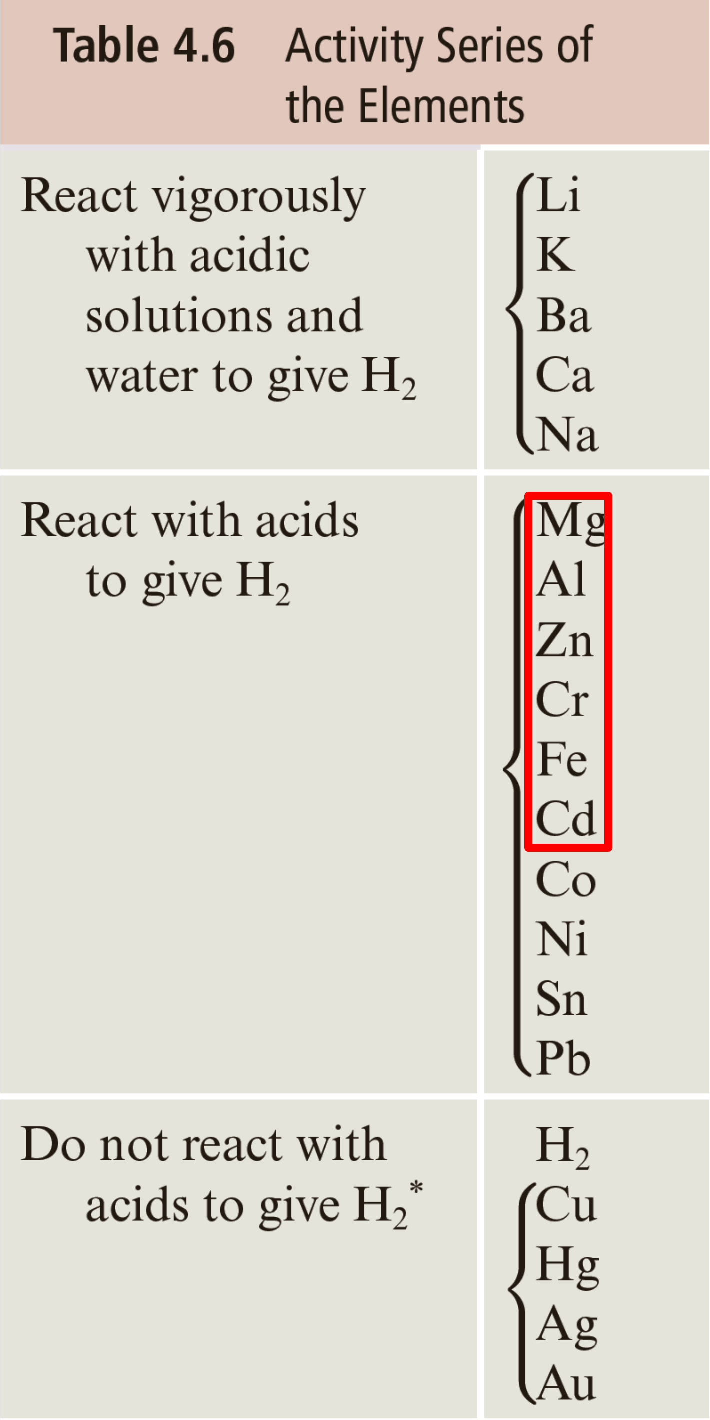


Table 4.6 Activity Series of the Elements

React vigorously with acidic solutions and water to give H_2	Li K Ba Ca Na
React with acids to give H_2	Mg Al Zn Cr Fe Cd Co Ni Sn Pb
Do not react with acids to give H_2*	H_2 Cu Hg Ag Au

4. **Combustion reaction** is *a reaction in which a substance reacts with oxygen, usually with the rapid release of heat to produce a flame.*

- ✓ The products include one or more oxides. Oxygen changes oxidation number from 0 to -2, so combustions are oxidation-reduction reactions.

$$2C_4H_{10}(g) + 13O_2(g) \longrightarrow 8CO_2(g) + 10H_2O(g)$$

$$4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$$

4.6 Balancing Simple Oxidation-Reduction Equations

(Q) Apply the half-reaction method to balance the following equation: $Mg(s) + N_2(g) \rightarrow Mg_3N_2(s)$

$$\overset{0}{\mathrm{M}}\mathrm{g}(s) + \overset{0}{\mathrm{N}}_2(g) \longrightarrow \overset{+2}{\mathrm{M}}\mathrm{g}_3\overset{-3}{\mathrm{N}}_2(s)$$

$$\mathrm{Mg} \longrightarrow \mathrm{Mg}^{2+} + 2e^- \qquad \text{(balanced oxidation half-reaction)}$$

$$\mathrm{N}_2 + 6e^- \longrightarrow 2\mathrm{N}^{3-} \qquad \text{(balanced reduction half-reaction)}$$

$$\begin{array}{r}
3 \times (\mathrm{Mg} \longrightarrow \mathrm{Mg}^{2+} + 2e^-) \\
1 \times (\mathrm{N}_2 + 6e^- \longrightarrow 2\mathrm{N}^{3-}) \\
\hline
3\mathrm{Mg} + \mathrm{N}_2 + \cancel{6e^-} \longrightarrow 3\mathrm{Mg}^{2+} + 2\mathrm{N}^{3-} + \cancel{6e^-}
\end{array}$$

$$\mathbf{3Mg + N_2 \longrightarrow 3Mg^{2+} + 2N^{3-}}$$

$$3\mathrm{Mg}(s) + \mathrm{N}_2(g) \longrightarrow \mathrm{Mg}_3\mathrm{N}_2(s)$$

4.66 Balance the following oxidation–reduction reactions by the half-reaction method.

a. $FeI_3(aq) + Mg(s) \rightarrow Fe(s) + MgI_2(aq)$

$Mg \rightarrow Mg^{2+} + 2e^-$ (oxidation half-reaction)

$Fe^{3+} + 3e^- \rightarrow Fe$ (reduction half-reaction)

$$3 \times (Mg \rightarrow Mg^{2+} + 2e^-)$$
$$\underline{2 \times (Fe^{3+} + 3e^- \rightarrow Fe)}$$
$$2Fe^{3+} + 3Mg + \cancel{6e^-} \rightarrow 2Fe + 3Mg^{2+} + \cancel{6e^-}$$

$$2Fe^{3+} + 3Mg \rightarrow 2Fe + 3Mg^{2+}$$

$$2FeI_3(aq) + 3Mg(s) \rightarrow 2Fe(s) + 3MgI_2(aq)$$

4.7 Molar Concentration

$$\text{Molarity } (M) = \frac{\text{moles of solute}}{\text{liters of solution}}$$

(Q) A sample of $NaNO_3$ weighing 0.38 g is placed in a 50.0 mL volumetric flask. The flask is then filled with water to the mark on the neck. What is the molarity of the resulting solution?

$$\text{Molarity} = \frac{4.\underline{4}7 \times 10^{-3}\text{ mol NaNO}_3}{50.0 \times 10^{-3}\text{ L soln}} = \mathbf{0.089\ \mathit{M}\ NaNO_3}$$

4.8 Diluting Solutions

$$M_i \times V_i = M_f \times V_f$$

(Q)You are given a solution of 14.8 *M* NH_3. How many milliliters of this solution do you require to give 100.0 mL of 1.00 *M* NH_3 ?

$$V_i = \frac{1.00\ \cancel{M} \times 100.0\text{ mL}}{14.8\ \cancel{M}} = \mathbf{6.76\ mL}$$

- ✓ Number of moles does not change

(Q) What is the molar concentration of Na^+ in a solution made by dissolving 1.59 g of Na_2CO_3 (molar mass = 106g/mol) in 100 mL H_2O?

4.9 Gravimetric Analysis

is *a type of quantitative analysis in which the amount of a species in a material is determined by converting the species to a product that can be isolated completely and weighed*.

(Q) A 1.000-L sample of polluted water was analyzed for lead(II) ion, Pb^{2+}, by adding an excess of sodium sulfate to it. The mass of lead(II) sulfate that precipitated was 229.8 mg. What is the mass of lead in a liter of the water? Give the answer as milligrams of lead per liter of solution.

✓ Solution: mass percentage of Pb in $PbSO_4$

$$\% \text{ Pb} = \frac{207.2 \text{ g/mol}}{303.3 \text{ g/mol}} \times 100\% = 68.32\%$$

Amount Pb in sample = 229.8 mg $PbSO_4$ X 0.6832 = 157.0 mg Pb

The water sample contains **157.0 mg Pb per liter.**

Exercise 4.14 You are given a sample of limestone, which is mostly $CaCO_3$, to determine the mass percentage of Ca in the rock. You dissolve the limestone in hydrochloric acid, which gives a solution of calcium chloride. Then you precipitate the calcium ion in solution by adding sodium oxalate, $Na_2C_2O_4$. The precipitate is calcium oxalate, CaC_2O_4. You find that a sample of limestone weighing 128.3 mg gives 140.2 mg of CaC_2O_4. What is the mass percentage of calcium in the limestone?

$$0.1402\text{ g } CaC_2O_4 \times \frac{1\text{ mol } CaC_2O_4}{128.10\text{ g } CaC_2O_4} \times \frac{1\text{ mol Ca}}{1\text{ mol } CaC_2O_4} \times \frac{40.08\text{ g Ca}}{1\text{ mol Ca}} = 0.0438\underline{66}\text{ g Ca}$$

$$\frac{0.0438\underline{6}6\text{ g Ca}}{0.1283\text{ g limestone}} \times 100\% = 34.1\underline{9}0 = 34.19\%$$

4.85 Copper has compounds with copper(I) ion or copper(II) ion. A compound of copper and chlorine was treated with a solution of silver nitrate, $AgNO_3$, to convert the chloride ion in the compound to a precipitate of AgCl. A 59.40-mg sample of the copper compound gave 86.00 mg AgCl.

a. Calculate the percentage of chlorine in the copper compound.

b. Decide whether the formula of the compound is CuCl or $CuCl_2$.

$$86.00\text{ mg AgCl} \times \frac{35.45\text{ mg Cl}^-}{143.32\text{ mg AgCl}} = 21.2\underline{7}1\text{ mg Cl}^-$$

$$\frac{21.2\underline{7}1\text{ mg Cl}^-}{59.40\text{ mg sample}} \times 100\% = 35.8\underline{0}9 = 35.81\%\text{ Cl}^-$$

$$\text{CuCl: } \frac{35.45\text{ mg Cl}^-}{99.00\text{ mg CuCl}} \times 100\% = 35.8\underline{0}8\%$$

$$\text{CuCl}_2\text{: } \frac{70.90\text{ mg Cl}^-}{134.45\text{ mg CuCl}_2} \times 100\% = 52.7\underline{3}3\%$$

4.10 Volumetric Analysis

Example 4.13 Calculating the Volume of Reactant Solution Needed

(Q) Consider the following reaction:

$\mathrm{H_2SO_4}(aq) + 2\mathrm{NaOH}(aq) \rightarrow 2\mathrm{H_2O}(l) + \mathrm{Na_2SO_4}(aq)$

Suppose a beaker contains 35.0 mL of 0.175 *M* H_2SO_4. How many milliliters of 0.250 *M* NaOH must be added to react completely with the sulfuric acid?

$$35.0 \times 10^{-3}\ \cancel{\mathrm{L\ H_2SO_4}}\ \mathrm{soln} \times \frac{0.175\ \cancel{\mathrm{mol\ H_2SO_4}}}{1\ \cancel{\mathrm{L\ H_2SO_4\ soln}}} \times \frac{2\ \cancel{\mathrm{mol\ NaOH}}}{1\ \cancel{\mathrm{mol\ H_2SO_4}}} \times \frac{1\ \mathrm{L\ NaOH\ soln}}{0.250\ \cancel{\mathrm{mol\ NaOH}}} = 4.90 \times 10^{-2}\ \mathrm{L\ NaOH\ soln\ (or\ 49.0\ mL\ NaOH\ soln)}$$

Exercise 4.15 consider the following reaction:

$$3NiSO_4(aq) + 2Na_3PO_4(aq) \rightarrow Ni_3(PO_4)_2(s) + 3Na_2SO_4(aq)$$

How many milliliters of 0.375 *M* $NiSO_4$ will react with 45.7 mL of 0.265 *M* Na_3PO_4?

$$0.0457\text{ L }Na_3PO_4 \times \frac{0.265\text{ mol }Na_3PO_4}{1\text{ L}} = 0.012\underline{1}1\text{ mol }Na_3PO_4$$

$$0.12\underline{1}1\text{ mol }Na_3PO_4 \times \frac{3\text{ mol }NiSO_4}{2\text{ mol }Na_3PO_4} \times \frac{1\text{ L }NiSO_4}{0.375\text{ mol }NiSO_4}$$

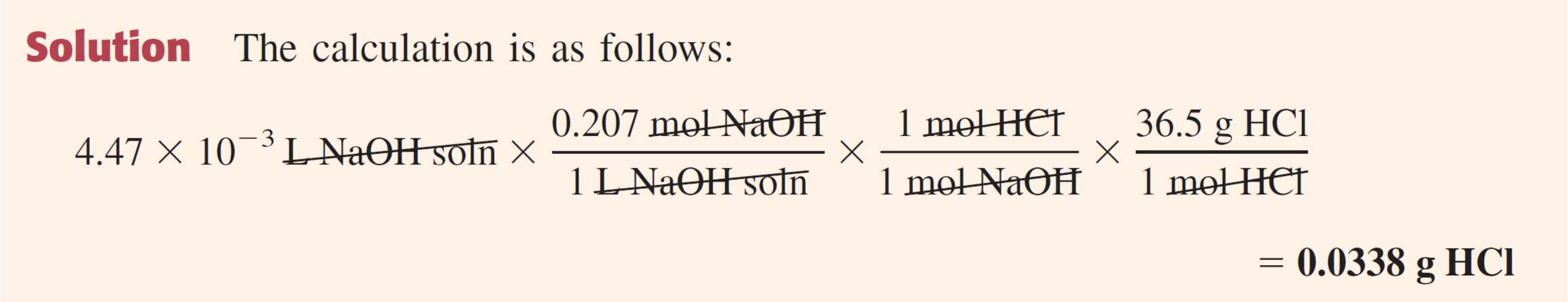
$$= 0.048\underline{4}4\text{ L (48.4 mL)}$$

Example 4.14

Calculating the Quantity of Substance in a Titrated Solution

(Q) A flask contains a solution with an unknown amount of HCl. This solution is titrated with 0.207 *M* NaOH. It takes 4.47 mL of the NaOH solution to complete the reaction. What is the mass of the HCl?

$$\mathrm{NaOH}(aq) + \mathrm{HCl}(aq) \rightarrow \mathrm{NaCl}(aq) + \mathrm{H_2O}(l)$$



Solution The calculation is as follows:

$$4.47 \times 10^{-3}\ \cancel{\mathrm{L\ NaOH\ soln}} \times \frac{0.207\ \cancel{\mathrm{mol\ NaOH}}}{1\ \cancel{\mathrm{L\ NaOH\ soln}}} \times \frac{1\ \cancel{\mathrm{mol\ HCl}}}{1\ \cancel{\mathrm{mol\ NaOH}}} \times \frac{36.5\ \mathrm{g\ HCl}}{1\ \cancel{\mathrm{mol\ HCl}}}$$

$$= \mathbf{0.0338\ g\ HCl}$$

4.91 How many milliliters of 0.150 M H_2SO_4 are required to react with 8.20 g of $NaHCO_3$, according to the following equation?

$H_2SO_4(aq) + 2NaHCO_3(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l) + 2CO_2(g)$

$$8.20 \text{ g NaHCO}_3 \times \frac{1 \text{ mol NaHCO}_3}{84.01 \text{ g NaHCO}_3} \times \frac{1 \text{ mol H}_2\text{SO}_4}{2 \text{ mol NaHCO}_3} \times \frac{1 \text{ L soln}}{0.250 \text{ mol H}_2\text{SO}_4}$$

$= 0.19\underline{5}2$ L (195 mL) soln

4.111 A stock solution of potassium dichromate, $K_2Cr_2O_7$, is made by dissolving 84.5 g of the compound in 1.00 L of solution. How many milliliters of this solution are required to prepare 1.00 L of 0.15 *M* $K_2Cr_2O_7$?

$$84.5\text{ g } K_2Cr_2O_7 \times \frac{1\text{ mol } K_2Cr_2O_7}{294.20\text{ g } K_2Cr_2O_7} = 0.287\text{ mol } K_2Cr_2O_7$$

Molarity = 0.287 mol $K_2Cr_2O_7$ / 1L = 0.287 M

$$M_1V_1 = M_2V_2 \rightarrow V_1 = M_2V_2 / M_1 = \frac{0.150\ M \times 1.00\text{ L}}{0.28\underline{7}2\ M} = 0.522\text{ L } (522\text{ mL})$$

4.113 A solution contains 6.0% (by mass) NaBr. The density of the solution is 1.046 g/cm^3. What is the molarity of NaBr?

Assume 100g sample → 6 g NaBr → moles NaBr = 6/102.89 = 0.0583 mol

d= mass/volume → V= mass/d = 100 g / 1.046 = 95.602 cm^3 = 0.0956 L

M = n/V = 0.0583/ 0.0956 = 0.61 M

4.132 Identify each of the following reactions as being a neutralization, precipitation, or reduction-oxidation reaction.

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

b. $Na_2SO_4(aq) + Hg(NO_3)_2(aq) \rightarrow HgSO_4(s) + 2NaNO_3(aq)$

c. $CsOH(aq) + HClO_4(aq) \rightarrow Cs^+(aq) + 2H_2O(l) + ClO_4^-(aq)$

d. $Mg(NO_3)_2(aq) + Na_2S(aq) \rightarrow MgS(s) + 2NaNO_3(aq)$

a.redox b. precipitation c. neutralization d. precipitation

4.135(modified) A 25-mL sample of 0.50 *M* NaOH is combined with a 75-mL sample of 0.30 *M* NaOH. What is the molarity of the resulting NaOH solution?

4.140 Potassium hydrogen phthalate (abbreviated as KHP) has the molecular formula $KHC_8H_4O_4$ and a molar mass of 204.22 g/mol. KHP has one acidic hydrogen. A solid sample of KHP is dissolved in 50 mL of water and titrated to the equivalence point with 22.90 mL of a 0.5010 *M* NaOH solution. How many grams of KHP were used in the titration?

4.74 What is the volume (in milliliters) of 0.100 *M* H_2SO_4 containing 0.949 g H_2SO_4?