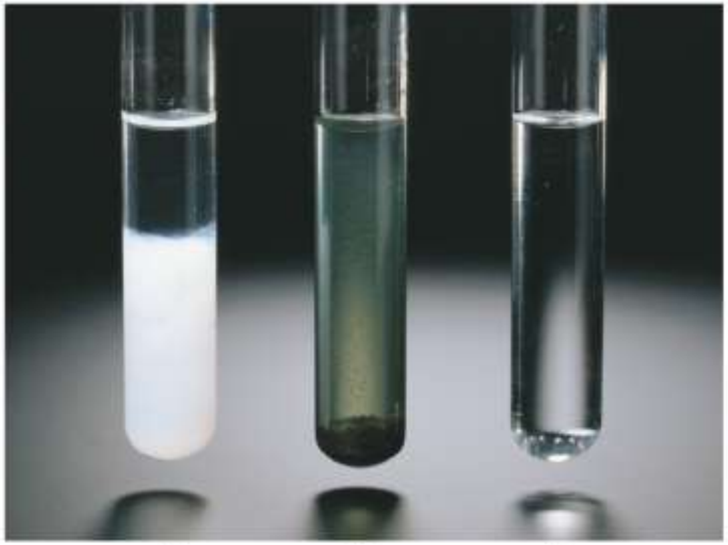
Petrucci • Harwood • Herring • Madura

Ninth Edition

GENERAL CHEMISTRY

Principles and Modern Applications



Chapter 5: Introduction to Reactions in Aqueous Solutions

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Contents

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5.1 The Nature of Aqueous Solutions

- Water
  - Inexpensive
  - Can dissolve a vast number of substances
  - Many substances dissociate into ions
  - Aqueous solutions are found everywhere
    - Seawater
    - Living systems

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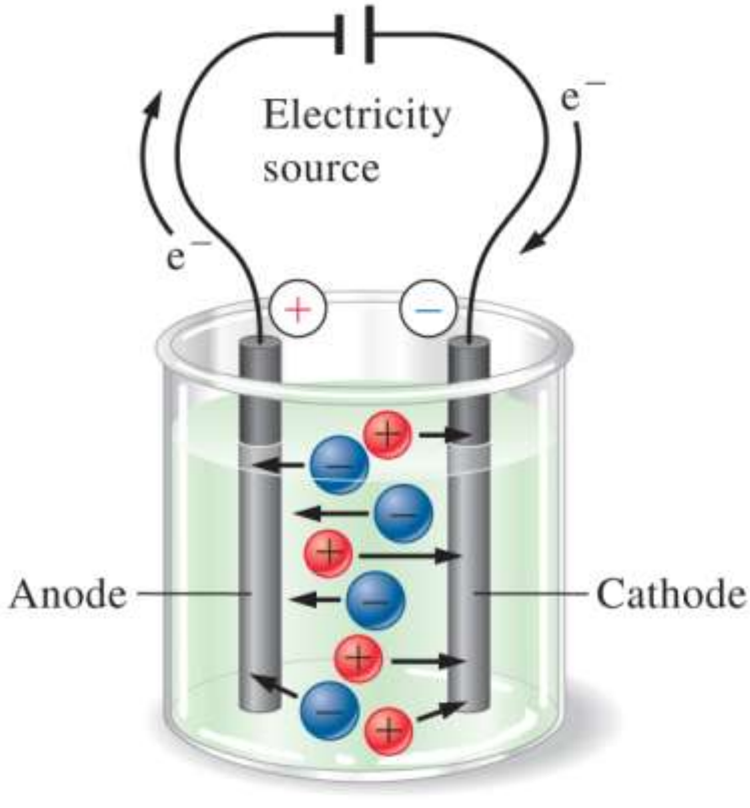
Electrolytes

- Some solutes can *dissociate* into ions.
- Electric charge can be carried.



Types of Electrolytes

- *Strong electrolyte* dissociates completely.
  - Good electrical conduction.
- *Weak electrolyte* partially dissociates.
  - Fair conductor of electricity.
- *Non-electrolyte* does not dissociate.
  - Poor conductor of electricity.

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Representation of Electrolytes using Chemical Equations

A strong electrolyte:

$$MgCl_2(s) \longrightarrow Mg^{2+}(aq) + 2\ Cl^-(aq)$$

A weak electrolyte:

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

A non-electrolyte:

$$CH_3OH(aq)$$

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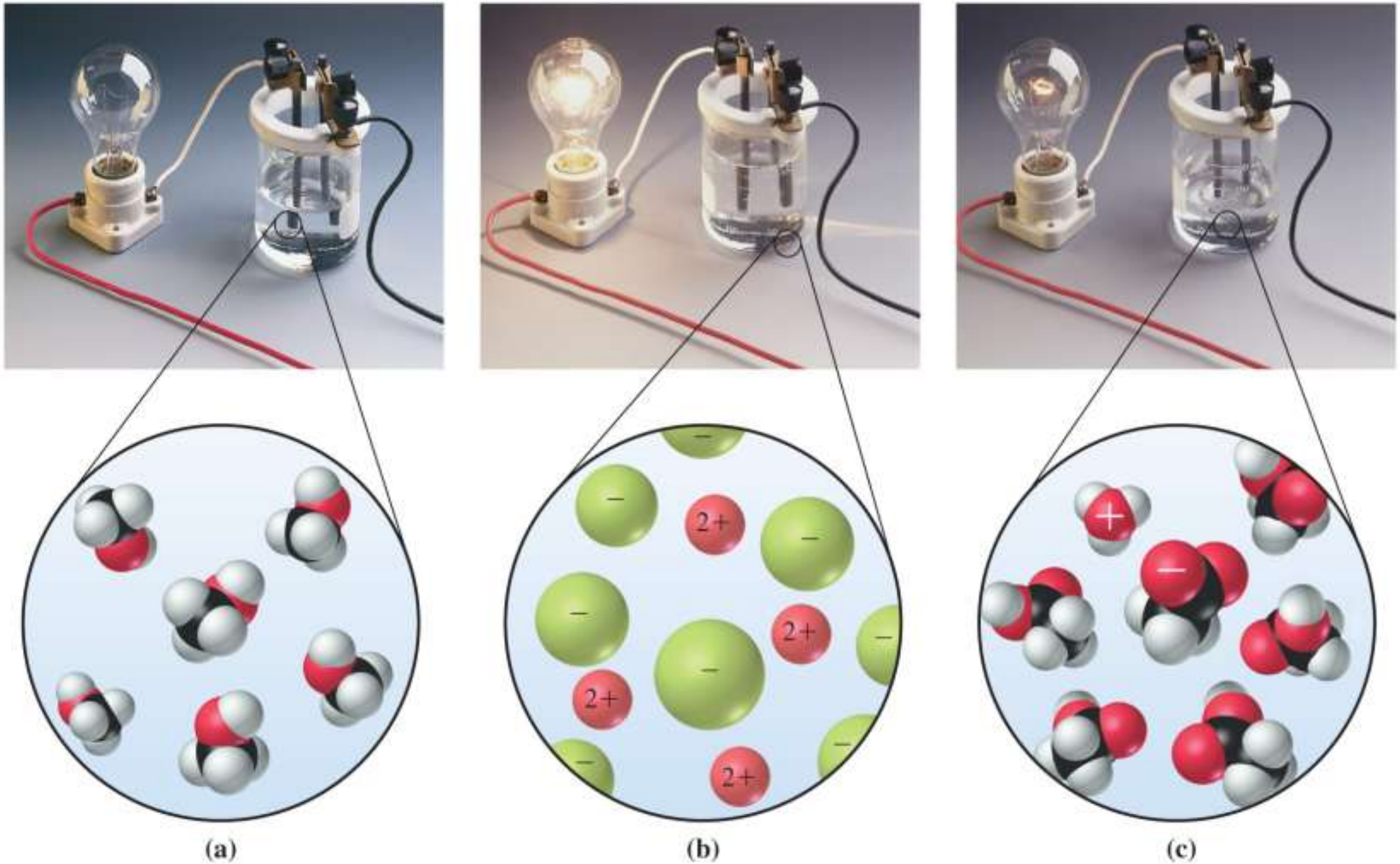
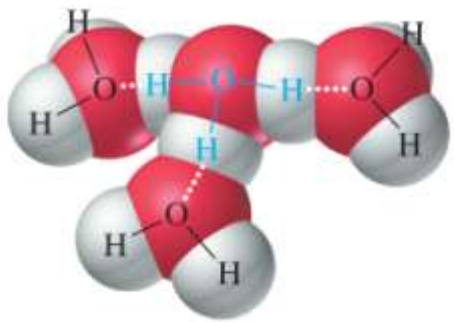
Three Types of Electrolytes



Solvation: The Hydrated Proton

Hydronium ion
H_3O^+

A hydrated proton
$H_5O_2{}^+$



A hydrated proton
$H_9O_4{}^+$

Relative Concentrations in Solution

$$MgCl_2(s) \longrightarrow Mg^{2+}(aq) + 2\ Cl^-(aq)$$

In 0.0050 M $MgCl_{2:}$

Stoichiometry is important.

$[Mg^{2+}] = 0.0050$ M $[Cl^-] = 0.0100$ M $[MgCl_2] = 0$ M

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EXAMPLE 5-1

Calculating Ion concentrations in a Solution of a Strong Electrolyte. What are the aluminum and sulfate ion concentrations in 0.0165 M $Al_2(SO_4)_3$?.

Write a Balanced Chemical Equation:

$$Al_2(SO_4)_3\,(s) \rightarrow 2\,Al^{3+}(aq) + 3\,SO_4^{2-}(aq)$$

Identify the Stoichiometric Factors :

$$\frac{2\text{ mol }Al^{3+}}{1\text{ mol }Al_2(SO_4)_3} \qquad \frac{3\text{ mol }SO_4^{2-}}{1\text{ mol }Al_2(SO_4)_3}$$

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EXAMPLE 7-3

Aluminum Concentration:

$$[Al] = \frac{0.0165 \text{ mol } Al_2(SO_4)_3}{1 \text{ L}} \times \frac{2 \text{ mol } Al^{3+}}{1 \text{ mol } Al_2(SO_4)_3} = 0.0330 \frac{\text{mol } Al^{3+}}{1 \text{ L}}$$

Sulfate Concentration:

$$[SO_4^{2-}] = \frac{0.0165 \text{ mol } Al_2(SO_4)_3}{1 \text{ L}} \times \frac{3 \text{ mol } SO_4^{2-}}{1 \text{ mol } Al_2(SO_4)_3} = 0.0495 \text{ M } SO_4^{2-}$$

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5-2 Precipitation Reactions

- Soluble ions can combine to form an *insoluble* compound.
- Precipitation occurs.
- A test for the presence of chloride ion in water.

$$Ag^{+}(aq) + Cl^{-}(aq) \rightarrow AgCl(s)$$

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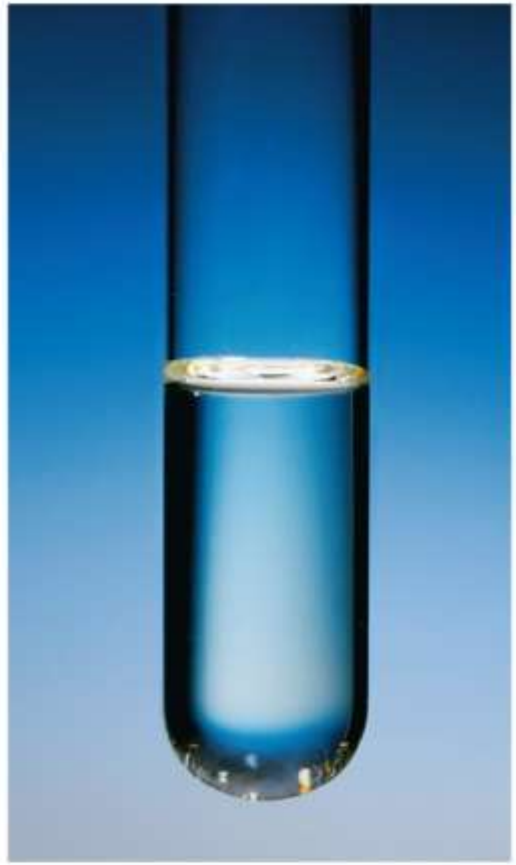
Silver Nitrate and Sodium Iodide

$AgNO_3(aq)$



$NaI(aq)$

$AgI(s)$

$Na^+(aq)$ $NO_3^-(aq)$

Net Ionic Equation

Overall Precipitation Reaction:

$$AgNO_3(aq) + NaI(aq) \rightarrow AgI(s) + NaNO_3(aq)$$

Complete ionic equation:

$$Ag^+(aq) + \cancel{NO_3^-(aq)} + \cancel{Na^+(aq)} + I^-(aq) \rightarrow AgI(s) + \overbrace{\cancel{Na^+(aq)} + \cancel{NO_3^-(aq)}}^{\text{Spectator ions}}$$

Net ionic equation:

$$Ag^+(aq) + I^-(aq) \rightarrow AgI(s)$$

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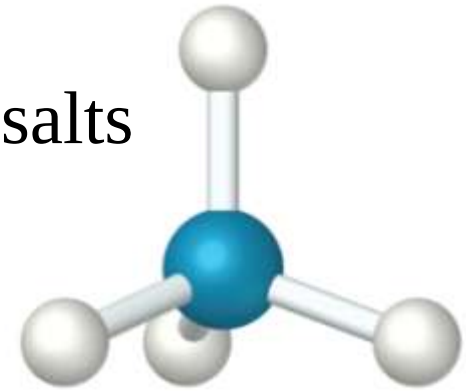
Solubility Rules

- Compounds that are *soluble*:
  - Alkali metal ion and ammonium ion salts

    Li^+, Na^+, K^+, Rb^+, Cs^+ NH_4^+



Ammonium ion

  - Nitrates, perchlorates and acetates

    NO_3^- ClO_4^- $CH_3CO_2^-$

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Solubility Rules

- Compounds that are *mostly soluble*:
  - Chlorides, bromides and iodides Cl^- Br^- I^-
    - Except those of Pb^{2+}, Ag^+, and Hg_2^{2+}.
  - Sulfates SO_4^{2-}
    - Except those of Sr^{2+}, Ba^{2+}, Pb^{2+} and Hg_2^{2+}.
    - $Ca(SO_4)$ is slightly soluble.

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Solubility Rules

- Compounds that are *insoluble*:
  - Hydroxides and sulfides HO^{-} S^{2-}
    - Except alkali metal and ammonium salts
    - Sulfides of alkaline earths are soluble
    - Hydroxides of Sr^{2+} and Ca2+ are slightly soluble.
  - Carbonates and phosphates CO_3^{2-} PO_4^{3-}
    - Except alkali metal and ammonium salts
  - Silver, Lead and Mercury Ag^{+} Pb^{2+} Hg_2^{2+}
    - Except nitrates, acetates and perchlorates

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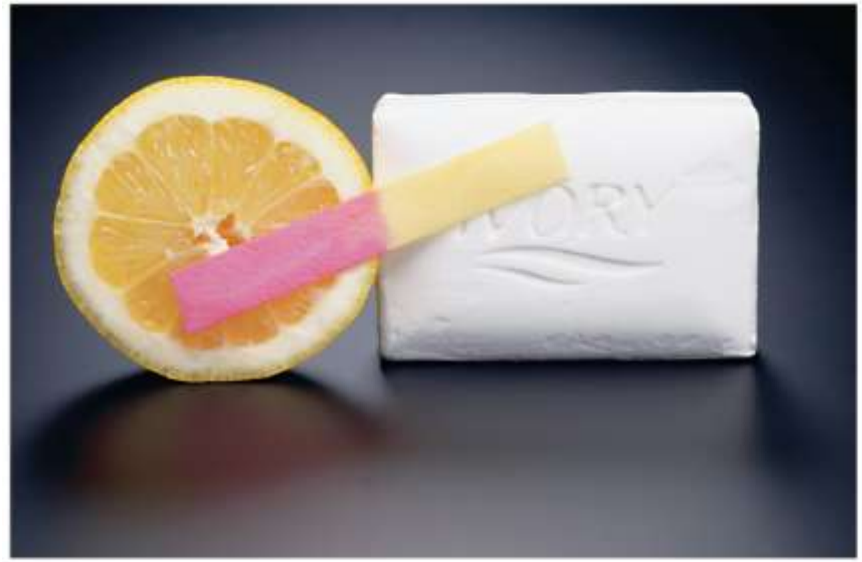
5-3 Acid-Base Reactions



- Latin *acidus* (sour)
  - Sour taste
- Arabic *al-qali* (ashes of certain plants)
  - Bitter taste
- Svante Arrhenius 1884 Acid-Base theory.

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Acids

- Acids provide H^+ in aqueous solution.
- Strong acids completely ionize:

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

- Weak acid ionization is not complete:

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

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Bases

- Bases provide OH^- in aqueous solution.

- Strong bases:

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

- Weak bases:

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

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Recognizing Acids and Bases.

- Acids have ionizable hydrogen ions.
  - CH_3CO_2H or $HC_2H_3O_2$
- Bases have OH^- combined with a metal ion.

  KOH

or can be identified by chemical equations

$$Na_2CO_3(s) + H_2O(l) \rightarrow HCO_3^-(aq) + 2\ Na^+(aq) + OH^-(aq)$$

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More Acid-Base Reactions

- Milk of magnesia $Mg(OH)_2$

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

$$Mg(OH)_2(s) + 2\ CH_3CO_2H(aq) \rightarrow$$
$$Mg^{2+}(aq) + 2\ CH_3CO_2^-(aq) + 2\ H_2O(l)$$

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More Acid-Base Reactions

- Limestone and marble.

$$CaCO_3(s) + 2\ H^+(aq) \rightarrow Ca^{2+}(aq) + H_2CO_3(aq)$$

But: $H_2CO_3(aq) \rightarrow H_2O(l) + CO_2(g)$

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

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TABLE 5.3 Some Common Gas-Forming Reactions

Ion	Reaction
HSO_3^-	$HSO_3^- + H^+ \longrightarrow SO_2(g) + H_2O(l)$
SO_3^{2-}	$SO_3^{2-} + 2\,H^+ \longrightarrow SO_2(g) + H_2O(l)$
HCO_3^-	$HCO_3^- + H^+ \longrightarrow CO_2(g) + H_2O(l)$
CO_3^{2-}	$CO_3^{2-} + 2\,H^+ \longrightarrow CO_2(g) + H_2O(l)$
S^{2-}	$S^{2-} + 2\,H^+ \longrightarrow H_2S(g)$
NH_4^+	$NH_4^+ + OH^- \longrightarrow NH_3(g) + H_2O(l)$

5-4 Oxidation-Reduction: Some General Principles

- Hematite is converted to iron in a blast furnace.

$$Fe_2O_3(s) + 3\ CO(g) \xrightarrow{\Delta} 2\ Fe(l) + 3\ CO_2(g)$$

- Oxidation and reduction always occur together.

Fe^{3+} is reduced to metallic iron.

$CO(g)$ is oxidized to carbon dioxide.

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Oxidation State Changes

- Assign oxidation states:

$$\overset{3+}{Fe_2}\overset{2-}{O_3}(s) + 3\ \overset{2+}{C}\overset{2-}{O}(g) \xrightarrow{\Delta} 2\ \overset{0}{Fe}(l) + 3\ \overset{4+}{C}\overset{2-}{O_2}(g)$$

Fe^{3+} is reduced to metallic iron.

CO(g) is oxidized to carbon dioxide.

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Thermite Reaction

$$Fe_2O_3(s) + 2\,Al(s) \rightarrow Al_2O_3(s) + 2\,Fe(l)$$

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Oxidation and Reduction

- Oxidation
  - O.S. of some element *increases* in the reaction.
  - Electrons are on the right of the equation
- Reduction
  - O.S. of some element *decreases* in the reaction.
  - Electrons are on the left of the equation.

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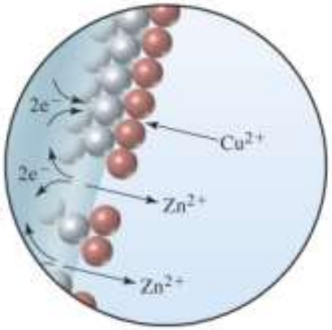
An Oxidation Reduction Reaction

(a) (b) (c)



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

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Oxidation and Reduction Half-Reactions

- A reaction represented by two half-reactions.

Oxidation: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2\ e^{-}$

Reduction: $Cu^{2+}(aq) + 2\ e- \longrightarrow Cu(s)$

Overall: $Cu^{2+}(aq) + Zn(s) \longrightarrow Cu(s) + Zn^{2+}(aq)$

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Balancing Oxidation-Reduction Equations

- Few can be balanced by inspection.
- Systematic approach required.

- The Half-Reaction (Ion-Electron) Method

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Balancing in Acid

- Write the equations for the half-reactions.
  - Balance all atoms except H and O.
  - Balance oxygen using H_2O.
  - Balance hydrogen using H^+.
  - Balance charge using e^-.
- Equalize the number of electrons.
- Add the half reactions.
- Check the balance.

EXAMPLE 5-6

Balancing the Equation for a Redox Reaction in Acidic Solution. The reaction described below is used to determine the sulfite ion concentration present in wastewater from a papermaking plant. Write the balanced equation for this reaction in acidic solution.

$$SO_3^{2-}(aq) + MnO_4^{-}(aq) \rightarrow SO_4^{2-}(aq) + Mn^{2+}(aq)$$

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EXAMPLE 5-6

Determine the oxidation states:

$$\overset{4+}{SO_3^{2-}}(aq) + \overset{7+}{MnO_4^-}(aq) \rightarrow \overset{6+}{SO_4^{2-}}(aq) + \overset{2+}{Mn^{2+}}(aq)$$

Write the half-reactions:

$$SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq) + 2\,e^-(aq)$$

$$5\,e^-(aq) + MnO_4^-(aq) \rightarrow Mn^{2+}(aq)$$

Balance atoms other than H and O:

Already balanced for elements.

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EXAMPLE 5-6

Balance O by adding H_2O:

$$H_2O(l) + SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq) + 2\,e^-(aq)$$

$$5\,e^-(aq) + MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + 4\,H_2O(l)$$

Balance hydrogen by adding H^+:

$$H_2O(l) + SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq) + 2\,e^-(aq) + 2\,H^+(aq)$$

$$8\,H^+(aq) + 5\,e^-(aq) + MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + 4\,H_2O(l)$$

Check that the charges are balanced: Add e^- if necessary.

EXAMPLE 5-6

Multiply the half-reactions to balance all e⁻:

$$\cancel{5\ H_2O(l)} + 5\ SO_3^{2-}(aq) \rightarrow 5\ SO_4^{2-}(aq) + \cancel{10\ e^-(aq)} + \cancel{10\ H^+(aq)}$$

$$\underset{6}{\cancel{16}}\ H^+(aq) + \cancel{10\ e^-(aq)} + 2\ MnO_4^-(aq) \rightarrow 2\ Mn^{2+}(aq) + \underset{3}{\cancel{8}}\ H_2O(l)$$

Add both equations and simplify:

$$5\ SO_3^{2-}(aq) + 2\ MnO_4^-(aq) + 6H^+(aq) \rightarrow$$

$$5\ SO_4^{2-}(aq) + 2\ Mn^{2+}(aq) + 3\ H_2O(l)$$

Check the balance!

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Balancing in Basic Solution

- OH^- appears instead of H^+.
- Treat the equation as if it were in acid.
  - Then add OH^- to each side to neutralize H^+.
  - Remove H_2O appearing on both sides of equation.
- Check the balance.

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Disproportionation Reactions

- The same substance is both oxidized and reduced.
- Some have practical significance
  - Hydrogen peroxide

$$2\ H_2O_2(aq) \rightarrow H_2O(l) + O_2(g)$$

  - Sodium thiosulphate

$$2\ S_2O_3(aq) + H^+(aq) \rightarrow S(s) + SO_2(g) + H_2O(l)$$

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5-6 Oxidizing and Reducing Agents.

- An oxidizing agent (oxidant):
  - Contains an element whose oxidation state *decreases* in a redox reaction

- A reducing agent (reductant):
  - Contains an element whose oxidation state *increases* in a redox reaction.

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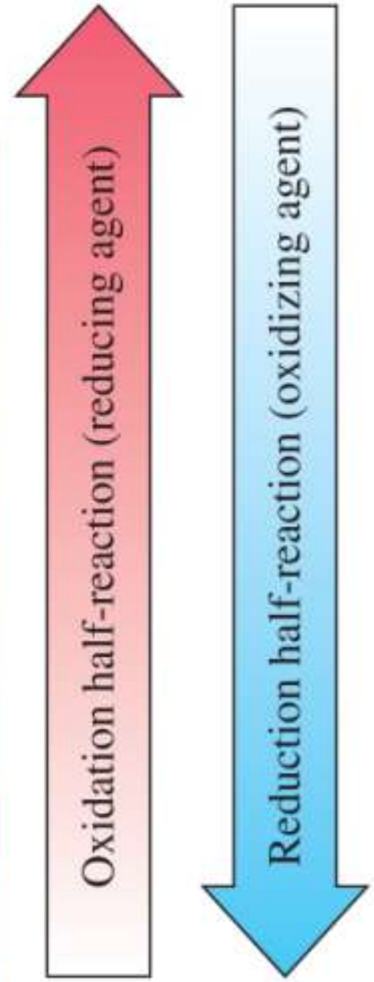
Oxidation States of Nitrogen

This species cannot be oxidized further

Compound or ion	Oxidation state
NO_3^-	+5
N_2O_4	+4
NO_2^-	+3
NO	+2
N_2O	+1
N_2	0
NH_2OH	−1
N_2H_4	−2
NH_3	−3

This species cannot be reduced further



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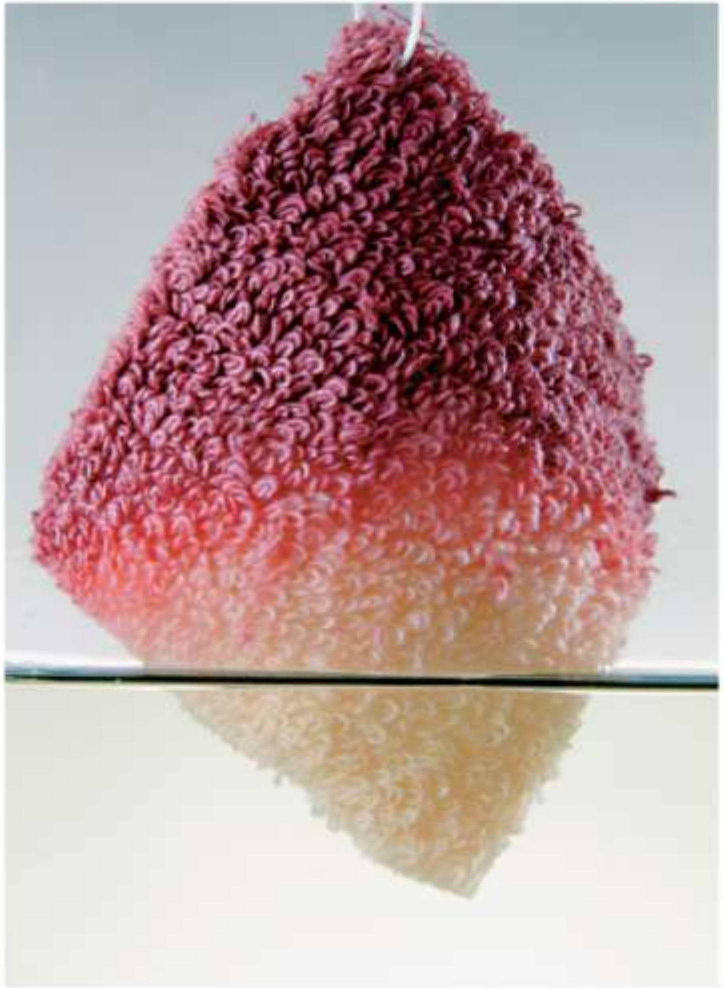
EXAMPLE 5-8

Identifying Oxidizing and Reducing Agents. Hydrogen peroxide, H_2O_2, is a versatile chemical. Its uses include bleaching wood pulp and fabrics and substituting for chlorine in water purification. One reason for its versatility is that it can be either an oxidizing or a reducing agent. For the following reactions, identify whether hydrogen peroxide is an oxidizing or reducing agent.



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EXAMPLE 7-3

$$\overset{}{H_2O_2(aq)} + 2\ \overset{2+}{Fe^{2+}}(aq) + 2\ H^+ \rightarrow 2\ H_2O(l) + 2\ \overset{3+}{Fe^{3+}}(aq)$$

Iron is oxidized and
peroxide is reduced.

$$5\ H_2O_2(aq) + 2\ \overset{7+}{Mn}O_4^-(aq) + 6\ H^+ \rightarrow$$

$$8\ H_2O(l) + 2\ \overset{2+}{Mn^{2+}}(aq) + 5\ O_2(g)$$

Manganese is reduced and
peroxide is oxidized.

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5-7 Stoichiometry of Reactions in Aqueous Solutions: Titrations.

- Titration
  - Carefully controlled addition of one solution to another.
- Equivalence Point
  - Both reactants have reacted completely.
- Indicators
  - Substances which change colour near an equivalence point.

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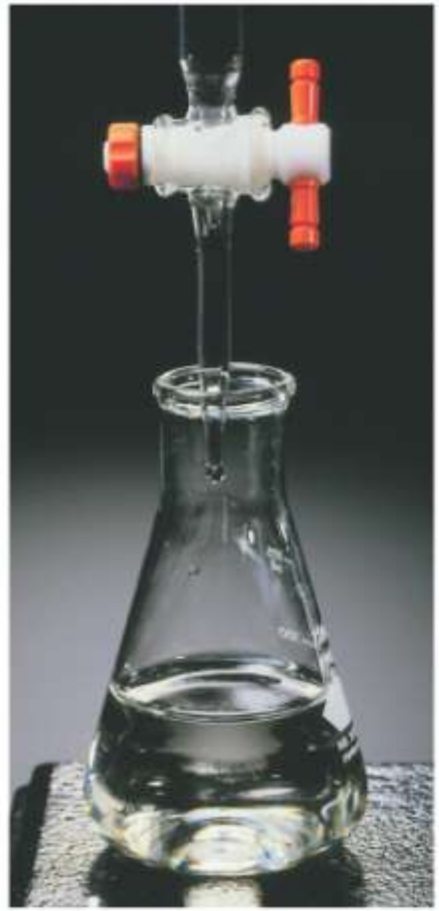
Indicators

5.0 mL CH_3CO_2H A few drops phenolpthalein



Add 0.1000 M NaOH

The “endpoint” (close to the equivalence point)

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EXAMPLE 5-10

Standardizing a Solution for Use in Redox Titrations. A piece of iron wire weighing 0.1568 g is converted to $Fe^{2+}(aq)$ and requires 26.42 mL of a $KMnO_4(aq)$ solution for its titration. What is the molarity of the $KMnO_4(aq)$?

$$5\ Fe^{2+}(aq) + MnO_4^-(aq) + 8\ H^+(aq) \rightarrow$$

$$5\ Fe^{3+}(aq) + Mn^{2+}(aq) + 4\ H_2O(l)$$

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EXAMPLE 5-10

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

Determine $KMnO_4$ consumed in the reaction:

$$n_{MnO_4^-} = 0.1568\ \cancel{g}\ Fe \times \frac{1\ \cancel{mol}\ Fe}{55.847\ \cancel{g}\ Fe} \times \frac{1\ \cancel{mol}\ Fe^{2+}}{1\ \cancel{mol}\ Fe} \times$$

$$\frac{1\ \cancel{mol}\ MnO_4^-}{5\ \cancel{mol}\ Fe^{2+}} \times \frac{1\ mol\ KMnO_4}{1\ \cancel{mol}\ MnO_4^-} = 5.615 \times 10^{-4}\ mol\ KMnO_4$$

Determine the concentration:

$$c_{KMnO_4} = \frac{5.615 \times 10^{-4}\ mol\ KMnO_4}{0.02624\ L} = 0.02140\ M\ KMnO_4$$

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End of Chapter Questions

- Try a different line of reasoning if you are stumped on a problem.
- Practice *Lateral Thinking*.