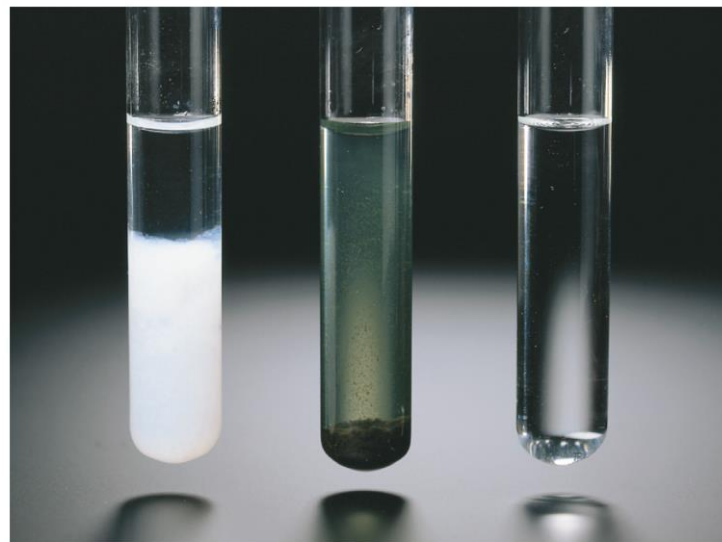


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Ninth
Edition

GENERAL CHEMISTRY

Principles and Modern Applications



Chapter 5: Introduction to Reactions in Aqueous Solutions

Philip Dutton
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- 5-6 Oxidizing and Reducing Agents
- 5-7 Stoichiometry of Reactions in Aqueous Solutions:
Titrations

➤ *Focus On Water Treatment*

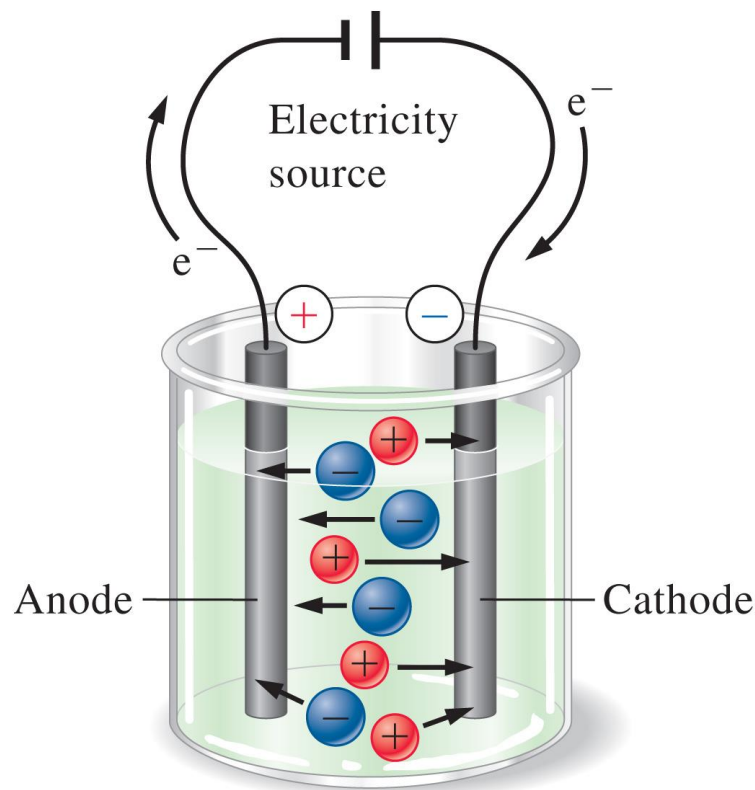
5.1 The Nature of Aqueous Solutions

◆ Water

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

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.

Representation of Electrolytes using Chemical Equations

A strong electrolyte:



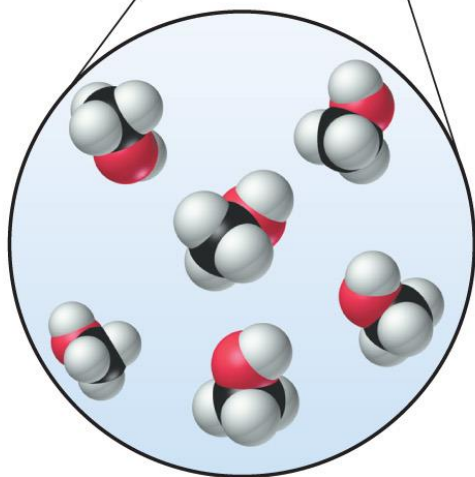
A weak electrolyte:



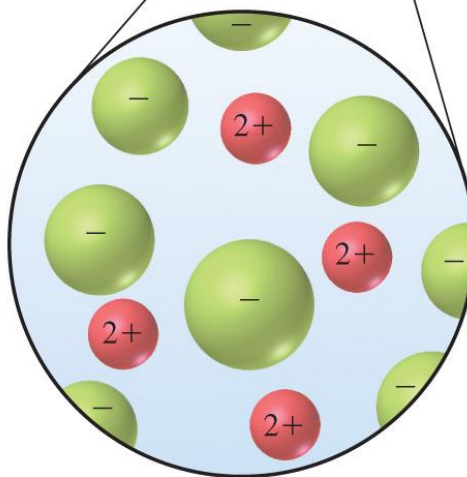
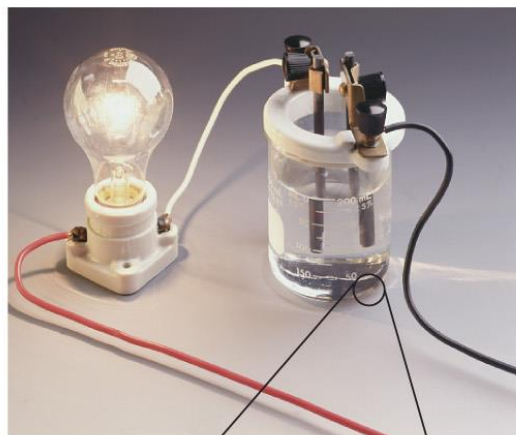
A non-electrolyte:



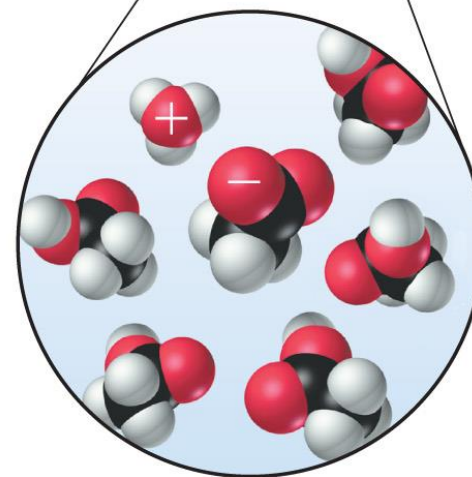
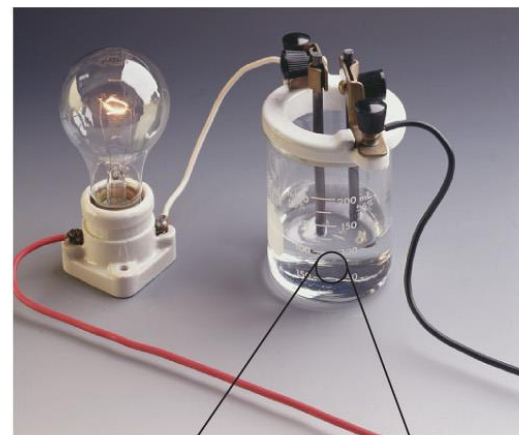
Three Types of Electrolytes



(a)

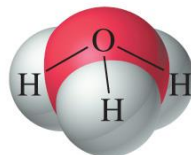


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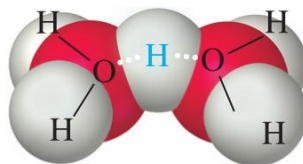


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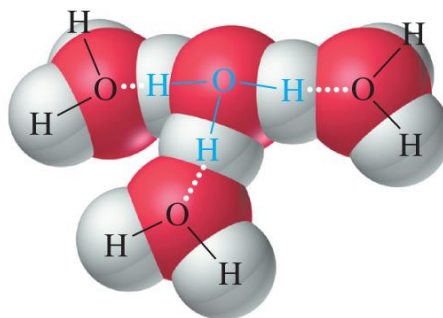
Solvation: The Hydrated Proton



Hydronium ion
 H_3O^+

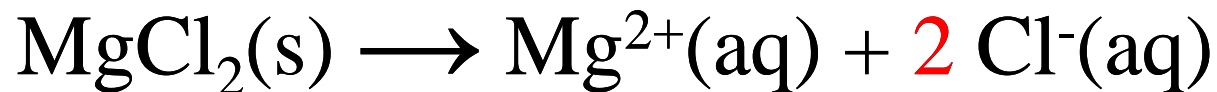


A hydrated proton
 H_5O_2^+



A hydrated proton
 H_9O_4^+

Relative Concentrations in Solution



In 0.0050 M MgCl_2 :

Stoichiometry is important.

$$[\text{Mg}^{2+}] = 0.0050 \text{ M} \quad [\text{Cl}^{-}] = 0.0100 \text{ M} \quad [\text{MgCl}_2] = 0 \text{ M}$$

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 $\text{Al}_2(\text{SO}_4)_3$?

Write a Balanced Chemical Equation:



Identify the Stoichiometric Factors :

$$\frac{2 \text{ mol Al}^{3+}}{1 \text{ mol Al}_2(\text{SO}_4)_3}$$

$$\frac{3 \text{ mol SO}_4^{2-}}{1 \text{ mol Al}_2(\text{SO}_4)_3}$$

EXAMPLE 7-3

Aluminum Concentration:

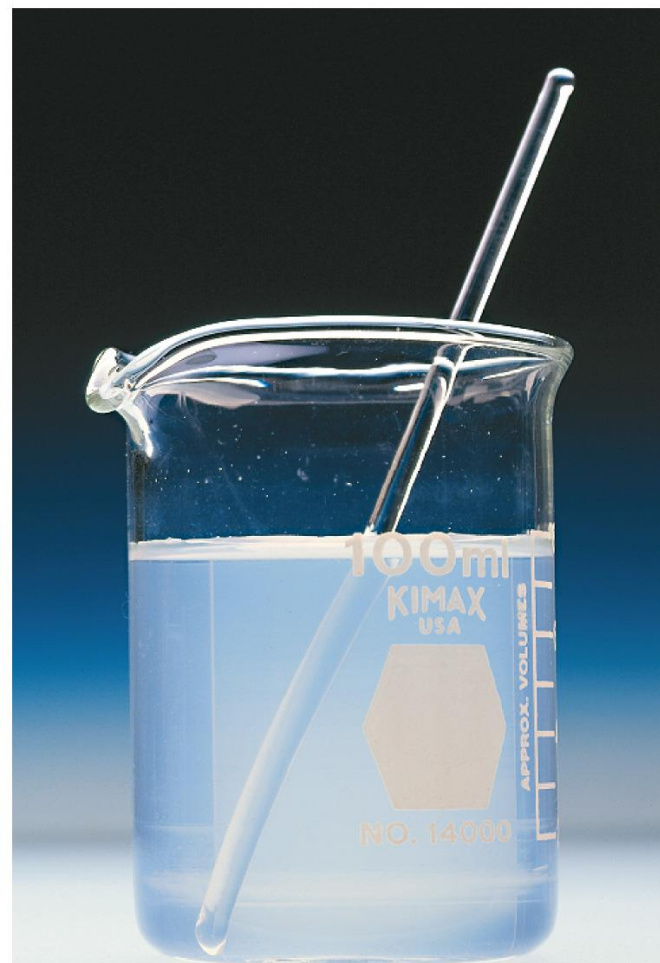
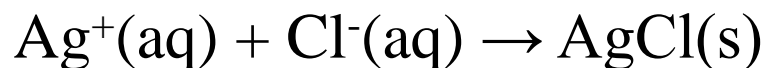
$$[\text{Al}] = \frac{0.0165 \text{ mol Al}_2(\text{SO}_4)_3}{1 \text{ L}} \times \frac{2 \text{ mol Al}^{3+}}{1 \text{ mol Al}_2(\text{SO}_4)_3} = 0.0330 \frac{\text{mol Al}^{3+}}{1 \text{ L}}$$

Sulfate Concentration:

$$[\text{SO}_4^{2-}] = \frac{0.0165 \text{ mol Al}_2(\text{SO}_4)_3}{1 \text{ L}} \times \frac{3 \text{ mol SO}_4^{2-}}{1 \text{ mol Al}_2(\text{SO}_4)_3} = 0.0495 \text{ M SO}_4^{2-}$$

5-2 Precipitation Reactions

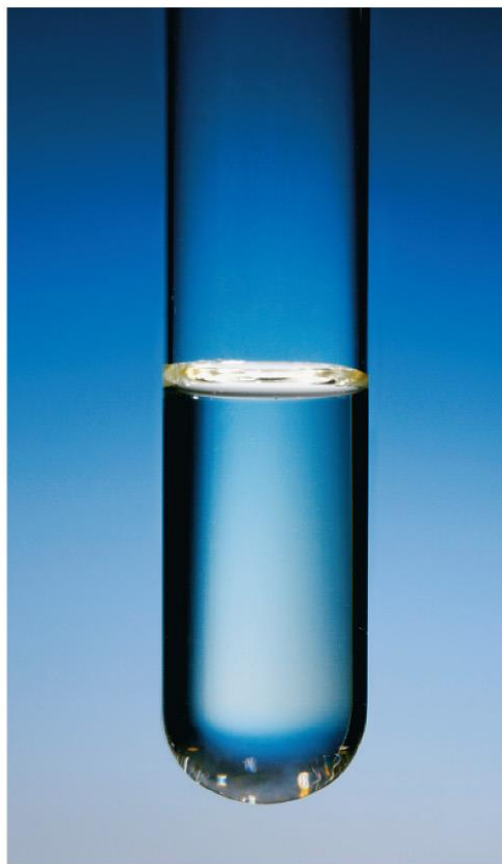
- ◆ Soluble ions can combine to form an *insoluble* compound.
- ◆ Precipitation occurs.
- ◆ A test for the presence of chloride ion in water.



Silver Nitrate and Sodium Iodide



$\text{AgNO}_3(\text{aq})$



$\text{NaI}(\text{aq})$

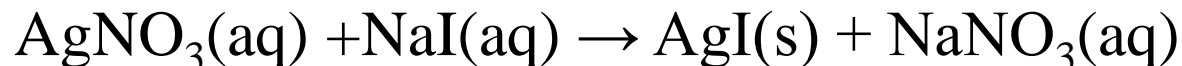


$\text{AgI}(\text{s})$

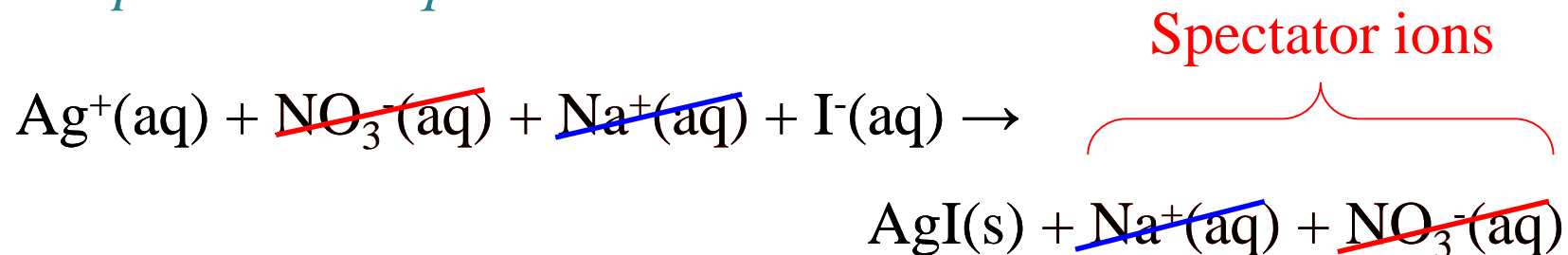
$\text{Na}^+(\text{aq}) \quad \text{NO}_3^-(\text{aq})$

Net Ionic Equation

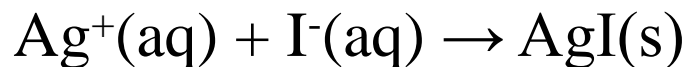
Overall Precipitation Reaction:



Complete ionic equation:



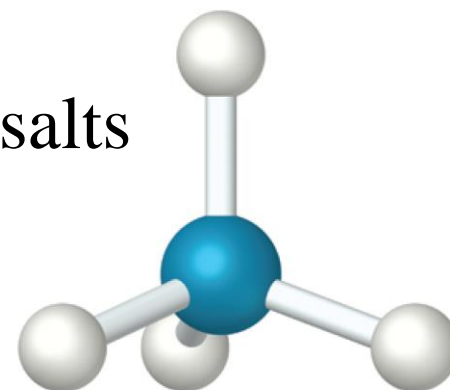
Net ionic equation:



Solubility Rules

◆ Compounds that are *soluble*:

- Alkali metal ion and ammonium ion salts



Ammonium ion

- Nitrates, perchlorates and acetates



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+} .
 - $\text{Ca}(\text{SO}_4)$ is slightly soluble.

Solubility Rules

◆ Compounds that are *insoluble*:

- Hydroxides and sulfides



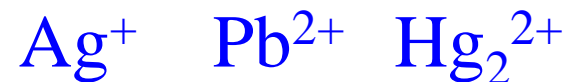
- Except alkali metal and ammonium salts
- Sulfides of alkaline earths are soluble
- Hydroxides of Sr^{2+} and Ca^{2+} are slightly soluble.

- Carbonates and phosphates



- Except alkali metal and ammonium salts

- Silver, Lead and Mercury



- Except nitrates, acetates and perchlorates

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.

Acids

◆ Acids provide H^+ in aqueous solution.

◆ Strong acids completely ionize:



◆ Weak acid ionization is not complete:



Bases

◆ Bases provide OH^- in aqueous solution.

◆ Strong bases:



◆ Weak bases:



Recognizing Acids and Bases.

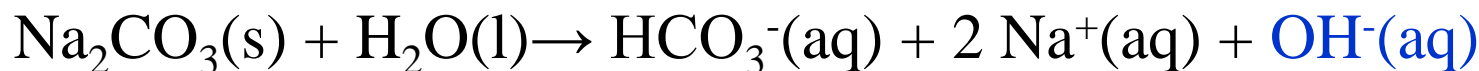
◆ Acids have ionizable hydrogen ions.



◆ Bases have OH^- combined with a metal ion.

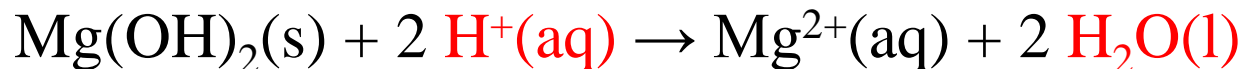


or can be identified by chemical equations



More Acid-Base Reactions

◆ Milk of magnesia



More Acid-Base Reactions

◆ Limestone and marble.

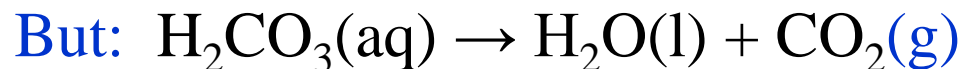
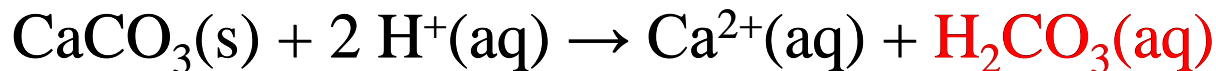
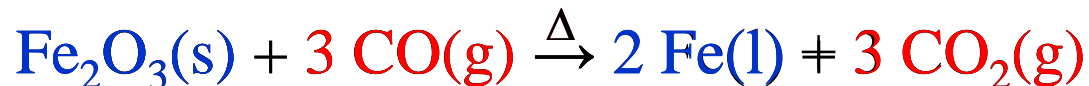


TABLE 5.3 Some Common Gas-Forming Reactions

Ion	Reaction
HSO_3^-	$\text{HSO}_3^- + \text{H}^+ \longrightarrow \text{SO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
SO_3^{2-}	$\text{SO}_3^{2-} + 2 \text{H}^+ \longrightarrow \text{SO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
HCO_3^-	$\text{HCO}_3^- + \text{H}^+ \longrightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
CO_3^{2-}	$\text{CO}_3^{2-} + 2 \text{H}^+ \longrightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
S^{2-}	$\text{S}^{2-} + 2 \text{H}^+ \longrightarrow \text{H}_2\text{S}(\text{g})$
NH_4^+	$\text{NH}_4^+ + \text{OH}^- \longrightarrow \text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{l})$

5-4 Oxidation-Reduction: Some General Principles

- ◆ Hematite is converted to iron in a blast furnace.



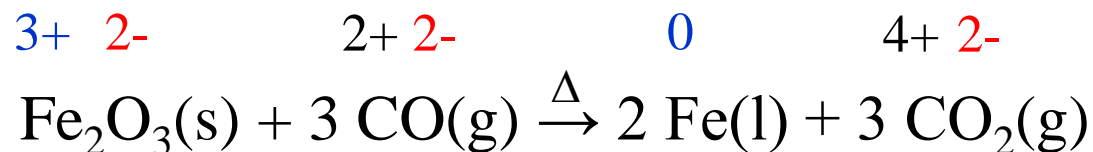
- ◆ Oxidation and reduction always occur together.

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

$\text{CO}(\text{g})$ is oxidized to carbon dioxide.

Oxidation State Changes

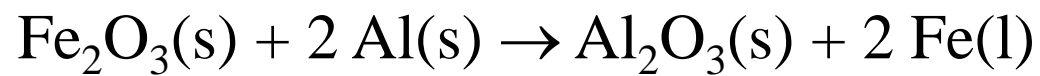
◆ Assign oxidation states:



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

$\text{CO}(\text{g})$ is oxidized to carbon dioxide.

Thermite Reaction



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.

An Oxidation Reduction Reaction



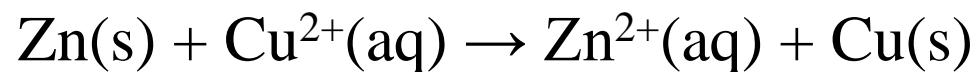
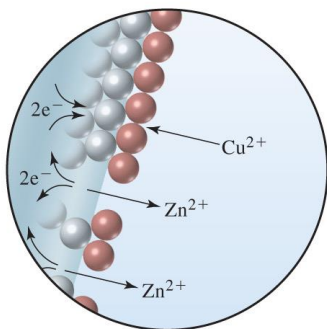
(a)



(b)



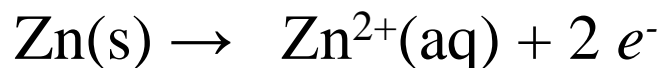
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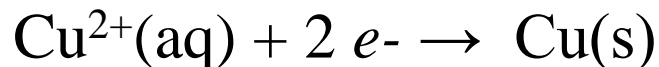
Oxidation and Reduction Half-Reactions

- ◆ A reaction represented by two half-reactions.

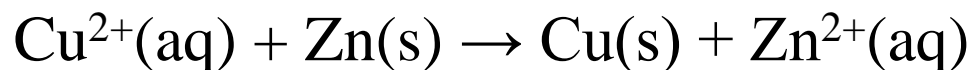
Oxidation:



Reduction:



Overall:



Balancing Oxidation-Reduction Equations

- ◆ Few can be balanced by inspection.
- ◆ Systematic approach required.
- ◆ The Half-Reaction (Ion-Electron) Method

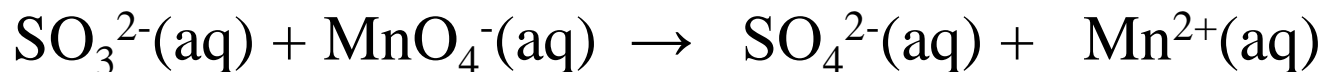
Balancing in Acid

- ◆ 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

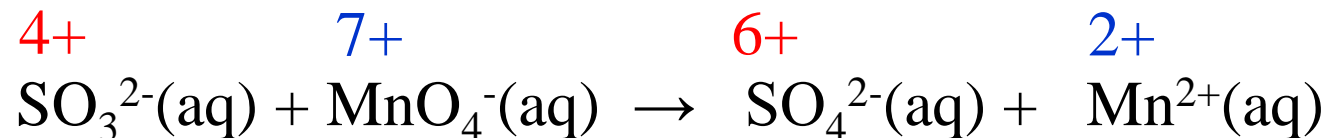
Balancing the Equation for a Redox Reaction in Acidic

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.

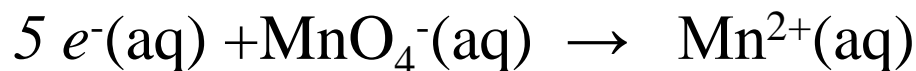


EXAMPLE 5-6

Determine the oxidation states:



Write the half-reactions:

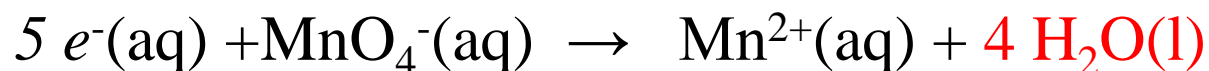
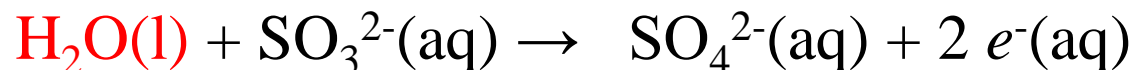


Balance atoms other than H and O:

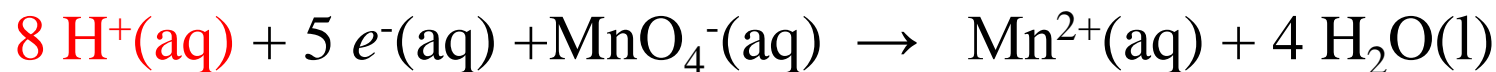
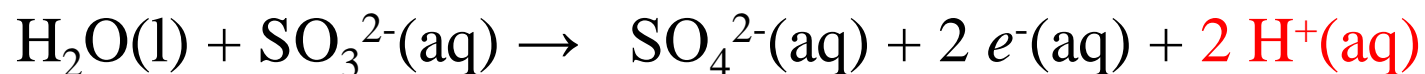
Already balanced for elements.

EXAMPLE 5-6

Balance O by adding H₂O:



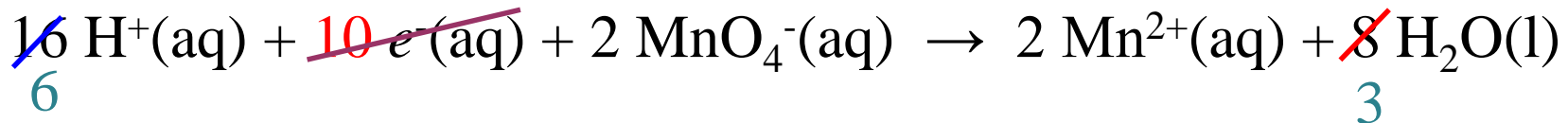
Balance hydrogen by adding H⁺:



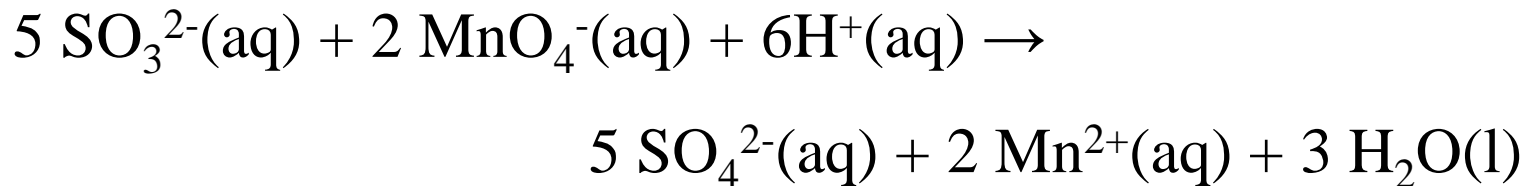
Check that the charges are balanced: Add e^{-} if necessary.

EXAMPLE 5-6

Multiply the half-reactions to balance all e^- :



Add both equations and simplify:



Check the balance!

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.

Disproportionation Reactions

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

- Hydrogen peroxide



- Sodium thiosulphate



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.

Oxidation States of Nitrogen

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 oxidized further

This species cannot be reduced further

Oxidation half-reaction (reducing agent)

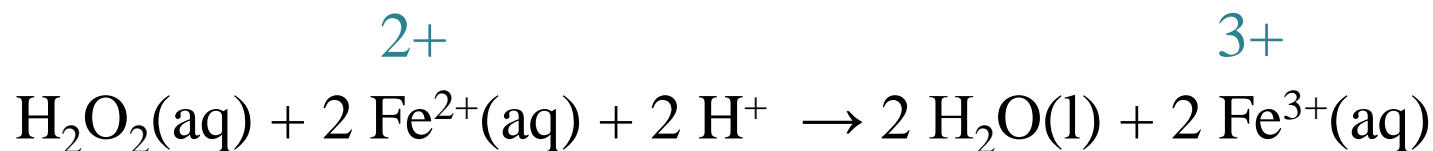
Reduction half-reaction (oxidizing agent)

EXAMPLE 5-8

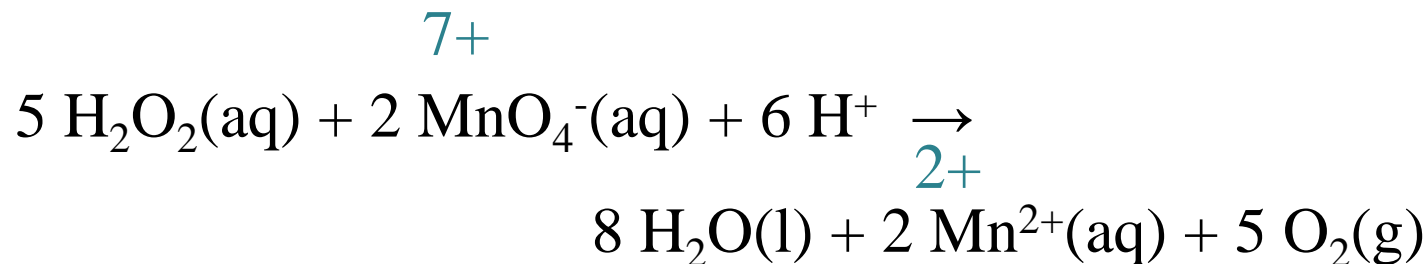
Identifying Oxidizing and Reducing Agents. Hydrogen peroxide, H_2O_2 , is a versatile chemical. Its uses include bleaching wood pulp and fabrics and substituting for chlorine in water purification. One reason for its versatility is that it can be either an oxidizing or a reducing agent. For the following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



EXAMPLE 7-3



Iron is oxidized and
peroxide is reduced.



Manganese is reduced and
peroxide is oxidized.

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

◆ Titration

- Carefully controlled addition of one solution to another.

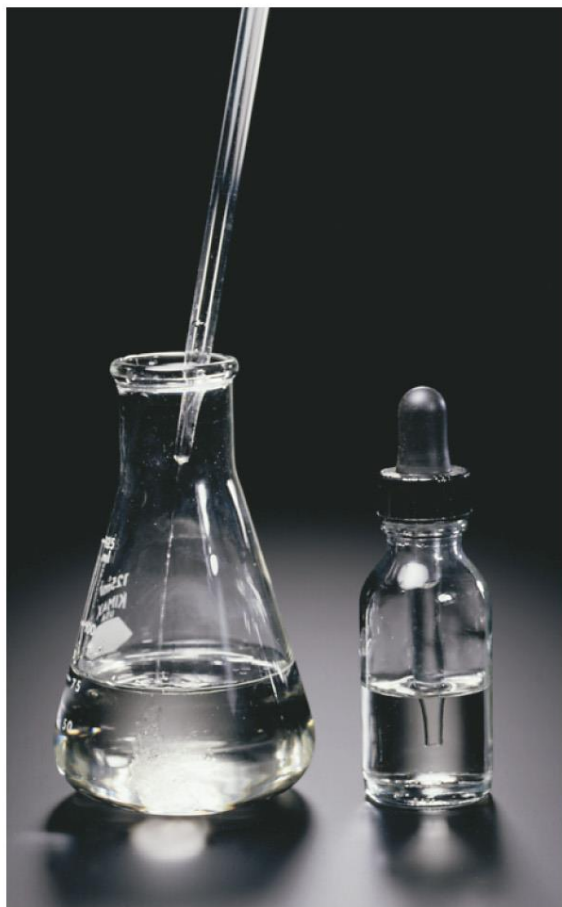
◆ Equivalence Point

- Both reactants have reacted completely.

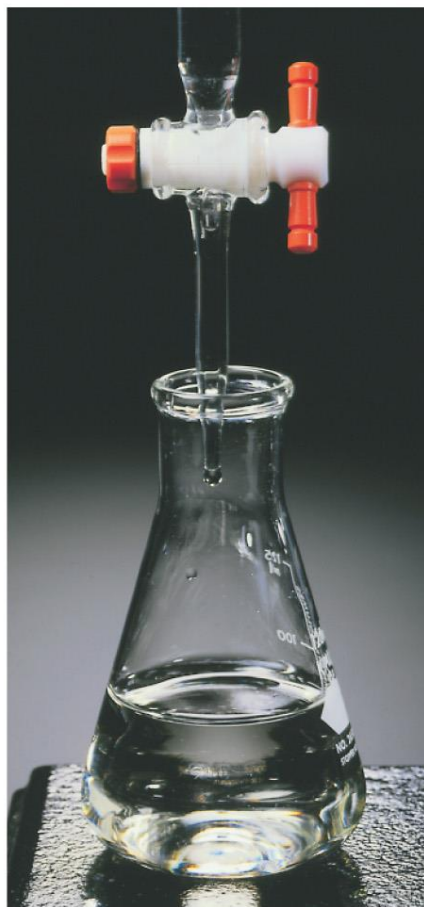
◆ Indicators

- Substances which change colour near an equivalence point.

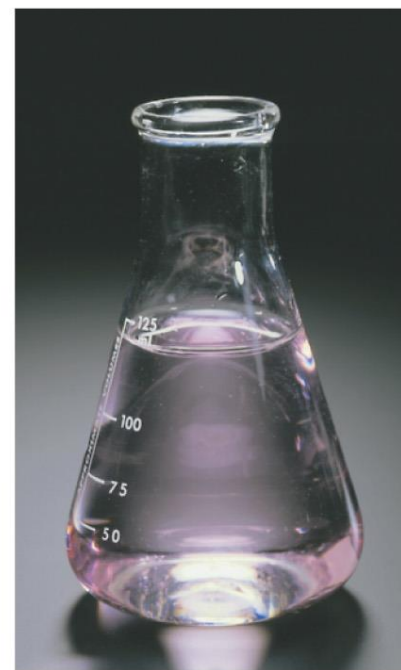
Indicators



5.0 mL $\text{CH}_3\text{CO}_2\text{H}$ A few drops
phenolphthalein



Add 0.1000 M NaOH

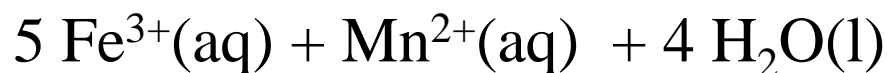
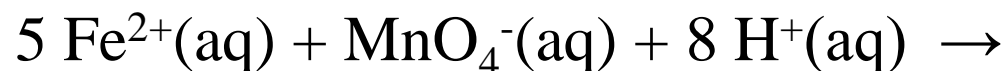


The “endpoint”
(close to the equivalence point)

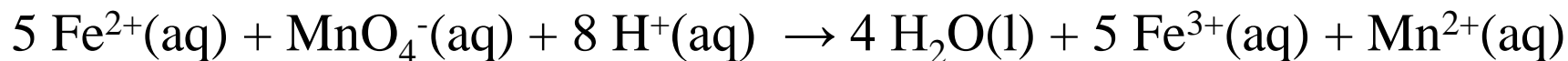
EXAMPLE 5-10

Standardizing a Solution for Use in Redox Titrations. A

piece of iron wire weighing 0.1568 g is converted to $\text{Fe}^{2+}(\text{aq})$ and requires 26.42 mL of a $\text{KMnO}_4(\text{aq})$ solution for its titration. What is the molarity of the $\text{KMnO}_4(\text{aq})$?



EXAMPLE 5-10



Determine KMnO_4 consumed in the reaction:

$$\begin{aligned} n_{\text{MnO}_4^{-}} &= 0.1568 \text{ g Fe} \times \frac{1 \text{ mol Fe}}{55.847 \text{ g Fe}} \times \frac{1 \text{ mol Fe}^{2+}}{1 \text{ mol Fe}} \times \\ &\quad \frac{1 \text{ mol MnO}_4^{-}}{5 \text{ mol Fe}^{2+}} \times \frac{1 \text{ mol KMnO}_4}{1 \text{ mol MnO}_4^{-}} = 5.615 \times 10^{-4} \text{ mol KMnO}_4 \end{aligned}$$

Determine the concentration:

$$c_{\text{KMnO}_4} = \frac{5.615 \times 10^{-4} \text{ mol KMnO}_4}{0.02624 \text{ L}} = 0.02140 \text{ M KMnO}_4$$

End of Chapter Questions

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

