# **Chapter 7**

#### **Oxidation-Reduction Reactions**





# Oxidation

- 400

- 300

200

- Historically oxidation meant reacting with oxygen.
  - $\begin{array}{rcl} 2\text{Zn}(s) \ + \ \text{O}_2(g) & \rightarrow & 2\text{ZnO}(s) \\ & \text{Zn} \ \rightarrow & \text{Zn}^{2+} \ + & 2\text{e}^- \\ & \text{or} & 2\text{Zn} \ \rightarrow & 2\text{Zn}^{2+} \ + & 4\text{e}^- \\ & \text{O} \ + & 2\text{e}^- \rightarrow & \text{O}^{2-} \\ & \text{or} \ & \text{O}_2 \ + & 4\text{e}^- \rightarrow & 2\text{O}^{2-} \end{array}$

## **Oxidation Redefined (1)**

- Many reactions that are similar to the reaction between zinc and oxygen were not considered oxidation.
- For example, both the zinc-oxygen reaction and the reaction between sodium metal and chlorine gas (described on the next slide) involve the transfer of electrons.

400

- 300

### Oxidation and Formation of Binary Ionic Compounds



# Similar to Oxidation of Zinc

 $2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$ Na  $\rightarrow$  Na<sup>+</sup> + e<sup>-</sup> or 2Na  $\rightarrow$  2Na<sup>+</sup> + 2e<sup>-</sup>  $Cl + e^- \rightarrow Cl^$ or  $Cl_2 + 2e^- \rightarrow 2Cl^-$ Oxidation = Loss of Electrons



#### **Oxidation Redefined (2)**

 To include the similar reactions in the same category, oxidation was redefined as any chemical change in which at least one element loses electrons.

400

- 300

200

#### **Zinc Oxide Reduction**

• The following equation describes one of the steps in the production of metallic zinc.

 $ZnO(s) + C(g) \rightarrow Zn(s) + CO(g)$ 

- Because zinc is reducing the number of bonds to oxygen atoms, historically, zinc was said to be *reduced*.
- When we analyze the changes taking place, we see that zinc ions are gaining two electrons to form zinc atoms.

 $Zn^{2+} + 2e^- \rightarrow Zn$ 

- 400

- 300

-200

100

• The definition of reduction was broadened to coincide with the definition of oxidation. According to the modern definition, when something gains electrons, it is *reduced*.

## Reduction

= 300

200

100

 The loss of electrons (oxidation) by one substance is accompanied by the gain of electrons by another (reduction). *Reduction* is any chemical change in which at least one element gains electrons.

## **Memory Aid**



400

- 300

-200

## Oxidizing and Reducing Agents

- A reducing agent is a substance that loses electrons, making it possible for another substance to gain electrons and be reduced. The oxidized substance is always the reducing agent.
- An oxidizing agent is a substance that gains electrons, making it possible for another substance to lose electrons and be oxidized. The reduced substance is always the oxidizing agent.

400

- 300

-200

## Identifying Oxidizing and Reducing Agents

 $2Zn(s) + O_2(g) \rightarrow 2ZnO(s)$ 

- $Zn \rightarrow Zn^{2+} + 2e^{-}$
- O +  $2e^- \rightarrow O^{2-}$

-400

- 300

-200

- Zinc atoms lose electrons, making it possible for oxygen atoms to gain electrons and be reduced, so zinc is the reducing agent.
- Oxygen atoms gain electrons, making it possible for zinc atoms to lose electrons and be oxidized, so O<sub>2</sub> is the oxidizing agent.

## Partial Loss and Gain of Electrons

 $N_2(g) + O_2(g) \rightarrow 2NO(g)$ 

- The N-O bond is a polar covalent bond in which the oxygen atom attracts electrons more than the nitrogen atom.
- Thus the oxygen atoms gain electrons *partially* and are reduced.
- The nitrogen atoms lose electrons partially and are oxidized.
- N<sub>2</sub> is the reducing agent.

400

- 300

-200

100

• O<sub>2</sub> is the oxidizing agent.

# Redox Terms (1)



# Redox Terms (2)

- Oxidation-Reduction Reaction
  - an electron transfer reaction
- Oxidation
  - complete or partial loss of electrons
- Reduction

- 300

200

- complete or partial gain of electrons
- Oxidizing Agent
  - the substance reduced; gains electrons, making it possible for something to lose them.
- Reducing Agent
  - the substance oxidized; loses electrons, making it possible for something to gain them.

# **Questions Answered by Oxidation Numbers**

Is the reaction redox?	If any atoms change their oxidation number, yes.
What's oxidized?	The element that increases its oxidation number
What's reduced?	The element that decreases its oxidation number
What's the reducing agent?	The substance with the element oxidized
What's the oxidizing agent?	The substance with the element reduced

#### **Steps for Determination of Oxidation Numbers**

• Step 1: Assign oxidation numbers to as many atoms as you can using the guidelines described on the next slide.

• Step 2: To determine oxidation numbers for atoms not described on the pervious slide, use the following guideline.

 The sum of the oxidation numbers for each atom in the formula is equal to the overall charge on the formula. (This includes uncharged formulas where the sum of the oxidation numbers is zero.)

- 300

-200

# **Oxidation Numbers**

uncharged element	0	no exceptions
monatomic ions	charge on ion	no exceptions
combined fluorine	-1	no exceptions
combined oxygen	-2	-1 in peroxides
covalently bonded hydrogen	+1	no exceptions

## More Types of Chemical Reactions

- Combination
- Decomposition
- Combustion
- Single Displacement



## Combination Reactions

 In combination reactions, two or more elements or compounds combine to form one compound.

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

 $C(s) + O_2(g) \rightarrow CO_2(g)$ 

400

- 300

200

100

 $MgO(s) + H_2O(I) \rightarrow Mg(OH)_2(s)$ 

## Decomposition Reactions

 In *decomposition reactions*, one compound is converted into two or more simpler substances.

Electric current  $2H_2O(I) \rightarrow 2H_2(g) + O_2(g)$ Electric current  $2NaCI(I) \rightarrow 2Na(I) + CI_2(g)$ 

400

- 300

200

## **Combustion Reactions**

 A combustion reaction is a redox reaction in which oxidation is very rapid and is accompanied by heat and usually light. The combustion reactions that you will be expected to recognize have oxygen, O<sub>2</sub>, as one of the reactants.

400

= 300

200

100

 $C_2H_5OH(I) + 3O_2(g)$  $\rightarrow 2CO_2(g) + 3H_2O(I)$ 

## **Combustion Products (1)**

- When any substance that contains carbon is combusted (or burned) completely, the carbon forms carbon dioxide.
- When a substance that contains hydrogen is burned completely, the hydrogen forms water.

400

- 300

100

 $\begin{array}{rl} 2C_{6}H_{14}(g) &+ 19O_{2}(g) \\ & \longrightarrow 12CO_{2}(g) &+ 14H_{2}O(I) \end{array}$ 

#### **Combustion Products (2)**

The complete combustion of a substance, like ethanol, C<sub>2</sub>H<sub>5</sub>OH, that contains carbon, hydrogen, and oxygen also yields carbon dioxide and water.

```
C_2H_5OH(I) + 3O_2(g) 
\rightarrow 2CO_2(g) + 3H_2O(I)
```

400

- 300

200

#### **Combustion Products (3)**

 When any substance that contains sulfur burns completely, the sulfur forms sulfur dioxide.

 $CH_3SH(g) + 3O_2(g)$ 

400

= 300

100

 $\rightarrow$  CO<sub>2</sub>(g) + 2H<sub>2</sub>O(I) + SO<sub>2</sub>(g)

# **Single Displacement**

Pure element displaces element in compound



## Single Displacement Reaction

 $Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$  $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ 

oxidation:  $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$ reduction:  $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$ 

400

- 300

# Single Displacement Reaction Example



# **Voltaic Cell**

400

= 300

200

100

 The system in which two halfreactions for a redox reaction are separated allowing the electrons transferred in the reaction to be passed between them through a wire is called *voltaic cell*.



## **Electrodes**

= 300

200

- The electrical conductors placed in the half-cells are called *electrodes*.
- They can be active electrodes, which participate in the reaction, or passive electrodes, which transfer the electrons into or out of a halfcell but do not participate in the reaction.

## Anode

400

- 300

200

- The **anode** is the site of oxidation.
- Because oxidation involves loss of electrons, the anode is the source of electrons. For this reason, it is described as the negative electrode.
- Because electrons are lost forming more positive (or less negative) species at the anode, the surroundings tend to become more positive. Thus anions are attracted to the anode.

## Cathode

400

- 300

200

- The *cathode* is the site of reduction.
- By convention, the cathode is the positive electrode.
- Because electrons come to the cathode and substances gain these electrons to become more negative (or less positive), the surroundings tend to become more negative. Thus cations are attracted to the cathode.

# Other Cell Components

400

- 300

200

- A device called a salt bridge can be used to keep the charges balanced.
- The portion of the electrochemical cell that allows ions to flow is called the electrolyte.

# Leclanché Cell or Dry Cell

400

- 300

200

100

Anode oxidation:  $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$ Cathode reduction:  $2MnO_2(s) + 2NH_4^+(aq) + 2e^ \rightarrow$  Mn<sub>2</sub>O<sub>3</sub>(s) + 2NH<sub>3</sub>(aq) + H<sub>2</sub>O(l) **Overall reaction:**  $Zn(s) + 2MnO_{2}(s) + 2NH_{4}^{+}(aq)$  $\rightarrow$  Zn<sup>2+</sup>(aq) + Mn<sub>2</sub>O<sub>3</sub>(s) + 2NH<sub>3</sub>(aq) + H<sub>2</sub>O(I)

# **Dry Cell Image**



## **Alkaline Batteries**

Anode oxidation:  $Zn(s) + 2OH^{-}(aq)$  $\rightarrow$  ZnO(s) + H<sub>2</sub>O(l) + 2e<sup>-</sup> Cathode reduction:  $2MnO_2(s) + H_2O(l) + 2e^{-1}$  $\rightarrow$  Mn<sub>2</sub>O<sub>3</sub>(s) + 2OH<sup>-</sup>(aq) **Overall reaction:**  $Zn(s) + 2MnO_2(s) \rightarrow ZnO(s) + Mn_2O_3(s)$ 



# **Electrolysis**

- *Voltage*, a measure of the strength of an electric current, represents the force that moves electrons from the anode to the cathode in a voltaic cell.
- When a greater force (voltage) is applied in the opposite direction, electrons can be pushed from what would normally be the cathode toward the voltaic cell's anode. This process is called *electrolysis*.
- In a broader sense, electrolysis is the process by which a redox reaction is made to occur in the nonspontaneous direction.

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

400

- 300

-200

## Primary and Secondary Batteries

- Batteries that are not rechargeable are called *primary batteries*.
- A rechargeable battery is often called a secondary battery or a storage battery.

400

- 300



# $Cd(s) + 2NiO(OH)(s) + 2H_2O(I)$ $\implies Cd(OH)_2(s) + 2Ni(OH)_2(s)$

# $NiO(OH)(s) + H_2O(I) + e^{-}$ $\implies Ni(OH)_2(s) + OH^{-}(aq)$

 $Cd(s) + 2OH^{-}(aq) \implies Cd(OH)_{2}(s) + 2e^{-}$ 

# Nickel-Cadmium Battery

 $Pb(s) + PbO_{2}(s) + 2HSO_{4}^{-}(aq) + 2H_{3}O^{+}(aq)$  $\implies 2PbSO_{4}(s) + 4H_{2}O(I)$ 

- 400

- 300

100

 $PbO_{2}(s) + HSO_{4}^{-}(aq) + 3H_{3}O^{+}(aq) + 2e^{-}$  $\implies PbSO_{4}(s) + 5H_{2}O(I)$ 

 $Pb(s) + HSO_4^{-}(aq) + H_2O(I)$  $\implies PbSO_4(s) + H_3O^{+}(aq) + 2e^{-}$ 

#### Lead Acid Battery

# **Lithium Batteries**

- Because lithium metal has a very low density, and because lithium can yield high voltages in batteries, lithium batteries have very high energy to mass ratios (or energy to volume ratios), making them ideal for powering electronic devices.
- The original lithium batteries used metallic lithium. The following slide shows a typical lithium-metal battery.

200

## **Lithium-Metal Battery**



## Lithium-Metal Battery (2)

- At the anode, lithium metal is oxidized to lithium ions, which migrate through the electrolyte to the cathode.
- At the cathode, lithium ions are inserted between manganese dioxide-carbon layers. Electrons must be gained at the cathode to maintain electrical neutrality.

- 300

-200

#### Problems with Lithium-Metal Batteries

- Lithium metal is very reactive, making lithium metal batteries somewhat dangerous.
- For this reason, modern lithium batteries are more likely to be lithium-ion batteries.

300

## Advantages of Lithium-Ion Batteries

- They are safe.
- Although lithium-ion batteries have a lower energy density than lithiummetal batteries, it is still high compared to other batteries...about twice the standard nickel-cadmium battery.
- Low self discharge
- Low maintenance

- 300

-200

### Limitations of Lithium-Ion Batteries

- Requires a protection circuit to maintain voltage and currents within safe limits.
- Expensive to manufacture.

- 300

• Subject to aging. A typical lifetime is two to three years.

### Differences in Lithium-Ion Batteries

- The technology for lithium-ion batteries is constantly evolving, leading to changes in the cathode, anode, and electrolyte.
- One example of a lithium-ion battery is shown on the next slide.

300



 $\begin{array}{rcl} \text{Li}_{n}\text{C}_{6} & \longrightarrow & n\text{Li}^{+}+6\text{C}+n\text{e}^{-} & & \text{CoO}_{2}+n\text{Li}^{+}+n\text{e}^{-} & \longrightarrow & \text{Li}_{n}\text{CoO}_{2} \\ & & \text{Li}_{n}\text{C}_{6}+\text{CoO}_{2} & \longrightarrow & 6\text{C}+\text{Li}_{n}\text{CoO}_{2} \end{array}$ 

## Lithium-Ion Battery (2)

- At the anode, lithium ions are trapped between graphite layers.
- During discharge, lithium ions move from the anode to the cathode through the electrolyte.
- When lithium ions are removed from the anode, electrons are lost to maintain electrical neutrality.
- When lithium ions move to the cathode, they are inserted into layers of cobalt dioxide.

- 300

-200

100

• Electrons must be gained at the cathode to maintain electrical neutrality.