REVIEW: TOPIC 8

NAME: ____________

DUE: ____________

REDOX

Unit 8 – Major Understandings

- ☆ 3.2d An oxidation-reduction (redox) reaction involves the transfer of electrons (e -).
- ☆ 3.2e Reduction is the gain of electrons.
- ☆ 3.2f A half-reaction can be written to represent reduction.
- ☆ 3.2g Oxidation is the loss of electrons.
- ☆ 3.2h A half-reaction can be written to represent oxidation.
- ☆ 3.3b In a redox reaction the number of electrons lost is equal to the number of electrons gained.
- ☆ 3.2i Oxidation numbers (states) can be assigned to atoms and ions. Changes in oxidation numbers indicate that oxidation and reduction have occurred.
- ☆ 3.2j An electrochemical cell can be either voltaic or electrolytic. In an electrochemical cell, oxidation occurs at the anode and reduction at the cathode.
- ☆ 3.2k A voltaic cell spontaneously converts chemical energy to electrical energy.
- ☆ 3.2l An electrolytic cell requires electrical energy to produce a chemical change. This process is known as electrolysis.

Introduction

Many reactions result from the transfer of electrons between atoms, and the term used for this oxidation-reduction transfer is **redox**.

A – Reduction

Reduction represents a gain, or apparent gain, of electrons. Any chemical change in which there is a decrease of the oxidation number is called reduction.

The particle that decreases in oxidation number is said to be reduced. Since it is the agent that causes the oxidation of another atom, it is referred to as the **oxidizing agent**.

B – Oxidation

Oxygen, having the second highest electronegativity rating of 3.4, after fluorine (4.0), was isolated over 100 years before fluorine, and its properties have become well known. Chemists found that whenever an element combined with oxygen, it had a tendency to lose electrons. This tendency of losing electrons was associated with the element oxygen and was called **oxidation**.

Oxidation represents a loss or an apparent loss of electrons. Any chemical change in which there is an increase in oxidation number – due to a loss of negative charge (electrons) – is called oxidation.

The particle that increases in oxidation number is said to be oxidized. Since it is the agent that causes the reduction of another, it is referred to as the **reducing agent**.

In other words, when attempting to identify the oxidizing or reducing agents, a simple rule could be applied. The item oxidized is the reducing agent, and the item reduced is the **oxidizing agent**.

Oxidation Numbers (States)

The oxidation number (oxidation state) of an atom is the charge which an atom has, or appears to have, when electrons are counted according to certain arbitrary rules. This oxidation number, although arbitrary, is a convenient notation for keeping track of the number of electrons involved in a chemical reaction. In assigning oxidation numbers, electrons shared between two unlike atoms are counted as belonging to the more electronegative atom. The electrons shared between two like atoms are divided equally between the sharing atoms.

Operational Rules for Determining Oxidation Number

Applying the general rules above, has resulted in the following operational rules.

- In the free elements, each atom has an oxidation number of zero (**0**). For example, hydrogen in H_2, sodium in Na, and sulfur in S_8; all have oxidation numbers of zero (**0**).
- In simple ions (ions containing one atom) the oxidation number is equal to the charge on the ion. These common ionic charges (oxidation states) can be found in the *Reference Tables* and the *Periodic Table of Elements*; for example, Na^{+}, Zn^{++}, Cl^{-}.
- When monatomic ions make up an ionic compound, the oxidation number of each ion is equal to its ionic charge. The algebraic sum of these charges is equal to zero (**0**). For example, in $CaCl_2$, calcium has an oxidation number of **+2** and each chlorine **-1**, giving chlorine a total charge of **-2**; therefore, the total charge of the compound adds up to zero (**0**). Iron in $FeCl_2$ has an oxidation number of **+2**, and each chlorine **-1**, which gives chlorine a total oxidation state of **-2**, so that the total sum of the positive and negative charges is again zero (**0**). In $FeCl_3$, iron has an oxidation number of **+3**, and each chlorine a **-1**, giving chlorine a total negative charge of **-3**, and the compound a total charge of zero (**0**).
- All metals in **Group 1** form only **1+** ions and their oxidation number is **+1** in all compounds.
- All metals in **Group 2** form only **2+** ions and their oxidation number is **+2** in all compounds.
- Oxygen has an oxidation number of **-2** in all its compounds except in peroxides (such as H_2O_2) when it is **-1** and in compounds with fluorine (OF and OF_2) when it may be **+1** or **+2**. For example, in H_2SO_4, oxygen has an oxidation number of **-2**.
- Hydrogen has an oxidation number of **+1** in all its compounds (such as HCl and H_2SO_4) except in the metal hydrides (such as LiH and CaH_2) when it is **-1**.
- For **polyatomic ions** (charged particles that contain more than one atom) the oxidation numbers of all the atoms must add up to the charge on the ion. For example, in SO_4^{2-} the four oxygen atoms contribute a total oxidation number of **-8**. Therefore, the sulfur must contribute an oxidation number of **+6** to give the ion a charge of **2-**.

All oxidation numbers must be consistent with the conservation of charge. For neutral molecules, the algebraic sum of the oxidation number of all the atoms must add up to zero. For example, in H_2SO_4, the two hydrogens contribute a total of **+2**, and the four oxygens contribute a total of **-8**. Therefore, the sulfur must contribute an oxidation number of **+6**.

C – Redox Reactions

Oxidation and reduction occur simultaneously – one cannot occur without the other. In oxidation and reduction, the increase and decrease of oxidation number results from a shift of electrons. The only way by which electrons can be shifted away from an atom (oxidation) is for them to be pulled toward another atom or ion (reduction). There is a conservation of charge as well as a conservation of mass in a redox reaction. Redox reactions fall into three categories: composition, decomposition or analysis, and single replacement reactions.

~~Composition~~ Reactions (SYNTHESIS)

$$\overset{0}{\mathbf{2Na}} + \overset{0}{\mathbf{Cl_2}} \rightarrow \overset{1+\ 1-}{\mathbf{2NaCl}}$$

In this reaction (above):

- Sodium's oxidation state changes from 0 to +1, and it is oxidized.
- Chlorine's oxidation state changes from 0 to -1, and it is reduced.

Decomposition or analysis reactions

$$\overset{1+\ 1-}{\mathbf{2HCl}} \rightarrow \overset{0}{\mathbf{H_2}} + \overset{0}{\mathbf{Cl_2}}$$

In this reaction:

- Hydrogen's oxidation state changes from +1 to 0, and it is reduced.
- Chlorine's oxidation state changes from -1 to 0, and it is oxidized.

Single replacement reactions

$$\overset{0}{\mathbf{Mg}} + \overset{1+\ 1-}{\mathbf{2HCl}} \rightarrow \overset{2+\ 1-}{\mathbf{MgCl_2}} + \overset{0}{\mathbf{H_2}}$$

In this reaction:

- Magnesium's oxidation state changes from 0 to +2, and it is oxidized.
- Hydrogen's oxidation state changes from +1 to 0, and it is reduced.

Note: Ionic or double replacement reactions are not usually redox reactions.

Balancing Simple Redox Equations

In any reaction, the loss of electrons by the species oxidized must be equal to the gain of electrons by the species reduced. As stated previous-ly, there is a conservation of charge as well as a conservation of mass in a redox reaction. For example:

$$\mathbf{Cu^0 + 2Ag^+ \rightarrow Cu^{2+} + 2Ag^0}$$

In the above reaction, the oxidation state of copper has changed from 0 to 2^+. This means that the copper atom has lost two of its electrons and has become a positive 2 ion. Meanwhile, two silver ions have each picked up one electron and have changed their oxidation state from positive one (+1) to zero (0). Another example includes the following reaction:

$$\mathbf{2Al^0 + 6H^+ \rightarrow 2Al^{3+} + 3H_2{}^0}$$

In the above reaction two aluminum atoms give up 3 electrons each to become 2 aluminum ions with a charge of positive 3. The six hydrogen ions have picked up the 6 electrons given up by the 2 aluminum atoms and have become 3 molecules of hydrogen.

Balancing Redox Reactions

In any reaction, the loss of electrons by the species oxidized must be equal to the gain of electrons by the species reduced. There is a conserva-tion of charge as well as a conservation of mass in a redox reaction.

One method for balancing the reaction between aqueous nitric acid and solid iodine follows. Given the unbalanced equation:

$$\mathbf{HNO_3 + I_2 \rightarrow HIO_3 + NO_2 + H_2O}$$

Proceed with the following steps:

1) Assign oxidation numbers to each element.

$$\overset{+1\,+5\,-2}{\mathbf{HNO_3}} + \overset{0}{\mathbf{I_2}} \rightarrow \overset{+1\,+5\ \ 2}{\mathbf{HIO_3}} + \overset{+4\,-2}{\mathbf{NO_2}} + \overset{+1\ -2}{\mathbf{H_2O}}$$

2) Determine the change in oxidation number (transfer of electrons) of the elements.

For nitrogen, $+5 \rightarrow +4$ (this shows a gain of 1 electron)
For iodine, $0 \rightarrow +5$ (this shows a loss of 5 electrons)

3) Write partial electronic equations for the materials oxidized and reduced.

$$\mathbf{N^{+5} + 1e^- \rightarrow N^{+4}}$$
$$\mathbf{I_2{}^0 \rightarrow 2I^{+5} + 10e^-}$$

4) Balance the electrons gained and lost by writing appropriate coefficients for the two half-reactions and cancel out the elec-trons gained and lost.

$$\mathbf{10N^{+5} + 10e^- \rightarrow 10N^{+4}}$$
$$\mathbf{2I^0 \rightarrow 2I^{+5} + 10e^-}$$
$$\mathbf{10N^{+5} + I_2{}^0 \rightarrow 10N^{+4} + 2I^{+5}}$$

This equation is the net equation and does not include any spectator ions or atoms that are not involved in the redox reaction.

5) Insert the coefficients from the net equation into the skeletal equation.

$$\mathbf{10HNO_3 + I_2 \rightarrow 2HIO_3 + 10NO_2 + H_2O}$$

6) Insert other coefficients consistent with the conservation of mat-ter, and balance by inspection.

$$\mathbf{10HNO_3 + I_2 \rightarrow 2HIO_3 + 10NO_2 + 4H_2O}$$

D – Corrosion (Rusting)

Corrosion is a gradual attack on a metal by its surroundings. When the metal returns to its ionic form, the usefulness of the metal may be destroyed. Corrosion is a redox reaction. Moisture, some gases in the air, and some chemicals contribute to corrosion.

Some metals, such as aluminum and zinc, form self-protective coatings. Aluminum is more susceptible to corrosion than iron. However, the corrosion of aluminum is not a serious problem, since the aluminum oxide formed can adhere tightly to the uncorroded aluminum beneath it and provide a protective layer that prevents further corrosion.

In the case of iron, the oxide formed from corrosion lacks the ability to adhere to the metal. It constantly flakes off, exposing fresh iron to corrosion.

- Anode iron is oxidized

$$\mathbf{Fe(s) \rightarrow Fe^{\pm 2} + 2e^-}$$

- Cathode oxygen is reduced

$$\mathbf{{}^1\!/_2O_2(g) + H_2O + 2e^- \rightarrow 2(OH)^-(aq)}$$

Adding the above half-reactions gives

$$\mathbf{Fe(s) + {}^1\!/_2O_2(g) + H_2O \rightarrow Fe(OH)_2(s)}$$

Further oxidation gives

$$\mathbf{2Fe(OH)_2(s) + {}^1\!/_2O_2 + H_2O \rightarrow 2Fe(OH)_3(s)}$$

This reddish, flaky product [$Fe(OH)_3$] is called **rust**. Ferrous corrosion is so widespread, that it is estimated to cost over 12 billion dollars a year in the United States alone.

Metals that corrode easily, like iron, may be protected by a variety of methods. Some methods include:

- Plating with self-protective metals like aluminum and zinc, or plating with corrosion-resistant metals like chromium and nickel.
- Sometimes, a more active metal like magnesium corrodes preferentially when it is connected to iron. This is called **cathode protection**. Magnesium plates are added to the hulls of sea going ships so that the magnesium corrodes and not the hull.
- The alloying of iron with corrosion resistant metals like nickel and chromium has produced stainless steel.
- Coating iron with paints, oils, or glass (porcelain) has proven effective against corrosion.

E – Half-Reactions

A redox reaction may be considered in two parts, one representing a loss of electrons (oxidation) and the other representing a gain of electrons (reduction). Each reaction is known as a half-reaction. A separate equation showing gain or loss of electrons (electronic equation) can be written for each half-reaction. For example:

$$\mathbf{\overset{0}{Mg} + \overset{0}{Cl} \rightarrow \overset{2+\ 1-}{MgCl_2}}$$

It can be represented as:

$$\mathbf{Mg^0 \rightarrow Mg^{2+} + 2e^-} \text{ (oxidation)}$$

$$\mathbf{Cl_2 + 2e^- \rightarrow 2Cl^-} \text{ (reduction)}$$

In the above reaction, Mg^0 is supplying the electrons and is considered the agent that causes the chlorine to be reduced. It is called the reducing agent. Substances with low ionization energies and low electronegativities are easily oxidized so they are called strong reducing agents.

On the other hand the Cl_2 is considered the agent that causes Mg to be oxidized. It is called the **oxidizing agent**. Elements with high electronegativities and ionization energies are more easily reduced and, therefore, are called strong oxidizing agents.

F – Electrochemical (Voltaic) Cells

Half-Cells

It is possible to set up reactions so that each half of a redox reaction takes place in a separate vessel. This occurs if the vessels are connected by an external conductor and a salt bridge or porous partition. This permits the migration of ions but does not allow the solutions to mix

Electrodes

The **electrode** at which reduction occurs in a cell is called a **cathode**. The cathode is identified as follows:

- In an electrochemical (voltaic) cell, the cathode is the positive electrode.
- In an electrolytic cell, the cathode is the negative electrode.

The electrode at which oxidation occurs in a cell is called the **anode**. The anode is identified as follows:

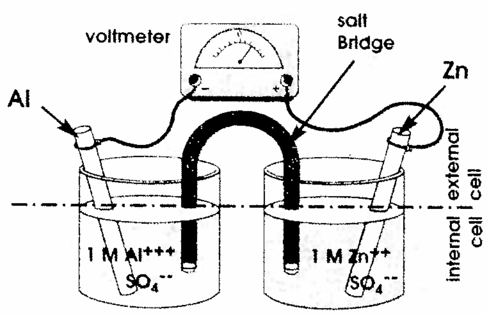
- In an electrochemical (voltaic) cell, the anode is the negative electrode.
- In an electrolytic cell, the anode is the positive electrode.

Chemical Cells – Electrochemical (Voltaic Cells)

Redox reactions that occur spontaneously may be employed to provide a source of electrical energy.

When the two half-cells of a redox reaction are connected by an external conductor and a salt bridge or a porous cup that allows the migration of ions, a flow of electrons (electric current) is produced. In a voltaic cell, a chemical reaction is used to produce a spontaneous electric current by converting chemical energy to electrical energy.

$$\overset{0}{Al} \xrightarrow[\text{(at anode)}]{\text{oxidation}} \overset{3+}{Al} + 3e^- \qquad \overset{2+}{Zn} + 2e^- \xrightarrow[\text{(at cathode)}]{\text{reduction}} \overset{0}{Zn}$$



In the figure at the right, when the voltmeter is connected to allow the flow of electrons, the aluminum metal strip which is immersed in a solution of $Al_2(SO_4)_3$ which contains both Al^{+++} and SO_4^{--} ions will supply the electrons which flow through the voltmeter to the zinc electrode. The excess of electrons allows the zinc ions in the solution of $Zn^{++}SO_4^{--}$ to pick up electrons at the zinc electrode and become zinc metal atoms Zn^0. In an electrochemical cell, oxidation occurs at the anode and reduction at the cathode.

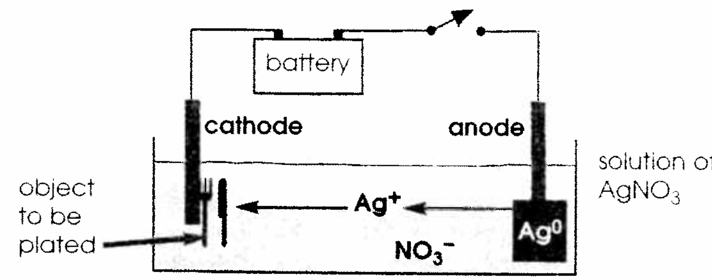
The aluminum metal atoms Al^0 each lost three electrons to become Al^{3+} ions. Since the loss of electrons takes place at the aluminum electrode it is called the anode, and the zinc electrode, where reduction takes place, is called the cathode. The E^0 values are established after setting up the two half-cell reactions

As the current continues, the flow of electrons diminishes until the cell reaches a state of equilibrium when the voltmeter will read zero.

Electrolytic Cells

Redox reactions that do not occur spontaneously can be forced to take place by supplying energy with an externally applied electric current. The use of an electric current to bring about a chemical reaction is called **electrolysis**. In an electrolytic cell, an electric current is used to produce a chemical reaction.

Silver, chrome, and stainless steel plating are processes that make use of this principle. In this process, an electric current is used to produce a chemical reaction. This results in the covering of a surface (usually a metallic item such as a spoon, car bumper, or trim) with a metal plating.



In the illustration above, the passage of one mole of electrons (6.02×10^{23} electrons) through the cathode will allow one mole of Ag^+ ions to be plated onto the object to be coated.

The procedure used is to make a solution of the salt that contains the plating metal ions and immerse the object to be plated (which is attached to the negative pole of a power pack) into the solution. Then, the flow of electric current is switched on. The concentration of the solution and the amount of time that the current is allowed to continue determines how thick the layer of plated material will be. In this process, reduction takes place at the cathode, which is negative in charge. The object to be plated is placed touching the cathode. Oxidation takes place at the anode, which is composed of the metal to be plated.

- **Predict the direction of electron flow**
- **Predict the direction of ion movement**

Unit Eight Redox

Key Concepts
- Oxidation Numbers
- Reduction
- Oxidation
- Balancing Redox
- Half-Reaction
- Types of Reactions; Single Replacement, Synthesis, Decomposition, Double Replacement
- Anode
- Cathode
- Voltaic Cell
- Salt Bridge
- Electrolytic Cell; Refining Metals, Electroplating, Electrolysis

I Reduction/Oxidation-REDOX

Any reaction that involves the transfer of electrons is a redox reaction. When a substance gains electrons it has gone through ***reduction***. When a substance loses electrons it has gone through ***oxidation.***

II Oxidation States

The ***oxidation state*** or apparent charge of an atom or element varies depending on how it is bonded. When there is a change in the oxidation state a redox reaction has taken place. If the oxidation number increase the substance has gone through ***oxidation***. If the oxidation number decreases the substance has gone through ***reduction.***
The rules for assigning oxidation states follow:

1. Free elements are 0
2. Group 1 =+1
3. Group 2 =+2
4. Oxygen normally = -2, exception peroxide = -1
5. Hydrogen normally = +1, exception when hydride = -1
6. Total sum of all charges in a molecule = 0
7. Total sum of all charges in a polyatomic ion = ion charge

III Redox Reactions

Types of Reactions

A. Single Replacement $A + BC \rightarrow B + AC$ use table J to predict which reaction will occur. More actives are found in compounds.

B. Synthesis $A + B \rightarrow AB$

C. Decomposition $AB \rightarrow A + B$

D. Double Replacement $AB + CD \rightarrow AD + CB$ (not a redox)

Half-Reactions show either the reduction or oxidation that is occurring during a redox reaction. . The overall reaction is the combination of the two half-reactions when the electrons have canceled out.

Oxidation is losing electrons and the oxidation number goes up, therefore the electrons are on the right and the Oxidation State on the right is higher.

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

Reduction is gaining electrons and the oxidation number goes down, therefore the electrons are on the left and the oxidation state is lower on the right.

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

Overall Reaction: $Zn + Cu^{+2} \rightarrow Zn^{+2} + Cu$

IV Balancing Redox

When a redox ***reaction is balanced*** both the charge and the mass are balanced. The same numbers of electrons need to be lost and gained.

Overall Equation $Cu^{2+} + Ag \rightarrow Cu + Ag^+$

1. Write the Half Reactions — Reduction $Cu^{2+} + 2\,e^- \rightarrow Cu$; Oxidation $Ag \rightarrow Ag^+ + 1\,e^-$

2. Balance Electrons by finding the least common multiple — Reduction x1 $Cu^{2+} + 2\,e^- \rightarrow Cu$; Oxidation x2 $2Ag \rightarrow 2Ag^+ + 2\,e^-$

3. Put the coefficients in the the overall equation. — $Cu^{2+} + 2Ag \rightarrow Cu + 2Ag^+$

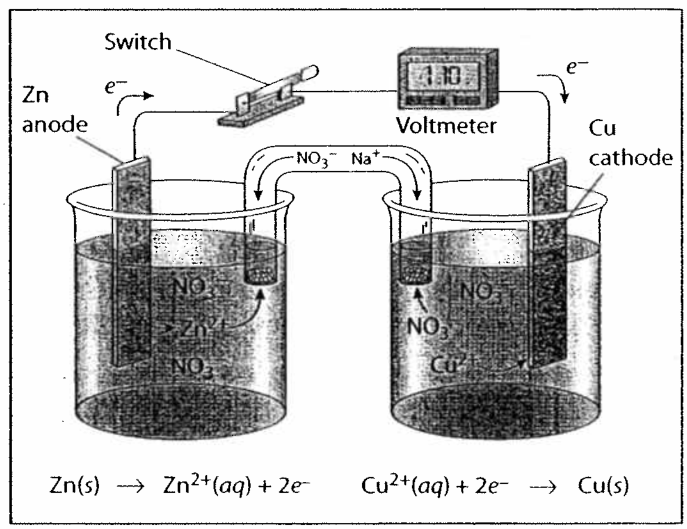
Important to check electrons and not just look at the number of atoms.

V Electrochemical Cells - Involves a chemical reaction and a floe of electrons from the anode to the cathode. The ***anode*** is the electrode where oxidation occurs. The ***cathode*** is the electrode where reduction takes place.

A ***Voltaic Cells***

These cells generate electricity and are spontaneous. The anode is negative and the cathode is positive. A ***salt bridge*** is needed to allow ions to migrate from one side to another.

a.) TABLE J. The metals at the top of the table are the most active and are the most likely to lose electrons and be found in a compound. The metals at the bottom of the table are the least active, which means they are less likely to lose electrons and are more likely to be found free in nature. Batteries are voltaic cells. Metals at the top of Table J want to go through oxidation and serve as anodes. Metals at the bottom of table J want to go through reduction and are the cathode. The electrons will move from the metal that is on the top of table J (ANODE) to the metal at the bottom of table J (CATHODE). The further apart the metals are on reference table J the activity series the more energy they generate.



B. *Electrolytic Cells*

These cells use electricity and are nonspontaneous. The anode is positive and the cathode is negative. Here a battery is need to force the electrons to flow. ***Electrolysis*** is the term used when electricity is used to cause a chemical reaction to take place.

a.)***Refining Metals*** is the process of producing a pure metal from a metallic compound. This occurs when an external power source is applied and the metal ions are reduced at the negative cathode.

b.)***Electroplating*** is the same process when the item to be plated is connected to the negative terminal of the power source, the cathode, and the ions reduce and form the pure metal.