OXIDATION NUMBERS

- The oxidation number of an atom is the number of electrons lost, gained or unequally shared by an atom. Oxidation numbers can be zero, positive or negative.

- Oxidation number of a monatomic ion is equal to the charge of the ion. For example:

NaCl

Na^+ = sodium has lost an electron O.N. = +1

Cl^- = chloride has gained an electron O.N. = –1

- In covalent compounds, the oxidation numbers are based on relative electronegativities.

- For non-polar covalent compounds each atom is assigned an oxidation number of 0 because they have the same electronegativity. For example:

	H—H		Cl—Cl	
EN	2.1	2.1	3.0	3.0
O.N.	0	0	0	0

- For polar covalent compounds, the element with the greater electronegativity is assigned the negative oxidation number, and the element with the lower electronegativity is assigned the positive oxidation number. For example:

	H—Cl	
EN	2.1	3.0
O.N.	+1	–1

- Many elements have multiple oxidation numbers. For example:

	N_2	N_2O	NO	N_2O_3	NO_2	N_2O_5	NO_3^-
O.N.. of N	0	+1	+2	+3	+4	+5	+5

OXIDATION NUMBER RULES

1. All elements in their free states have oxidation number of zero.
   Examples: Na, Cu, Mg, H_2, O_2, Cl_2

2. Hydrogen is +1, except when combined with metals, where it is −1.
   Examples: NaH, CaH_2

3. Oxygen is −2, except in peroxides, where it is −1 and OF_2 , where it is +2.
   Examples:H_2O_2 , Na_2O_2

4. For monatomic ions, O.N. equals the charge of the ion.
   Examples: $Na^+ = +1$, $Cl^- = -1$

5. The algebraic sum of the oxidation number of elements in a compound is equal to zero.

6. The algebraic sum of the oxidation numbers in a polyatomic ion is equal to the charge of the ion.

Examples:

1. Determine the oxidation number of sulfur in sulfuric acid (H_2SO_4)

2. Determine the oxidation number of carbon in calcium carbonate ($CaCO_3$)

3. Determine the oxidation number of each underlined element in the compounds shown below:

   a) $\underline{S}O_2$

   b) $H_3\underline{P}O_4$

   c) $H\underline{C}_2H_3O_2$

REDOX REACTIONS

- **Oxidation-reduction (redox)** is a chemical process in which the oxidation number of an element is changed.

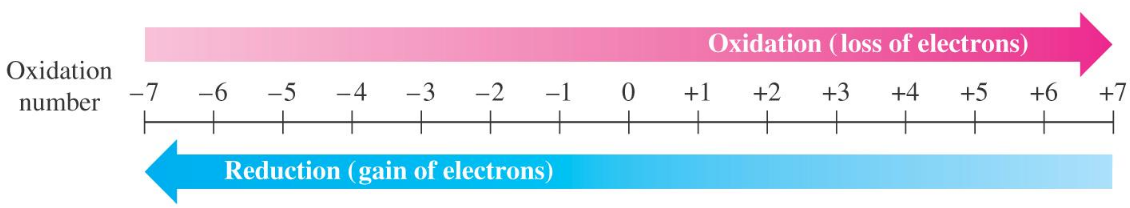
- **Oxidation** occurs when the oxidation number of an element increases as a result of losing electrons.

$$Ag^{0} \xrightarrow{\text{loss of 1 e}^{-}} Ag^{+}$$

- **Reduction** occurs when the oxidation number of an element decreases as a result of gaining electrons.

$$Cu^{2+} \xrightarrow{\text{gain of 2 e}^{-}} Cu^{0}$$

- In a redox reaction oxidation and reduction occur simultaneously, one cannot occur in the absence of the other.



<u>Examples:</u>
For each reaction below, determine the oxidized and reduced species, and the number of electrons transferred:

1. $2\ Ca\ (s) + O_2\ (g) \longrightarrow 2\ CaO\ (s)$

2. $HF + KOH \longrightarrow KF + H_2O$

OXIDIZING AND REDUCING AGENTS

- **Oxidizing agent:** The substance that causes an increase in the oxidation state of another substance. The oxidizing agent is reduced in a redox reaction.

$$Cu^0 + 2\,Ag^+ \longrightarrow Cu^{2+} + 2\,Ag^0$$

- **Reducing agent:** The substance that causes a decrease in the oxidation state of another substance. The reducing agent is oxidized in a redox reaction.

$$Cu^0 + 2\,Ag^+ \longrightarrow Cu^{2+} + 2\,Ag^0$$

Examples:

Identify the oxidizing and reducing agents in the reactions shown below:

1. $$Zn\,(s) + H_2SO_4\,(aq) \longrightarrow ZnSO_4\,(aq) + H_2\,(g)$$

   Reaction can be more clearly seen in the net ionic form:

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

   Oxidizing agent:________________ Reducing agent:_________________

2. $$Ca\,(s) + H_2O\,(l) \longrightarrow Ca(OH)_2\,(aq) + H_2\,(g)$$

   Oxidizing agent:________________ Reducing agent:_________________

HALF-REACTIONS

- Redox reactions can be separated into two ***half-reactions***: oxidation and reduction.
- In an ***oxidation*** half-reaction the electrons are lost, and therefore represented as product:

$Cu^0 (s) \rightarrow Cu^{2+} (aq) + 2\ e^-$ **oxidation half-reaction**

- In a reduction half-reaction the electrons are gained, and therefore represented as reactant:

$Ag^+ (aq) + e^- \rightarrow Ag^0 (s)$ **reduction half-reaction**

- When two half-reactions are added together, the number of electrons must be equalized in order to cancel one-another.

$2\ (Ag^+ + e^- \rightarrow Ag)$ **reduction half-reaction**

$2\ Ag^+ + 2\ e^- \rightarrow 2\ Ag$ **reduction half-reaction**

- The sum of the two half-reactions would then equal the overall reaction.

$Cu^0 \rightarrow Cu^{2+} + 2\ e^-$ **oxidation half-reaction**

$2\ Ag^+ + 2\ e^- \rightarrow 2\ Ag$ **reduction half-reaction**

$Cu^0 + 2\ Ag^+ + \cancel{2\ e^-} \rightarrow Cu^{2+} + 2\ Ag + \cancel{2\ e^-}$ **Overall reaction**

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

Examples:

1. Write oxidation and reduction half-reactions the following reaction:

$$Mg\ (s) + Br_2\ (l) \rightarrow MgBr_2\ (s)$$

Oxidation half-reaction:

Reduction half-reaction:

2. Write oxidation and reduction half-reactions for the following reaction:

$$Cl_2\ (g) + 2\ NaBr\ (l) \rightarrow Br_2\ (l) + 2\ NaCl\ (aq)$$

Oxidation half-reaction:

Reduction half-reaction:

ACTIVITY SERIES OF METALS

- **Activity series** is a listing of metallic elements in descending order of reactivity. Hydrogen is also included in the series since it behaves similar to metals.

- Activity series tables are available in textbooks and other sources.

- Elements listed higher will displace any elements listed below them. For example Na will displace any elements listed below it from one of its compounds.

$$2\ Na\ (s)\ +\ MgCl_2\ (aq) \rightarrow 2\ NaCl\ (aq) + Mg\ (s)$$

$$Na\ (s)\ +\ AgCl\ (aq)\ \rightarrow\ NaCl\ (aq)\ +\ Ag\ (s)$$

- Elements listed lower will not displace any elements listed above them. For example Ag cannot displace any elements listed above it from one of its compounds.

$$Ag\ (s)\ +\ CuCl_2\ (aq)\ \rightarrow\ \text{No Reaction}$$

$$Ag\ (s)\ +\ HCl\ (aq)\ \rightarrow\ \text{No Reaction}$$

Table 17.3 Activity Series of Metals

Ease of oxidation ↑			
	K	$\longrightarrow$	$K^+ + e^-$
	Ba	$\longrightarrow$	$Ba^{2+} + 2\,e^-$
	Ca	$\longrightarrow$	$Ca^{2+} + 2\,e^-$
	Na	$\longrightarrow$	$Na^+ + e^-$
	Mg	$\longrightarrow$	$Mg^{2+} + 2\,e^-$
	Al	$\longrightarrow$	$Al^{3+} + 3\,e^-$
	Zn	$\longrightarrow$	$Zn^{2+} + 2\,e^-$
	Cr	$\longrightarrow$	$Cr^{3+} + 3\,e^-$
	Fe	$\longrightarrow$	$Fe^{2+} + 2\,e^-$
	Ni	$\longrightarrow$	$Ni^{2+} + 2\,e^-$
	Sn	$\longrightarrow$	$Sn^{2+} + 2\,e^-$
	Pb	$\longrightarrow$	$Pb^{2+} + 2\,e^-$
	H_2	$\longrightarrow$	**$2\,H^+ + 2\,e^-$**
	Cu	$\longrightarrow$	$Cu^{2+} + 2\,e^-$
	As	$\longrightarrow$	$As^{3+} + 3\,e^-$
	Ag	$\longrightarrow$	$Ag^+ + e^-$
	Hg	$\longrightarrow$	$Hg^{2+} + 2\,e^-$
	Au	$\longrightarrow$	$Au^{3+} + 3\,e^-$

Examples:

Use activity series to complete each reaction below. If no reaction occurs, write "No Reaction".

1. $Pb\ (s)\ +\ HCl\ \rightarrow$

2. $Zn\ (s)\ +\ MgCl_2\ (aq)\ \rightarrow$

3. $Ni\ (s)\ +\ CuCl_2\ (aq)\ \rightarrow$

4. $Mg\ (s)\ +\ AlCl_3\ (aq)\ \rightarrow$

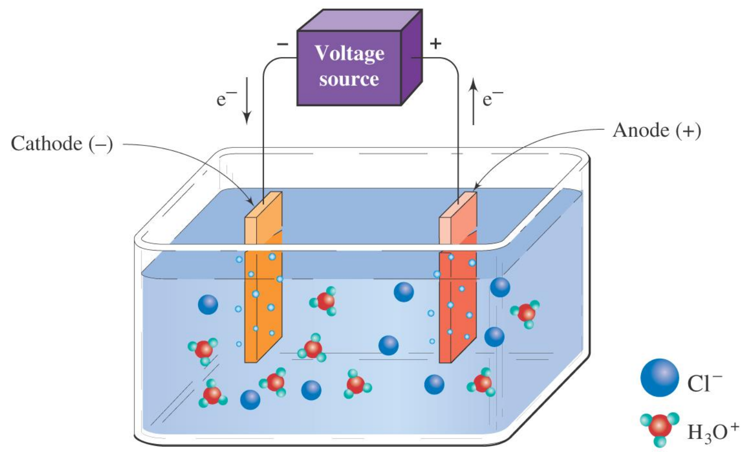
ELECTROLYSIS

- The process by which electrical energy is used to bring about a non-spontaneous chemical change is called ***electrolysis***. For example water can be decomposed to its elements through electrolysis:

$$2\ H_2O\ (l) \xrightarrow[\text{current}]{\text{electric}} 2\ H_2\ (g)\ +O_2\ (g)$$

- The apparatus in which electrolysis is performed is called ***electrolytic cell***. The cell consists of a positive electrode (***anode***) and a negative electrode (***cathode***).

- In an electrolytic cell electrical energy from the voltage source is used to bring about non-spontaneous redox reactions. For example, the electrolysis of HCl is shown below.



- The cations migrate toward the cathode (–) and are reduced.

$2\ H^+\ (aq)\ +2\ e^- \rightarrow H_2\ (g)$ **Reduction half-reaction**

- The anions migrate toward the anode (+) and are oxidized.

$2\ Cl^-\ (aq) \rightarrow Cl_2\ (g) +\ 2\ e^-$ **Oxidation half-reaction**

- The overall reaction can be obtained by adding the two half-reactions.

$2\ HCl\ (aq) \rightarrow H_2\ (g)\ +\ Cl_2\ (g)$ **Overall reaction**

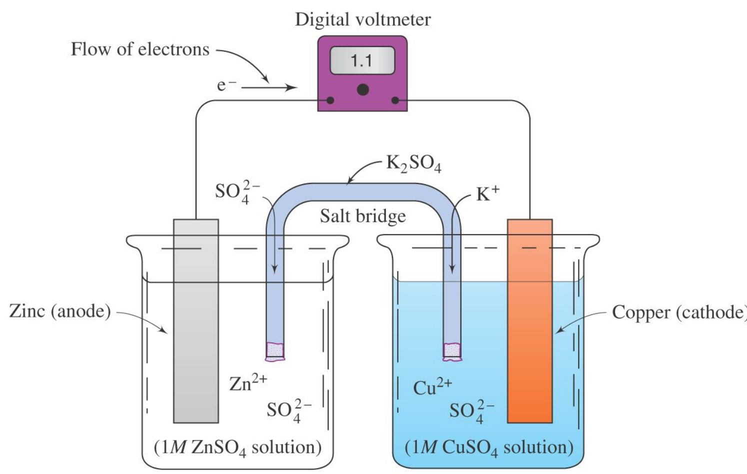
VOLTAIC CELLS

- A ***voltaic cell*** is a cell that produces electrical energy from a spontaneous chemical reaction. A voltaic cell is also known as a galvanic cell.

- The oxidation of a more active metal by a less active metal is a spontaneous reaction that can produce electrical energy. For example:

$$Zn\ (s) + CuSO_4\ (aq) \rightarrow ZnSO_4\ (aq) + Cu\ (s)$$

- When this reaction is carried out in a voltaic cell, electrical energy is produced.



- The oxidation half-reaction occurs at the anode (Zn).

$$Zn\ (s) \rightarrow Zn^{2+}\ (aq) + 2\ e^- \qquad \textbf{Oxidation half-reaction}$$

- The reduction half-reaction occurs at the cathode (Cu).

$$Cu^{2+}\ (aq) + 2\ e^- \rightarrow Cu\ (s) \qquad \textbf{Reduction half-reaction}$$

- The overall reaction can be obtained by adding the two half-reactions.

$$Zn\ (s) + Cu^{2+}\ (aq) \rightarrow Zn^{2+}\ (aq) + Cu \qquad \textbf{Overall reaction}$$

Examples:

1. In the voltaic cell shown below, (a) write the overall reaction, (b) identify the anode and cathode, and (c) write half-reaction for each electrode.