# V. Electrochemistry

## Oxidation Numbers

**oxidation number**: the apparent charge of an atom in a compound/ion if all bonds are considered to be ionic.

## Rules for Assigning Oxidation Numbers

(1) The oxidation number for an atom in an element is zero.
ex. Na, $O_2$, He etc. all have an oxidation number equal to zero

(2) The oxidation number of an ion is equal to its charge.
ex. for NaCl, $Na^+$ has an oxidation number of +1 and $Cl^-$ has an oxidation number of -1

(3) In a compound, hydrogen usually has an oxidation number of +1.
ex. HBr, $H^+$ has an oxidation number of +1 and $Br^-$ has an oxidation number of -1.

The exception is for metal hydrides, where hydrogen has an oxidation number of -1.
ex. LiH, $Li^+$ has an oxidation number of +1 and hydrogen has an oxidation number of -1.

(4) In a compound, oxygen usually has an oxidation number of -2.
ex. $K_2O$, $K^+$ has an oxidation number of +1 and $O^{2-}$ has an oxidation number of -2.

The exception is for peroxides, where oxygen has an oxidation number of -1.
ex. hydrogen peroxide, $H_2O_2$, $H^+$ has an oxidation number of +1 and oxygen has an oxidation number of -1

(5) In neutral compounds, the oxidation numbers of atoms must add up to zero. In an ion, the oxidation numbers of all atoms must add up to the total charge.

ex. Assign oxidation numbers to each element in the following compounds/ions.

(1) $SO_3^{2-}$ (2) $Cr_2O_3$ (3) $KMnO_4$ (4) $HPO_4^-$ (5) $Fe_3O_4$

* fractional oxidation numbers are possible! In this case, the oxidation number represents an average of all of that the atoms of the substance.

## Reduction Oxidation (Redox) Reactions

A Redox reaction is one that involves a change of oxidation number.

**Oxidation**: a chemical reaction in which the oxidation number of an atom increases as a result of *losing electrons*.
**Reduction**: a chemical reaction in which the oxidation number of an atom decreases as a result of *gaining electrons*.
**Oxidizing agent**: the substance that is *reduced* in a redox reaction.
**Reducing agent**: the substance that is *oxidized* in a redox reaction.

Just remember: LEO says GER (losing electrons oxidation/gaining electrons reduction)

ex. Assign oxidation numbers to each element. Determine if the reaction is a redox reaction.

(1) $2Na + Cl_2 \rightarrow 2NaCl$

(2) $Na_2CO_3 + CaCl_2 \rightarrow 2NaCl + CaCO_3$

(3) $CuCl_2 + 2Ag \rightarrow 2AgCl + Cu$

ex. Determine if each change represents oxidation or reduction.

(1) $Co^{2+} \rightarrow Co$ (2) $2Cl^{-} \rightarrow Cl_2$ (3) $Fe^{3+} \rightarrow Fe^{2+}$ (4) $Sn^{2+} \rightarrow Sn^{4+}$

ex. Assign oxidation numbers to each atom and determine which element is being oxidized and which element is being reduced. Identify the oxidizing agent and the reducing agent.

ex. $SO_4^{2-} + 8I^{-} + 8H^{+} \rightarrow S^{2-} + 4I_2 + 4H_2O$

ex. $2NO_3^{-} + 8H^{+} + 3Cu \rightarrow 2NO + 4H_2O + 3Cu^{2+}$

**Balancing Redox Equations**

**Half Reaction Method**

(1) Write separate equations for the oxidation and reduction half reactions.
(2) For each half reaction:
- balance all the elements
- balance the charge by adding electrons

(3) Add the two half reactions together. If necessary multiply one or both of the reactions by a number in order to equalize the number of electrons in the two half reactions. Cancel identical species.

ex. Balance each Redox equation using the half reaction method.

(1) $Pb^{4+} + Mg \rightarrow Pb + Mg^{2+}$

(2) $Cl_2 + Na \rightarrow Cl^{-} + Na^{+}$

(3) $Ce^{4+} + Sn^{2+} \rightarrow Ce^{3+} + Sn^{4+}$

(4) $Al + Cu^{2+} \rightarrow Al^{3+} + Cu$

(5) $Al + F_2 \rightarrow Al^{3+} + F^{-}$

## Balancing Redox Equations in Acidic Solution

(1) Write separate equations for the oxidation and reduction half reactions.

(2) For each half reaction:

- balance all the elements except oxygen and hydrogen.
- balance the oxygen atoms by adding $H_2O$
- balance the hydrogen atoms by adding $H^+$
- balance the charge by adding electrons

(3) Add the two half reactions together. If necessary multiply one or both of the reactions by a number in order to equalize the number of electrons in the two half reactions. Cancel identical species.

ex. Balance each Redox equation occurring in Acidic Solution.

(1) $MnO_2 + Cl^- \rightarrow Mn^{2+} + Cl_2$

(2) $Cr_2O_7^{2-} + SO_2 \rightarrow Cr^{3+} + SO_4^{2-}$

(3) $Os + IO_3^- \rightarrow OsO_4 + I_2$

**Balancing Redox Equations in Basic Solution**

(1) Write separate equations for the oxidation and reduction half reactions.

(2) For each half reaction:

- balance all the elements except oxygen and hydrogen.
- balance the oxygen atoms by adding $H_2O$
- balance the hydrogen atoms by adding $H^+$
- balance the charge by adding electrons

(3) Add the two half reactions together. If necessary multiply one or both of the reactions by a number in order to equalize the number of electrons in the two half reactions. Cancel identical species.

(4) For a basic solution, add the same number of $OH^-$ as there are $H^+$ ions to both sides of the reaction. ($H^+$ will be eliminated from one side of the reaction by forming $H_2O$ and $OH^-$ will remain on the other side of the reaction)

ex. Balance each Redox equation occurring in Basic Solution.

(1) $HClO_2 + I^- \rightarrow Cl_2 + HIO$

(2) $MnO_4^- + NO_2^- \rightarrow MnO_2 + NO_3^-$

(3) $ClO_3^- + N_2H_4 \rightarrow NO_3^- + Cl^-$

## Disproportionation Reactions

In a disproportionation reaction, a single substance is both oxidized and reduced.

ex. Balance the following reaction in acidic solution:

$I_2 \rightarrow I^- + IO^-$

ex. Balance the following reaction in basic solution:

$Cl_2 \rightarrow ClO_3^- + Cl^-$

## Reduction OxidationTitrations

Redox Titrations involve redox reactions.

ex. In acidic solution, $MnO_4^-$ reacts with $Fe^{2+}$ to produce $Mn^{2+}$ and $Fe^{3+}$.
Write the balanced chemical equation for this reaction. What volume of 0.02118 M $KMnO_4$ solution is required to titrate 42.00 mL of 0.1040 M $Fe(NO_3)_2$?

ex. A sample of tin ore (impure) weighing 0.300 g was dissolved in acid to produce $Sn^{2+}$ ions. The solution was then titrated with 8.08 mL of 0.0500 M $KMnO_4$ solution. In acidic solution, $Sn^{2+}$ reacts with $MnO_4^-$ to produce $Sn^{4+}$ and $Mn^{2+}$. Write the balanced chemical equation for this reaction. Determine the mass of pure tin in the sample of tin ore. Determine the percent tin in the sample of tin ore.

**Predicting Redox Reactions**

Common Reduction Reactions:

| **Reactants (oxidizing agent)** | **Products formed** |
|---|---|
| $MnO_4^-$ (acidic solution) | $Mn^{2+}$ |
| $MnO_2$ | $Mn^{2+}$ |
| $MnO_4^-$ (basic or neutral solution) | $MnO_2$ |
| $Cr_2O_7^{2-}$ (acidic solution) | $Cr^{3+}$ |
| $CrO_4^{2-}$ (basic solution) | $CrO_2^-$ |
| halogens (ex. $Cl_2$) | halide ions (ex. $Cl^-$) |
| metal ions (ex. $Cu^{2+}$) | metals (ex. Cu) |
| metall*ic* ions (higher oxidation number) (ex. $Fe^{3+}$) | metall*ous* ions (lower oxidation number) (ex. $Fe^{2+}$) |
| $H_2O$ | $H_2 + OH^-$ |

Common Oxidation Reactions:

| **Reactants (reducing agent)** | **Products formed** |
|---|---|
| halide ions (ex. $Cl^-$) | halogens (ex. $Cl_2$) |
| $S_2O_3^{2-}$ | $S_4O_6^{2-}$ |
| $C_2O_4^{2-}$ | $CO_2$ |
| metals (ex. Cu) | metal ions (ex. $Cu^{2+}$) |
| metall*ous* ions (lower oxidation number) (ex. $Fe^{2+}$) | metall*ic* ions (higher oxidation number) (ex. $Fe^{3+}$) |
| $H_2O_2$ | $O_2 + H_2O$ |
| $H_2O$ | $O_2 + H^+$ |

| Common multivalent metals | Common metals with only one charge |
|---|---|
| $Fe^{3+}/Fe^{2+}$<br>$Cu^{2+}/Cu^+$<br>$Pb^{4+}/Pb^{2+}$<br>$Sn^{4+}/Sn^{2+}$<br>$Co^{3+}/Co^{2+}$<br>$Cr^{3+}/Cr^{2+}$<br>$Ni^{3+}/Ni^{2+}$ | $Ag^+$<br>$Zn^{2+}$<br>$Cd^{2+}$<br>$Al^{3+}$ |

Complete and balance the following reactions:
(1) A strip of lead metal is added to a solution of silver nitrate.

(2) An acidic solution of potassium dichromate is added to a solution of iron (II) nitrate

(3) An alkaline (basic) solution of potassium permanganate and tin (II) nitrate are mixed

(4) Liquid bromine is added to a solution of potassium iodide.

(5) Cadmium nitrate is mixed with chromium (II) nitrate

## Standard Reduction Potentials

In order to determine if a redox reaction will occur spontaneously, each reduction reaction is assigned a standard reduction potential (E°) measured in volts (V). Standard reduction potentials given are for standard conditions: at a temperature of 25 ºC, all gases at 1.00 atm and all solutions having a concentration equal to 1.0 M. Standard reduction potentials are relative to the reduction of hydrogen, which is assigned a voltage of zero. *The higher the reduction potential, the more easily the element/compound is reduced. The lower the reduction potential, the more easily the element/compound is oxidized.*
Note: If the reduction reaction is reversed and is written as an oxidation, the sign on the voltage is reversed. Multiplying the reaction by a number does NOT change the voltage.

The overall voltage for a reaction can be determined by adding the voltages for the reduction half reaction and the oxidation half reaction. If the overall voltage is positive, the reaction is spontaneous. If the overall voltage is negative the reaction is non-spontaneous.

ex. Which of the following substances is the strongest oxidizing agent? $F_2$, $Cd^{2+}$, $Na^+$, or $Br_2$

ex. Which of the following substances is the strongest reducing agent? Rb, $Cl^-$, Hg, or $Sn^{2+}$

ex. Determine the voltage for each half-reaction. Determine the overall voltage. Is the reaction spontaneous or non-spontaneous?

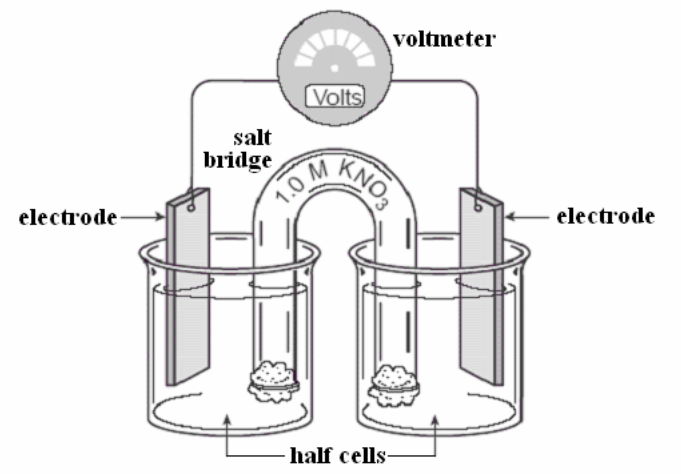
(1) $Cl_2 + Cd \rightarrow 2Cl^- + Cd^{2+}$

(2) $2I^- + Zn^{2+} \rightarrow I_2 + Zn$

(3) $F_2 + 2Li \rightarrow 2F^- + 2Li^+$

## Electrochemical Cells

Electrochemical or galvanic cells convert the chemical energy of redox reactions into electrical energy. In an electrochemical cell, the reduction half reaction and the oxidation half reaction are separated into two half cells. Each half cell consists of an electrode and a solution. There may also be a liquid or a gas that is part of the redox reaction. The electrons transferred during the redox reaction create a current that moves through a wire connecting the two half cells. In order to complete the circuit, a salt bridge also connects the two half cells. A salt bridge is a glass tube filled with an electrolyte (ie. $KNO_3$). The voltage produced by the redox reaction (E° cell) is measured using a voltmeter.



The overall redox reaction in an electrochemical cell is always spontaneous (always has a positive overall voltage). The half cell where **oxidation** occurs is called the **anode** and the half cell where **reduction** occurs is called the **cathode**. Electrons are produced at the anode and travel through the wire towards the cathode where they are consumed.

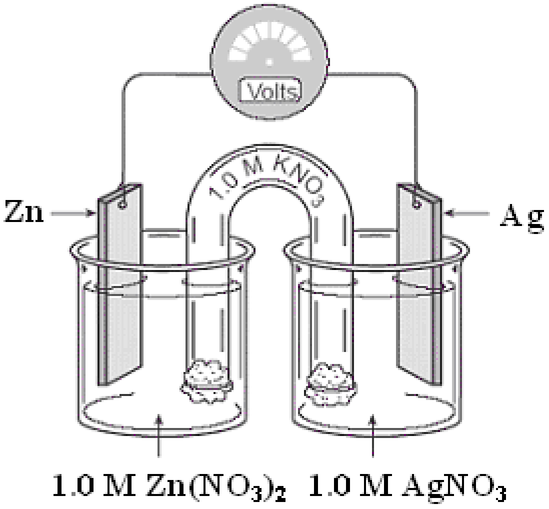
The metal electrode of the anode will generally decrease in mass as the metal is oxidized and the metal electrode of the cathode will generally increase in mass as the metal ions in the solution are reduced.

In the salt bridge, ions migrate in order to keep the half cells neutral (uncharged). The cation in the salt bridge (ie. $K^+$) migrates towards the cathode and the anion in the salt bridge (ie. $NO_3^-$) migrates towards the anode.

**Line Notation**

Electrochemical cells can be represented using line notation. Anode components are listed on the left and cathode components are listed on the right. The half cells are separated by a double vertical line: "||". Phase boundaries are indicated by a single vertical line: "|".

ex. Consider the following electrochemical cell.



(a) Write the cathode half reaction. Label the cathode.

(b) Write the anode half reaction. Label the anode.

(c) Write the overall reaction.

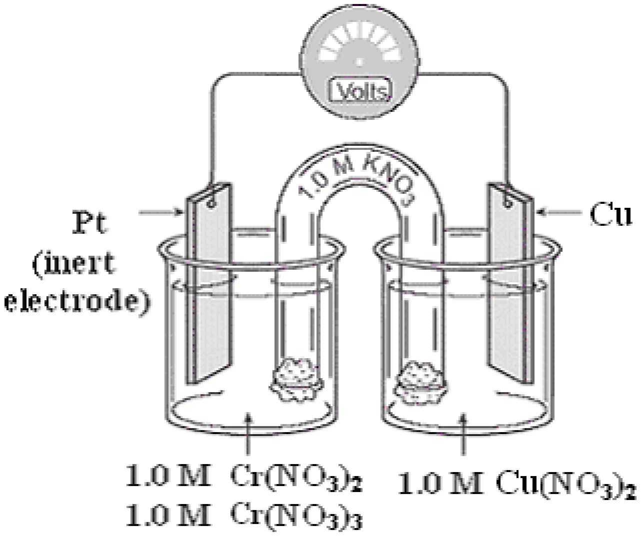
(d) Calculate the cell voltage. ($E^o_{cell}$)

(e) On the diagram, show electron flow and ion migration.

(f) Which electrode loses mass and which electrode gains mass?

(g) Give the line notation for this electrochemical cell.

ex. Consider the following electrochemical cell.



(a) Write the cathode half reaction. Label the cathode.

(b) Write the anode half reaction. Label the anode.

(c) Write the overall reaction.

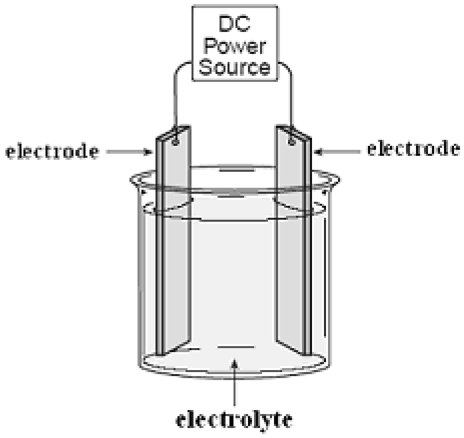
(d) Calculate the cell voltage. ($E^o_{cell}$)

(e) On the diagram, show electron flow and ion migration.

(f) Give the line notation for this electrochemical cell.

**Electrolytic Cells**

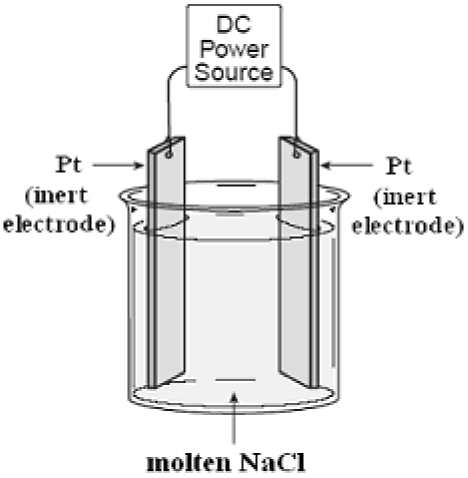
Electrolytic cells convert electrical energy into chemical energy in order to cause a non-spontaneous reaction to occur.
In an electrolytic cell, electrical energy is supplied by a power source (ie. a battery).



In order to determine the reaction taking place at the cathode, list all possible reduction reactions and the voltage of each. The reduction reaction that takes place is the one with the highest voltage.
In order to determine the reaction taking place at the anode list all possible oxidation reactions and the voltage of each. The oxidation reaction that takes place is the one with the highest voltage.
The power supply required to operate the electrolytic cell will be equal to the overall voltage for the electrolytic cell.

There are three basic types of electrolytic cells.
Type I: Inert electrodes (ie. platinum or graphite), molten electrolyte

ex. Consider the following electrolytic cell.



(a) Write the cathode half reaction.

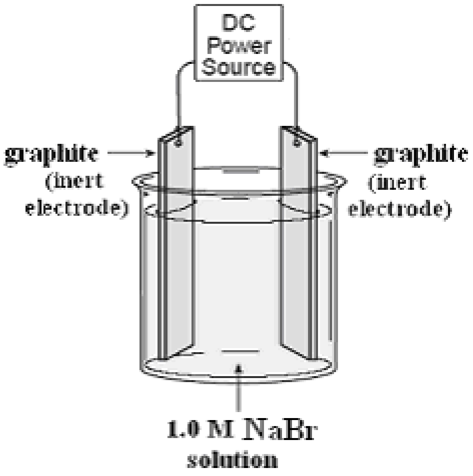
(b) Write the anode half reaction.

(c) Write the overall reaction.

(d) Calculate the power that must be supplied to operate the cell.

Type II: Inert electrodes (ie. platinum or graphite), electrolyte solution

ex. Consider the following electrolytic cell.



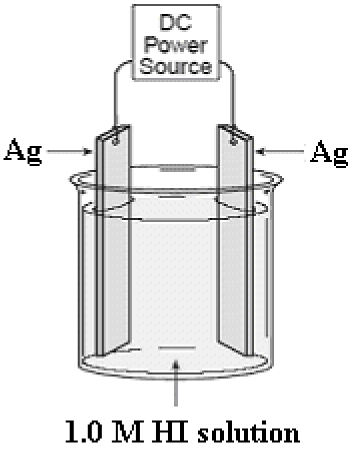
(a) Write the cathode half reaction.

(b) Write the anode half reaction.

(c) Write the overall reaction.

(d) Calculate the power that must be supplied to operate the cell.

Type III: Reactive electrodes, electrolyte solution
ex. Consider the following electrolytic cell.



(a) Write the cathode half reaction.

(b) Write the anode half reaction.

(c) Write the overall reaction.

(d) Calculate the power that must be supplied to operate the cell.

**Current Calculations**
In an electrolytic cell, the current supplied by the power source can be related to the mass change of an electrode.

Current is calculated according to the following equation:

$$I = \frac{q}{t}$$

where: I =Current (Amperes, A) 1 amp = 1 Coulomb/second
q = charge (coulombs, C) 1 mole of electrons has a charge of 1 Faraday; 1 Faraday = 96500 Coulombs
t = time (seconds)

ex. Consider the half reaction: $Cu^{2+} + 2e^{-} \rightarrow Cu$. What mass of copper is produced if 10.0 A is applied over 30.0 minutes?

ex. Consider the half reaction: $Ag^{+} + e^{-} \rightarrow Ag$. How long must a 5.00 A current be applied to produce 10.5 g of silver metal?