Chem 115 POGIL Worksheet - Week #6
Oxidation Numbers, Redox Reactions, Solution Concentration,
Titrations, First Law, and Enthalpy

Why?

In addition to metathetical reactions, electron transfer reactions often occur in solutions.   When electrons are transferred from one chemical species to another oxidation and reduction are said to have occurred.   These kinds of reactions are very important in natural and synthetic processes.   One way of tracking these changes is to look at assigned oxidation numbers on each element in the chemical species involved in the reaction.

To round out our discussions of solution reactions, we need to address the quantitative relationships between reactants and products.   Up to now, we have used the connection between mass and moles to do this.   When dealing with solutions, it is usually more convenient to analyze the stoichiometry in terms of mole-based solution concentration terms. An important application of this is the analytical technique of titration, used to determine the amount of a substance, such as an acid or base, in a solution.   It is based on the quantitative relationships between volume an and the mole-based solution concentration molarity.

In addition to mass changes, chemical reactions involve heat changes.   Like mass-based stoichiometry, these heat changes are quantitative.   One of the most important physical relationships governing heat change is the First Law of Thermodynamics.   Most often we will consider this in terms of a thermodynamic function called enthalpy.   Knowing about the First Law and enthalpy is essential to understanding the relationship between heat and chemical reactions. Considerations of heats of chemical reactions are important in many fields, ranging from nutrition to the search for more efficient fuels.

Learning Objectives
·   Understand the rules for assigning oxidation numbers
·   Understand the concepts of oxidation and reduction in terms of oxidation numbers
·   Understand solution concentration in terms of molarity
·   Know the connection between molarity, volume, and moles or millimoles of solute
·   Understand the difference between analytical concentration and actual species concentration
·   Understand the techniques of titration and the quantitative relationships on which it is based
·   Know the First Law of Thermodynamics
·   Understand the relationships between heat, work, internal energy, and enthalpy

Success Criteria
·   Be able to assign oxidation numbers to elements in chemical species
·   Be able to identify when a species is being oxidized or reduced
·   Be able to calculate molarity of a solution
·   Be able to convert between molarity, volume, and moles or millimoles
·   Be able to assess the actual ion concentrations in a strong electrolyte solution
·   Be able to carry out stoichiometry calculations using molarities and volumes of solutions

·   Be able to carry out titration calculations
·   Be able to calculate heat and temperature changes
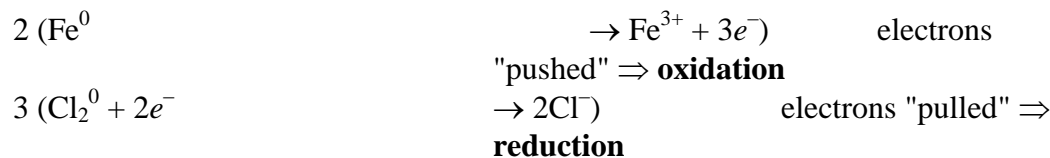·   Be able to apply the First Law of Thermodynamics

Prerequisite
·   Have read sections 4.4 through 4.6 in the text.
·   Have read sections 5.1 through 5.4 in the text.

Information (Redox and Oxidation Numbers)

A reaction in which one species transfers electrons to another is called an **oxidation-reduction reaction**, also called a **redox reaction**.   For example, consider the reaction of metallic iron with chlorine gas to form ionic iron(III) chloride:

$$2 \ Fe(s) + 3 \ Cl_2(g) \rightarrow 2 \ FeCl_3(s) \equiv 2 \ [Fe^{3+}][Cl^-]_3$$

We can think of this as the net transfer of six electrons from two iron atoms to three chlorine molecules:

$$2 \ (Fe^0 \rightarrow Fe^{3+} + 3e^-) \quad \text{electrons "pushed"} \Rightarrow \textbf{oxidation}$$
$$3 \ (Cl_2^0 + 2e^- \rightarrow 2Cl^-) \quad \text{electrons "pulled"} \Rightarrow \textbf{reduction}$$

In essence, the Fe "pushes" electrons and the Cl_2 "pulls" electrons, thereby effecting electron transfer.   On this basis, we have the following definitions:

Oxidation - loss of electrons by a substance
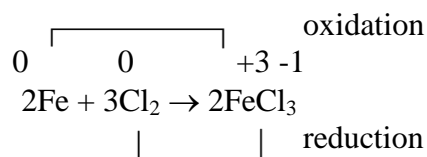**Reduction** - gain of electrons by a substance

Oxidation and reduction always involve transfer of electrons.   Therefore, *there is never oxidation without reduction and vice versa in a redox reaction.*   Oxidizing something must cause something else to be reduced and vice versa.   Therefore, the substance oxidized is seen to be the agent of the other substance's reduction, and the substance reduced is seen to be the agent of the other substance's oxidation.   This leads to the following definitions:

Oxidizing agent (oxidant)   a substance that causes another substance to be oxidized and is itself reduced.
Reducing agent (reductant)   a substance that causes another substance to be reduced and is itself oxidized.

The transfer of electrons from one species to another changes the electron count and distribution about the atoms in both.   One way of reflecting this is through changes in assigned **oxidation numbers**.   Oxidation numbers are real or hypothetical charges on atoms, assigned by the following rules:

·   Atoms in elements are assigned 0.

·   All simple monatomic ions have oxidation numbers equal to their charges.   (e.g., all Group IA ions are +1; all group IIA ions are +2; all the following ions have oxidation numbers given by their charges - Fe^{2+}, Al^{3+}, S^{2-}, N^{3-})

·   Fluorine is always -1 in its compounds.

·   Halogens are usually -1, except when a central atom or when combined with a more electronegative[1] element   (e.g., assign I as -1 in NI_3, but +3 in ICl_3).

·   Oxygen is -2 in most of its compounds, except in peroxides (H_2O_2, Na_2O_2) where it is -1.

·   Hydrogen is usually +1, except in hydrides with electropositive elements, particularly with metal cations, where it is -1 (e.g., NaH, CaH_2, BH_4^-).

·   The sum of all oxidation numbers for a neutral compound is zero; the sum is the charge on the species for a complex ion.

When a species is oxidized, one of its atoms goes to a higher (more positive or less negative) oxidation number.   When a species is reduced, one of its atoms goes to a lower (less positive or more negative) oxidation number.   For example, in the reaction between metallic iron and gaseous chlorine, the oxidation state of Fe goes from 0 to +3, making this an oxidation, and the oxidation number of each Cl goes from 0 to −1, making this a reduction.
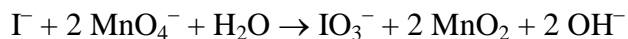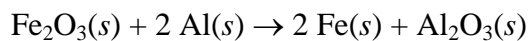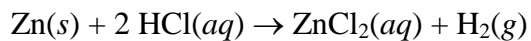
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\begin{array}{c}
\overset{\displaystyle\qquad\text{oxidation}}{\underset{\displaystyle\underbrace{\hphantom{+3-1}}_{\text{reduction}}}{\underbrace{\overbrace{\quad\quad\quad}}_{}\ }}\\
\underset{0}{2Fe} + \underset{0}{3Cl_2} \rightarrow \underset{+3\ -1}{2FeCl_3}
\end{array}
$$

Key Questions

1. Assign the oxidation numbers of each element in the following chemical species: HCl, H_2O, NH_3, NO_3^-, $K_2Cr_2O_7$, Hg_2Cl_2, $HgCl_2$, $Al(OH)_3$, Na_3PO_4

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[1]We will discuss electronegativity in more detail later.   For now, electronegativity can be defined as the ability of an atom in a compound to attract electrons to itself.   In the periodic table, electronegativity increases left to right and bottom to top; e.g., O < F, I < Cl, Cl < O.   Overall, the most electronegative elements are in the upper right, and the least electronegative elements are in the lower left of the periodic table.

Exercises

2. Which element is oxidized and which element is reduced in the following reactions?

$Zn(s) + 2\ HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$

$Fe_2O_3(s) + 2\ Al(s) \rightarrow 2\ Fe(s) + Al_2O_3(s)$

$14\ HNO_3 + 3\ Cu_2O \rightarrow 6\ Cu(NO_3)_2 + 2\ NO + 7\ H_2O$

$I^- + 2\ MnO_4^- + H_2O \rightarrow IO_3^- + 2\ MnO_2 + 2\ OH^-$

Information (Solution Concentration)

Solution concentration is a statement of the amount of solute present in a solution relative to either the amount of solvent or the amount of solution. The most frequently used expression of concentration in chemistry is **molarity** (symbol M). Molarity is defined numerically by: