**Vocabulary**

**Electrochemistry :** the study of the interchange of chemical and electrical energy

**Redox reaction :** a transfer of electrons from the reducing agent to the oxidizing agent

**Oxidation:** a loss of electrons (an increase in the oxidation number)

**Reduction:** a gain of electrons (a decrease in the oxidation number)

**Half-reactions:** a redox reaction broken in to two parts, one half with the oxidation and the other half with the reduction

**Salt bridge:** the connection between the two solutions

**Galvanic cell:** device in which chemical energy is changed to electrical energy

**Anode:** the electrode at which oxidation occurs *(an-ox)*

**Cathode:** the electrode at which reduction occurs *(red-cat)*

**Cell potential, (Ecell):** potential difference between the oxidation and reduction

**Volt:** the unit of electrical potential (J/C)

**Standard hydrogen electrode:** a platinum electrodes in contact with 1M H+ ions bathed by H2 gas at 1 atm

**Standard reduction potentials, E :** likelihood for the reduction to occur with all solutes at 1M or 1 atm

**Concentration cell**: cell with both electrodes having identical components but at different concentrations

**Nernst equation:** converts cells that are at nonstandard conditions to standard conditions *E* = *E* - ln(Q) RT nF

**Glass electrode:** contains a reference solution of dilute hydrochloric acid in contact with a thin glass membrane

**Lead storage battery:** lead serves as the anode and lead coated with lead dioxide serves as the cathode

**Electrolytic cell:** an apparatus that uses electrical energy to produce chemical change for nonspontaneous cells

**Electrolysis:** forcing a current through a cell to produce a chemical change ; used for nonpontaneous cells

**Ampere:** measure of current in coulombs per second (C/s). Often used to help convert the number of electrons flowing (current) to the rate of reaction in time

**Electrochemistry:**

**Introduction**

Chemical reactions which have the capacity to occur spontaneously are in a position to generate electrical energy under appropriate conditions. Chemical reactions or processes which do not have the capacity to take place spontaneously can be induced to do so if an appropriate quantity of electrical energy is supplied under appropriate conditions. Both types of chemical changes are regarded as being *electrochemical* in nature. For implementing changes of either type it is necessary to have an electrolyte in which at least two electrodes are dipped. Such a set-up is generally called a *cell*, and cells from which electrical energy is derived are known as electrochemical cells (or Galvanic cells or Voltaic cells).

Those to which electrical energy has to be fed to drive chemical reactions are known as electrolytic cells. In a nutshell, therefore, in an electrolytic cell, electrical energy supplied from an outside source causes a spontaneous reaction to occur. A galvanic cell, on the other hand, harnesses a spontaneous reaction to generate electric current. In either, the electrode at which oxidation occurs is called the anode, and the electrode at which reduction occurs is called the cathode. Electrolytic cells have numerous commercial applications. Many galvanic cells are of commercial importance. The content of this chapter basically deals with the two different areas of electrical energy as described above. It should also be pointed out in passing that there is one other area which is equally important and represents bulk utility of electrical energy; examples include arc furnaces and heating appliances. This involved area is familiarly called *electrothermics*; however, the present text does not enter into the realm of these significantly important technological areas.

For electrochemical reactions, a **redox reaction** can be separated in two, **oxidation** which occurs at the anode and **reduction** that occurs at the cathode. Redox reactions exchange electrons.

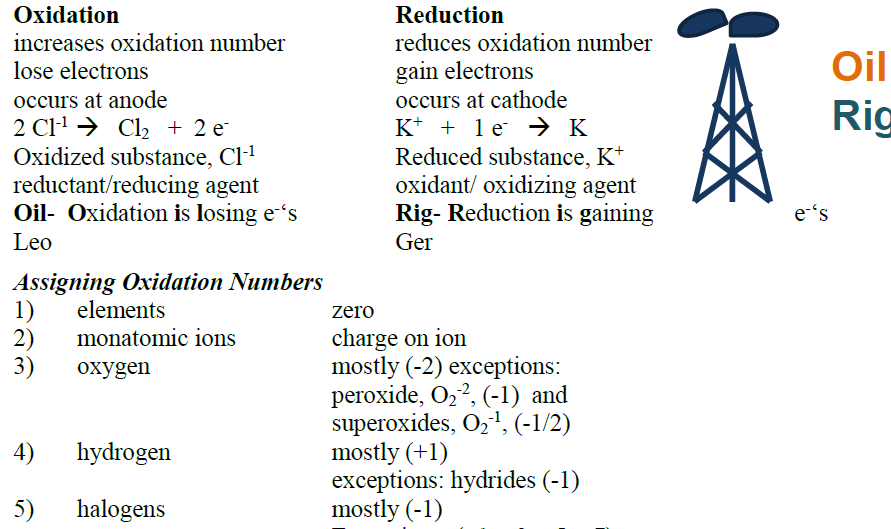
When balancing a reaction, remember to **balance**…

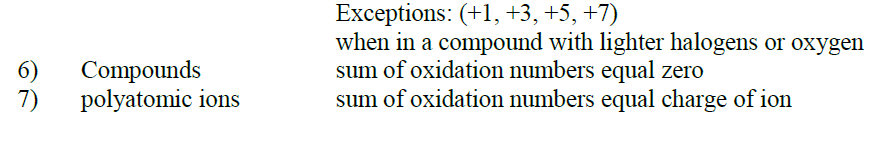
(1) the number of electrons lost = electrons gained

(2) the atoms on either side of the reaction must balance

(3) the total charge on either side of the reaction must balance.

Learn the half reaction method of balancing for electrochemistry reactions. This method splits apart the oxidation half reaction from the reduction half reaction.



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**Practice:**

Determine the oxidation number of each element in the following list.

a) Cl2

b) MgCl2

c) Al(ClO)3

d) Ni(ClO2)2

e) V(ClO3)5

f) KClO4

g) K2Cr2O7

h) C2H4O

i) C3H8

Note: in most cases oxidation states are positive or negative integers. On occasion atoms within a compound may have an average fractional oxidation state. It is acceptable because the oxidation states are an imposed bookkeeping scheme, not an actual quantity.

***Balancing Redox Rxns Using the Half Rxn Method***

1) Assign oxidation numbers to each atom in the equation.

2) Determine what is oxidized and what is reduced.

3) Split the skeleton equation into two half reactions label appropriately as oxidation or reduction reactions.

4) Complete and balance each half reaction

a) Balance atoms (except O and H) starting with the atom that changes oxidation state.

b) Include electrons as products in the oxidation reaction and reactants in the reduction reaction

c) If the solution is acidic: balance electric charges by adding H+1 ions, balance the O’s by adding H2O, verify all atoms balance

d) If the solution is basic: balance electric charges by adding OH-1 ions, add H2O to balance the O and H atoms, verify all atoms balance.

5) Combine the two half reactions to obtain overall equation

a) Multiply each half reaction by the factor needed to have equivalent electrons lost and gained.

b) Simplify and reduce to the lowest whole number ratio

6) Check balancing

a) atoms

b) sum of charges of reactants equal to those of products

c) number on electrons lost and gained

**Example 1:** *Balance the following with the half reaction method.*

**a)** I2 (s) + S2O3 -2 (aq) I-1 (aq) + S4O6-2 (aq)

b) Al (s) + SO4-2 (aq) Al+3 (aq) + SO2 (g) (acidic conditions)

**REDOX EQUATIONS:** Answers to this additional practice found on website **Balance the following, identify species that oxidizes/reduces**

1. Al + Pb+2 Al+3 + Pb

2. Cu + NO3-1 + H+1 Cu+2 + NO2 + H2O

3. Zn + NO3-1 + H+1 = Zn+2 + NH4+1 + H2O

4. HI + HNO3 = I2 + NO + H2O

5. OH-1 + Cl2 = Cl-1 + ClO-1 + H2O

6. Cr+3 + MnO4-1 Cr2O7-

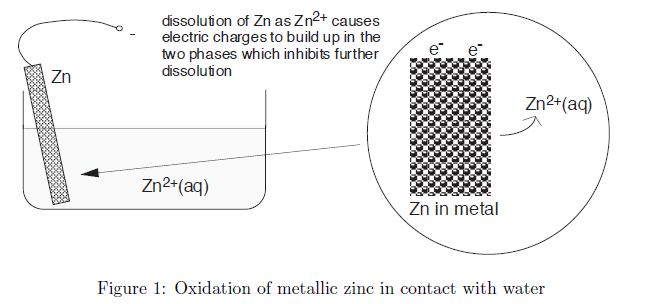
**Chemistry and electricity**

The connection between chemistry and electricity is a very old one, going back to Allesandro Volta's discovery, in 1793, that electricity could be produced by placing two dissimilar metals on opposite sides of a moistened paper. In 1800, Nicholson and Carlisle, using Volta's primitive battery as a source, showed that

an electric current could decompose water into oxygen and hydrogen. This was surely one of the most signi¯cant experiments in the history of chemistry, for it implied that the atoms of hydrogen and oxygen were associated with positive and negative electric charges, which must be the source of the bonding forces

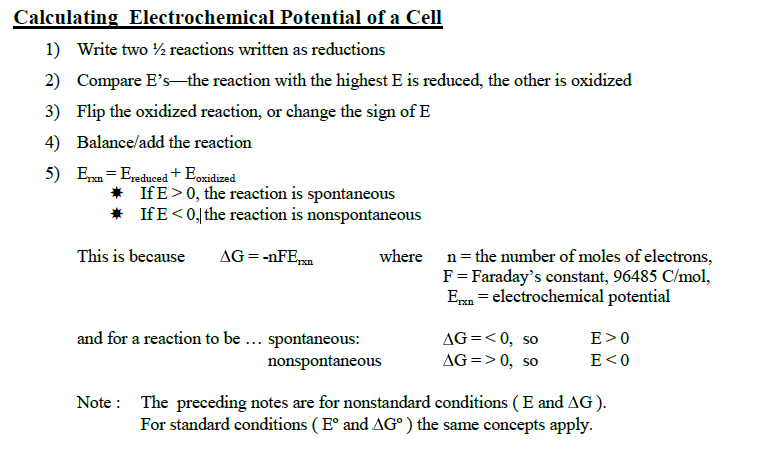
between them. By 1812, the Swedish chemist Berzelius could propose that all atoms are electri¯ed, hydrogen and the metals being positive, the nonmetals negative. In electrolysis, the applied voltage was thought to overpower the attraction between these opposite charges, pulling the electri¯ed atoms apart in

the form of *ions* (named by Berzelius from the Greek for \travellers"). It would be almost exactly a hundred years later before the shared electron pair theory of G.N. Lewis could o®er a signi¯cant improvement over this view of chemical bonding.



Meanwhile, the use of electricity as a means of bringing about chemical change continued to play a central role in the development of chemistry. Humphrey Davey prepared the ¯rst elemental sodium by electrolysis of a sodium hydroxide melt. It was left to Davey's former assistant, Michael Faraday, to show that

there is a quantitative relation between the amount of electric charge and the quantity of electrolysis product. James Clerk Maxwell immediately saw this as evidence for the \molecule of electricity", but the world would not be receptive to the concept of the electron until the end of the century.



***The Nernst Equation:***

The Nernst equation is used to relate a cell’s electrochemical potential, *E*, that is not at standard conditions (1 atm. 25 ◦C, 1 M solutions) with an electrochemical potential that is at standard conditions, *E* .

