CHEMISTRY 112 LECTURE
EXAM I Material

PART I THERMOCHEMISTRY
Chapter 6

Thermodynamics is the study of heat and its relationship to other kinds of energy (chemical or electrical).
Thermochemistry is the study of heat released or absorbed during chemical reactions.

I. Energy

- **Internal Energy = kinetic energy + potential energy**

- **Kinetic energy** is energy due to the motion of the object =thermal energy

- **Potential energy** is the energy due to the objects position or composition

- **Energy Transfer –** Energy is transferred from **a system to it's surroundings and vice versa**

$$\text{Internal Energy} = \Delta E = E_{final} - E_{initial}$$

II. State Functions
State Functions are properties that on dependent upon its present state and not dependent upon the pathway to the present state. For example: the Internal energy (E) of a system is a state function = its value depends only on the state of the system and not how it arrived at that state.

III. First Law of Thermodynamics
The Total Energy of the Universe is constant - Energy can neither be created or destroyed

IV. Heat and Work
Heat, q, is the heat transferred to or from a system during a reaction. It is the energy that flows to or from a system due to the difference of °T

$$q = m \text{ x } C \text{ x } \Delta T$$
$$q = \textit{Mass X Specific heat capacity (J/g } ^oC) \textit{ X } \Delta T$$

Work,w, is the energy exchange when a force ,F, moves an object a certain distance.

$$w = F \text{ X } D$$
$$w = \text{ Force X Distance}$$
$$w = - P \Delta V$$

Internal Energy = ΔE = q + w

III. Units of Energy
Joule,J

Calorie,Cal

VI. Enthalpy, H (Heat content of a substance)

Change of Enthalpy,ΔH, is the heat given off or absorbed by a system at constant pressure. For reactions, the change of enthalpy is the

Heat of Reaction:

$$\textbf{Heat of Reaction} = \Delta H_{rxn} = H_{final} - H_{initial}$$

$$\text{and} \quad \Delta H_{rxn} = q$$

Mechanics of reactions:

VII. Calorimetry
The **Heat Capacity** of a substance is the amount of heat required to change its temperature 1 °

The **Specific Heat** of a substance is the amount of heat required to change 1 gram of the substance its temperature 1 K

Problem: Calculate the amount of heat required to heat 35.0 g of Al from 55.0°C to 75.0°C.
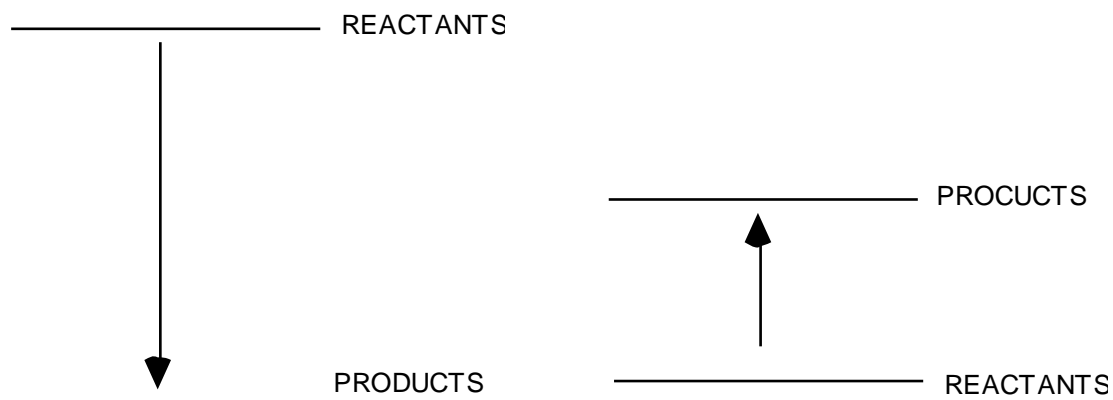
Specific Heat of Al = 0.908 $\frac{J}{g \ K}$

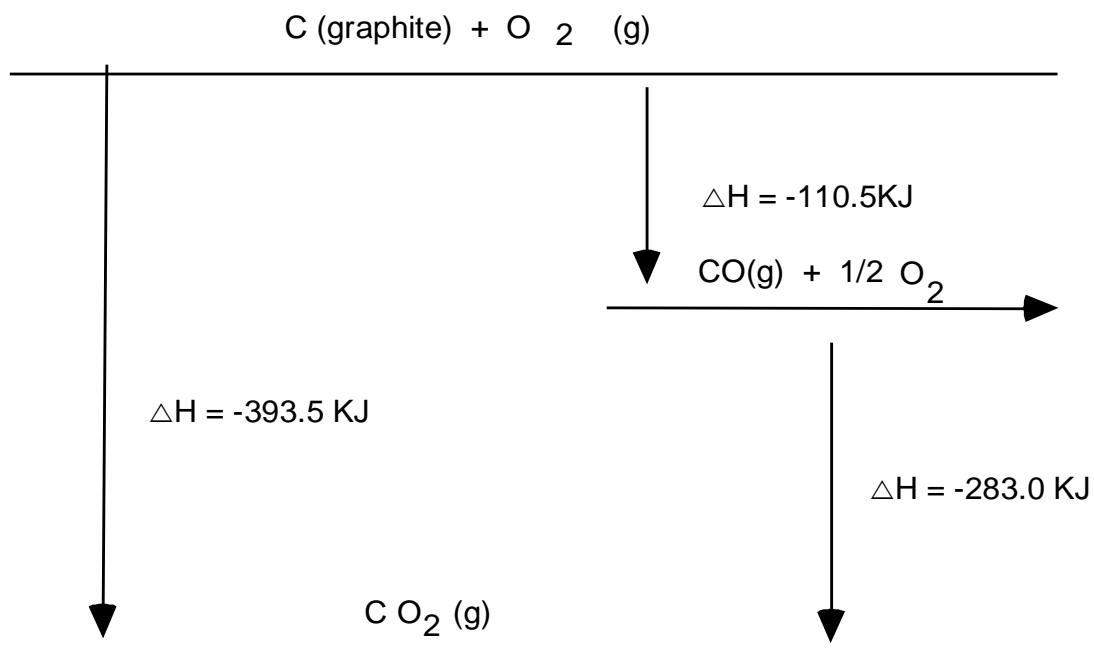The **Heat Capacity** of a substance is the amount of heat required to change its temperature 1 °

Example 6.8 , page 269 in Textbook: A Coffee – Cup Calorimeter

VII. Law of Hess-Law of constant heat summation

A. Enthalphy, $\triangle H$ $\triangle H_{rxn} = \triangle H_{products} - \triangle H_{reactants}$

——————————— REACTANTS

——————————— PROCUCTS

——————————— PRODUCTS   ——————————— REACTANTS

B. Energy diagram

C (graphite) + O$_2$ (g)

$\triangle H = -110.5KJ$

CO(g) + 1/2 O$_2$

$\triangle H = -393.5$ KJ

$\triangle H = -283.0$ KJ

C O$_2$ (g)

C. Energy Equations:

  1. Additon of equations

    C (graphite) + O$_2$(g) $\rightarrow$ CO(g) + 1/2 O$_2$ $\triangle H = -110.5$ KJ

    CO (g) + 1/2 O$_2$ (g) $\rightarrow$ CO$_2$ $\triangle H = -283.0$ KJ

2. Multiplying:

$$HI(g) \rightarrow 1/2\ H_2(g)\ +\ 1/2\ I_2(s)$$ $\triangle H = -25.9\ KJ$

3. Reversing:

$$1/2\ H_2(g)\ +\ 1/2\ I_2(s) \rightarrow HI(g)$$ $\triangle H = +25.9\ KJ$

4. Problem:

Find $\triangle H$ for $2\ NH_3\ (g)\ +\ 3\ N_2O(g) \rightleftarrows 4N_2(g)\ +\ 3\ H_2O\ (l)$
Given:

$$4\ NH_3\ (g)\ +\ 3\ O_2(g) \rightarrow 2\ N_2(g)\ +\ 6\ H_2O\ (l)$$ $\triangle H = -1531\ KJ$

$$N_2O(g)\ +\ H_2(g) \rightarrow N_2(g)\ +\ H_2O\ (l)$$ $\triangle H = -367.4\ KJ$

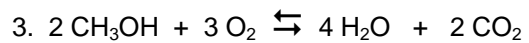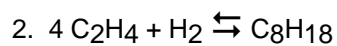$$H_2O\ (l) \rightarrow H_2(g)\ +\ 1/2\ O_2(g)$$ $\triangle H = +285.9\ KJ$
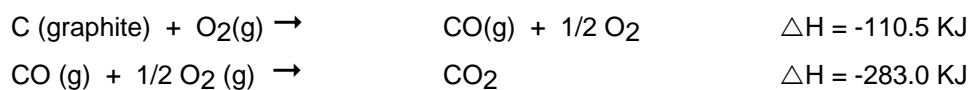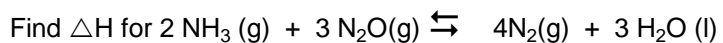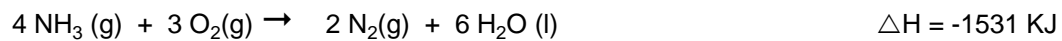
Warning! You need to print out more Exam 1 lecture outline pages!

VIII. Bond Energies and Bond Lengths Chapter 9 Pages 409-413

Bond Energy Page 410 in Tro
 Calculate the the ΔH for the following reactions using bond energies:

1. $CH_4(g) + Cl_2(g) \rightleftarrows CH_3Cl(g) + HCl(g)$

2. $4 C_2H_4 + H_2 \rightleftarrows C_8H_{18}$

3. $2 CH_3OH + 3 O_2 \rightleftarrows 4 H_2O + 2 CO_2$

PART II   FREE ENERGY AND THERMODYNAMICS
Chapter 17

Thermodynamics is the study of heat and its relationship to other kinds of energy (chemical, light, mechanical or electrical).

Thermochemistry is the study of heat released or absorbed during chemical reactions.

I. Second Law of Themodynamics: Predicting a spontaneous change

Spontaneous Change

Nonspontaneous Change

A. Entropy,S
Entropy, S, is a measure of the disorder or randomness of a system. It is a state function

$$\textbf{Entropy Change} = \Delta S_{rxn} = S_{final} - S_{initial}$$

B. Second Law of Thermodynamics
For a spontaneous reaction, total entropy always increases for a system and its surroundings:

$$S_{universe} = S_{system} + S_{surroundings}$$

$S_{universe} > 0$ for a spontaneous reaction

$S_{universe} < 0$ for a non-spontaneous reaction

Predicting an entropy change for a reaction:

	ΔS	Spontaneous/nonspontaneous
1. $2 Fe_2O_3(s) \rightarrow 4 Fe(s) + 3 O_2(g)$		
2. $H_2O(s) \rightarrow H_2O(l) \rightarrow H_2O(g)$		
3. $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$		
4. $CO_2(g) \rightarrow CO_2(s)$		

C. Gibbs Free Energy

Background: Reaction Spontaneity: ΔS vs ΔH

Gibbs Free Energy is used to determine the spontaneity of a reaction:

$$\text{Change in Free Energy} = \Delta G° = \Delta H° - T\Delta S°$$

Note: $\Delta G° = 0$ for elements

D. Third Law of Thermodynamics

The entropy, S, of a pure crystal at 0 K is zero

E. Thermodynamics and Equilibrium.

$$\Delta G° = -RT \ln K$$

$\Delta G° < 0$ K>1 Products are favored at equilibrium

$\Delta G° = 0$ K=1 Products = reactants at equilibrium

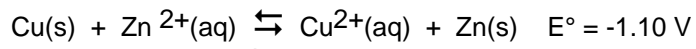$\Delta G° > 0$ K<1 Reactants are favored at equilibrium

F. Thermodynamics and Standard Potential, E°.

$$\Delta G°_{rxn} = -nFE°$$

G. Problems:

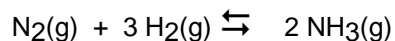1. Calculate the $\Delta G°$ for the following redox reaction:

    $Cu(s) + Zn^{2+}(aq) \rightleftarrows Cu^{2+}(aq) + Zn(s)$ $E° = -1.10$ V
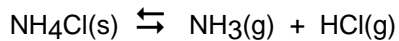
    $F = 9.6485 \times 10^4 \frac{J}{V\ mol}$

2. Calculate the equilibrium constant, K_p, for the following reaction at 25.0°C   if $\Delta G°$ is - 32.9 kJ:

    $$N_2(g) + 3 H_2(g) \rightleftarrows 2 NH_3(g)$$

3. Calculate $\Delta G°$, for the following reaction at 25.0°C if K_p is 1.1×10^{-16}:

    $$NH_4Cl(s) \rightleftarrows NH_3(g) + HCl(g)$$

4. Given the following $\Delta G°$ values: I^- (aq) = - 51.7 kJ/mol

                                                                Cl^- (aq) = -131.2 kJ/mol

    Calculate $E°$ for the following reaction: $Cl_2 + 2\ I^-$ (aq) $\rightleftarrows$ $2\ Cl^-(aq) + I_2$

5. Calculate K for the following reaction: $2\ SO_2 + O_2 \rightleftarrows 2\ SO_3$

      $\Delta G_f°\ SO_2 = - 300.8$ kJ/mol

      $\Delta G_f°\ SO_3 = - 370.4$ kJ/mol

Chapter 18

I. **BACKGROUND**

Electrochemistry - The interchange of chemical and electrical energy

A. Redox reaction

B. Half reactions

C. Oxidation numbers are used in a book keeping method to keep track of the number of electrons lost or gained in by an atom in a redox equation

OXIDATION NUMBERS

1. The oxidation number for oxygen is usually -2.
    Exceptions: O_2 and peroxides

    (O--O bond → ex. H_2O_2, Na_2O_2, and BaO_2 and etc.)

2. The oxidation number of hydrogen is usually +1.
    Exceptions: H_2 and hydrides   Ex. NaH, BaH_2, and etc.

3. Oxidation numbers of an atom or group of atoms is equal to the charge on the species:

a. The oxidation number on free elements is zero.

    Ex. Hg, Fe, Cr, Mn....etc.

b. The oxidation number for elements when combined with themselves is zero
   Ex. H_2, S_8, Br_2....etc.)

c. The oxidation number of a monatomic ion is equal to its charge.

| ION	OXIDATION NUMBER
K^{1+}	+1
Ca^{2+}	+2
Fe^{3+}	+3
S^{2-}	-2

d. The sum of the oxidation numbers of the elements in a compound is equal to zero

    SO_2 SO_3

    $CrCl_3$ $CrCl_6$

    CO_2 CO

e. The sum of the oxidation numbers of the elements in a polyatomic ion is equal to its net charge.

    CO_3^{2-} $C_2O_4^{2-}$

    BrO^- BrO_3^-

    SO_4^{2-} SO_3^{2-}

f. The sum of the oxidation numbers of the elements in a polyatomic ion is equal to its net charge.

    Na_2CO_3 FeC_2O_4 $Sn_3(PO_4)_4$

    HBrO $Zn(BrO_3)_2$ Cu_2SO_3
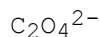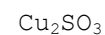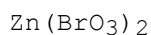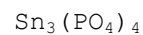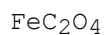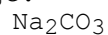
D.   Redox equations/ Reducing and Oxidizing agents:

1. A Reducing agent is the species causing the reduction of another species (it is being oxidized)
2. A Oxidizing agent is the species causing the oxidation of another species (it is being reduced)

Redox reactions: $Zn° + Fe^{+2} \rightarrow Zn^{+2} + Fe°$
Half reactions:

Problems:

Textbook Problem

E. Balancing Redox Reaction - Half- Reaction Method:

In Acidic Solution:

$H_2C_2O_4$(aq) + MnO_4^-(aq) → Mn^{2+}(aq) + CO_2(g)   (acidic)

1. Write the two half- reactions (Oxidation and reduction reaction)

2. Balance the atoms undergoing oxidation and reduction/ all other atoms other than "O" and "H"

3. Balance atoms and charges in each half-reaction.
    a. Use H_2O to balance O atoms.

    b. Use H^+ to balance H atoms

    c. Use e^- to balance positive charges

4. Multiply each half-reaction by some integer so the the number of e^- lost in the Oxidation half-reaction equals the number of e^- gained in the Reduction half-reaction

5. Add the half - reactions together, canceling species that appear on both sides. The e^- must completely cancel and not be present in the end.

In Basic Solution:

$Bi^° (s) + Cl^- (aq) + Hg(OH)_3^- \rightarrow BiCl_4^- + Hg^°$

1. Write the two half- reactions (Oxidation and reduction reaction)

2. Balance the atoms undergoing oxidation and reduction/ all other atoms other than "O" and "H".

3. Balance atoms and charges in each half-reaction.
   a. Use H_2O to balance O atoms.

   b. Use H^+ to balance H atoms

   c. Neutralize H^+ by adding the same number of OH^- to each side of the equation

   d. Use e^- to balance positive charges

4. Multiply each half-reaction by some integer so the the number of e^- lost in the Oxidation half-reaction equals the number of e^- gained in the Reduction half-reaction

5. Add the half - reactions together, canceling species that appear on both sides. The e^- must completely cancel and not be present in the end.
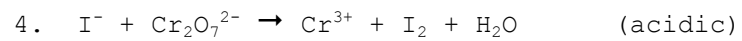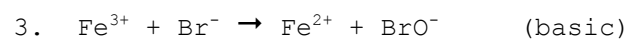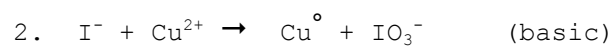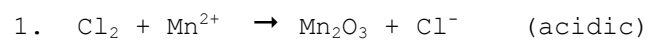
Practice

Balance the following redox reactions:

1. $Cl_2 + Mn^{2+} \rightarrow Mn_2O_3 + Cl^-$ (acidic)

2. $I^- + Cu^{2+} \rightarrow Cu^{\circ} + IO_3^-$ (basic)

3. $Fe^{3+} + Br^- \rightarrow Fe^{2+} + BrO^-$ (basic)

4. $I^- + Cr_2O_7^{2-} \rightarrow Cr^{3+} + I_2 + H_2O$ (acidic)

G. Electrochemical Cells

1. **Electrochemical Cells** are systems that allow electrons to flow from a reducing agent to an oxidizing agent.

2. **Types of Electrochemical Cells:**

   a. Voltaic Cells are electrochemical cells that produce electricity (flow of electrons) when a spontaneous redox reaction occurs. A battery is a voltaic cell. Voltaic cells are also known as galvanic cells

   b. Electrolytic Cells are electrochemical cells that require electricity (flow of electrons) for a non-spontaneous redox reaction to occur.

3. An Example of an Electrochemical Cell:

Diagram:
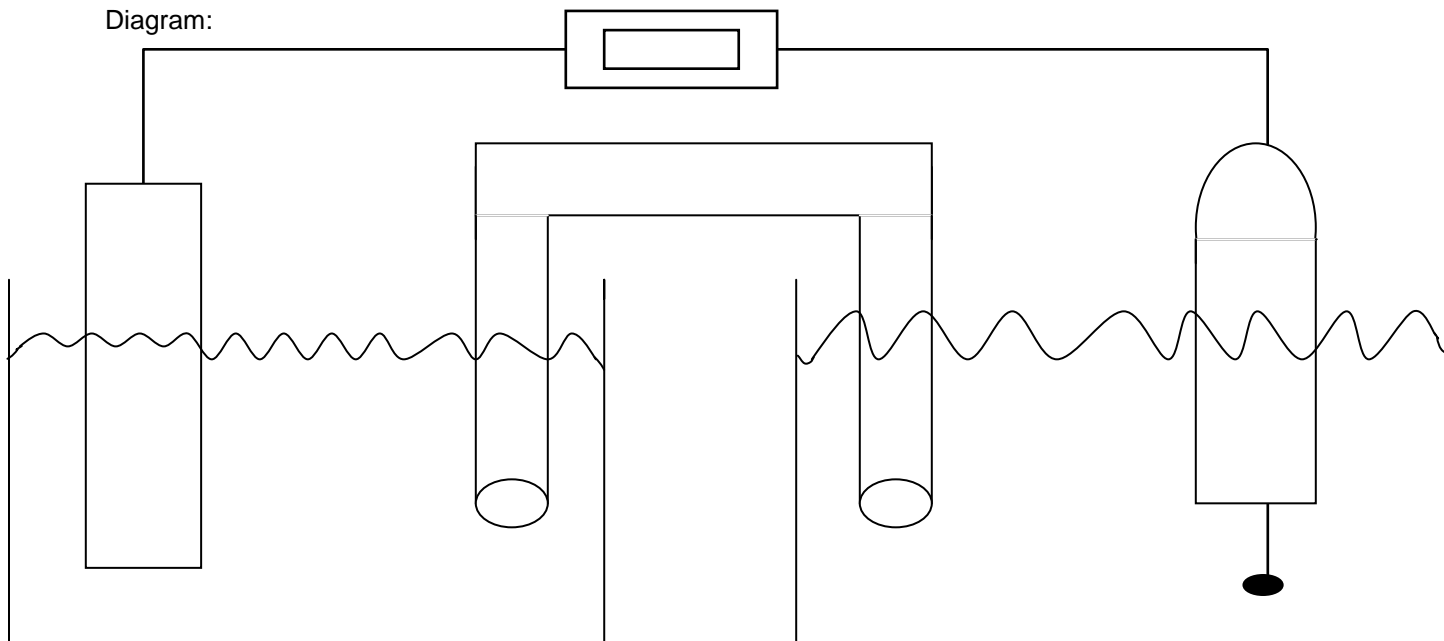
The Balanced Equation:

Oxidation occurs at the **ANODE**

Reduction occurs at the **CATHODE**

An **electrolyte** is a substance which allows the flow of ions

A **salt bridge** is a device for maintaining a balance of ion charges in the cell compartments.

3. Electrochemical Cell Notation: Oxidation || Reduction
    (Schematic Cell representation)

$$Cu° | \ Cu^{2+}(aq) \ || \ Ag^+(aq) | \ Ag° \ (s)$$

$$Zn° | \ ZnCl_2(1.2M) \ || \ CuCl_2(0.50M) | \ Cu°$$

Electrochemical Cell Notation continued:

$$Fe° | Fe(NO_3)_3 (1.0M) \; || \; H^+ (0.10M) \; | \; H_2 \; (0.90atm), \; Pt$$

$$Ag° \; | \; AgBr(sat'd) \; , \; Br^- (0.04M) \; || \; H^+ (1.00 \times 10^{-4}) \; | \; H_2 \; _{(0.90 \; atm)}, \; Pt$$
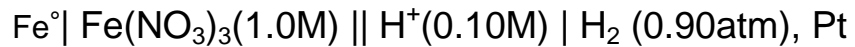
<u>Voltaic Cells:</u>
(also known as galvanic cells)
Danielle cell: **John Daniell invented the first battery to generate   electricity**

$$Cu(s) + Zn^{2+} \longrightarrow Zn(s) + Cu^{2+}$$
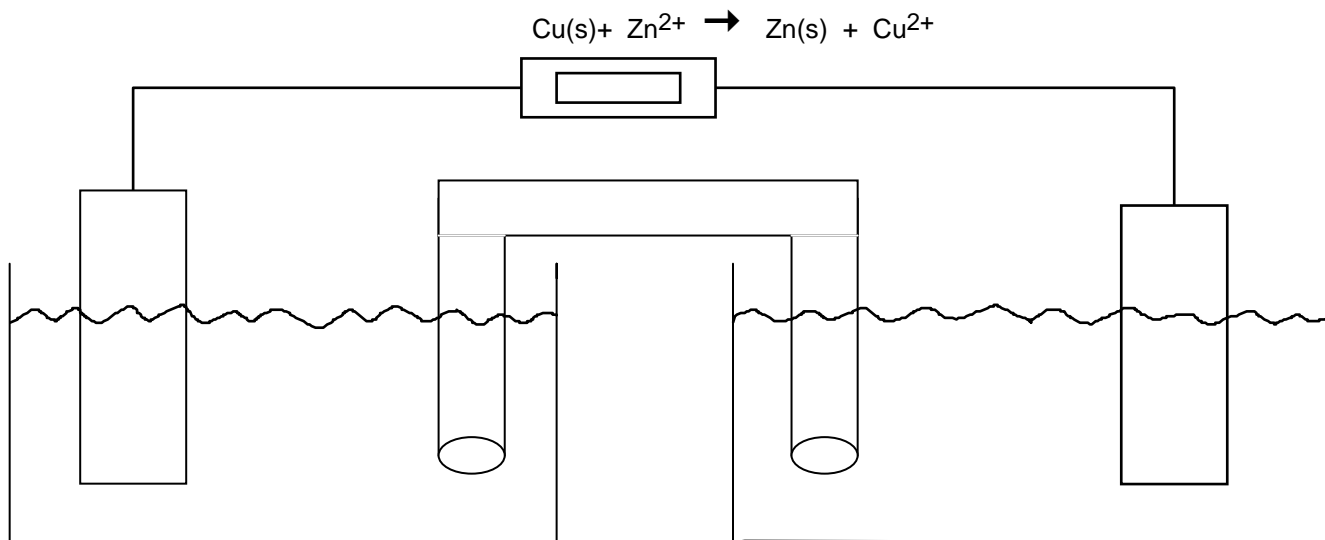
H. Cell Potentials

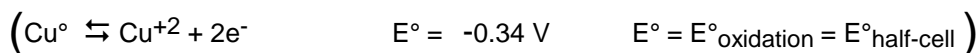The force that pushes the electrons away from the anode (- charged electrode) and pulls the electrons towards the cathode (+ charged electrode) is an electrical potential called the <u>electromotive force</u> (emf), An electromotive force is also known as the cell potential (E) and cell voltage

$Cu^{+2} + 2e^- \leftrightharpoons Cu°$ $E° =$ 0.34 V $E° = E°_{reduction} = E°_{half-cell} =$ Half Cell potential

                                              V = Volts

                                              E° = standard cell potential

$\left(Cu° \leftrightharpoons Cu^{+2} + 2e^- \right.$ $E° =$ -0.34 V $E° = E°_{oxidation} = E°_{half-cell} \left. \right)$

Some Examples of Standard Cell potentials

$Au^{+3} + 3e^- \leftrightharpoons Au°$ $E° =$ 1.50 V

$Ag^+ \ + 1e^- \leftrightharpoons Ag°$ $E° =$ .80 V

$Fe^{+2} + 2e^- \leftrightharpoons Fe°$ $E° =$ .77 V

$Cu^{+2} + 2e^- \leftrightharpoons Cu°$ $E° =$ .34 V

$Zn^{+2} + 2e^- \leftrightharpoons Zn°$ $E° =$ -.76 V

$2H^+ \ + 2e^- \leftrightharpoons H_2$ $E°_{reference} =$ 0 V   Standard hydrogen electrode (SHE)

1. The larger the E°, the higher the tendency the species will undergo reduction

2. E° indicates that the cell potentials (half-cell) were measured at standard conditions, more later.

3. E $_{species}$ is measured against: $2H^+ \ + 2e^- \leftrightharpoons H_2$ $°E = 0$

   ie. .....all other potentials are measured relative to the Hydrogen reduction reaction

4. By convention all half-reactions are written as reductions.
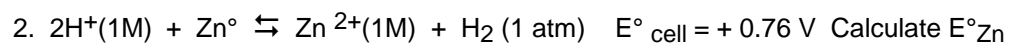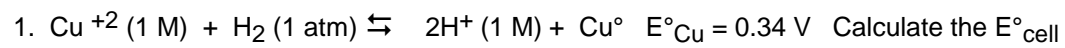
Calculations involving Cell Potentials:

$$\mathbf{E°_{cell} = E°_{cathode} \ - \ E°_{anode}}$$

$$\mathbf{E°_{cell} = E°_+ \ - \ E°_-}$$

            species undergoing reduction   species undergoing oxidation

EXAMPLES

1. Cu^{+2} (1 M) + H_2 (1 atm) $\leftrightarrows$ $2H^+$ (1 M) + $Cu°$ $E°_{Cu}$ = 0.34 V   Calculate the $E°_{cell}$

2. $2H^+$(1M) + $Zn°$ $\leftrightarrows$ Zn^{2+}(1M) + H_2 (1 atm) $E°_{cell}$ = + 0.76 V Calculate $E°_{Zn}$

3. Calculate the E°$_{cell}$ for the following:

$$Zn° (s) + Ni^{2+}(1\ M) \leftrightarrows Zn^{2+} (1\ M) + Ni°(s)$$
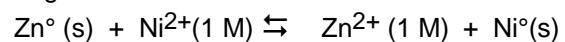
I. Standard Reduction Potential Table

A listing of common reduction half-reactions
1. The more positive the E°, the higher the tendency the species will undergo reduction.

2. The more negative the E°, the higher the tendency the species will undergo oxidation.

$Au^{+3} + 3e^- \leftrightarrows Au°$ E° =   1.50 V

$Ag^+ + 1e^- \leftrightarrows Ag°$ E° =   .80 V

$Fe^{+2} + 2e^- \leftrightarrows Fe°$ E° =   .77 V

$Cu^{+2} + 2e^- \leftrightarrows Cu°$ E° =   .34 V

$Zn^{+2} + 2e^- \leftrightarrows Zn°$ E° =   -.76 V

I . Relative Strengths of Oxidizing and Reducing Agents
The more positive the E° value the more the reaction tends to occur as written:

For a spontaneous reaction:
A stronger oxidizing agent will react with the stronger reducing agent to produce a weaker oxidizing agent and weaker reducing agent

II. Predicting E° (potential) and the direction of a Redox Reaction

A redox reaction is the sum of two half-reactions, one for oxidation and the other for reduction

Consider the following:

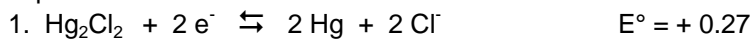The sum of the two half reactions E° (oxidation and reduction) would be the E° for the overall redox reaction:

To write Spontaneous Redox Reactions:

1. Reverse one of the half-rxns into an oxidation step such that the sum of the two 1/2 reactions $E°$ give a positive $E°_{cell}$

2. Add the two half-rxns to obtained an overall redox reaction in such a way that the number of electrons cancel from both sides of the equation.

*NOTE: Changing the "balancing" coefficients of a half-rxn does **NOT** change the $E°$ value. An electrode potential, $E°$ is an intensive property, one that does not depend on the amount of substance present.   The potential is the ratio of energy to charge, when the coefficients are changed (increasing the amount of substance) both the energy and charge increases proportionally and therefore: the energy to charge ratio does not change: The potential, $E°$, does not change.
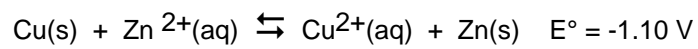
Examples:

1. $Hg_2Cl_2 + 2 e^- \rightleftarrows 2 Hg + 2 Cl^-$ $E° = + 0.27$

    $PbSO_4 + 2 e^- \rightleftarrows Pb + SO_4^{2-}$ $E° = + 0.36$

2. $Al^{3+} + 3 e^- \rightleftarrows Al$ $E° = - 1.67$

    $Br_2 + 2 e^- \rightleftarrows 2 Br^-$ $E° = + 1.09$

3. $MnO_4^- + 2 H_2O + 3 e^- \rightleftarrows MnO_2 + 4 OH^-$ $E° = + 0.50$ V

         $Sn^{4+} + 2 e^- \rightleftarrows Sn^{2+}$ $E° = + 0.141$ V

III. Cell Potential, E°, and Free Energy, G°.

G° and E°:

$$\Delta G°_{rxn} = -nFE°$$

Problems:

1. Calculate the $\Delta G°$ for the following redox reaction:

   $Cu(s) + Zn^{2+}(aq) \rightleftarrows Cu^{2+}(aq) + Zn(s)$ E° = -1.10 V

   $F = 9.6485 \times 10^4 \frac{J}{V \, mol}$

2. Given the following $\Delta G°$ values:

   I^- (aq) = - 51.7 kJ/mol

   Cl^- (aq) = -131.2 kJ/mol

   Calculate E° for the following reaction: $Cl_2 + 2 I^-$ (aq) $\rightleftarrows$ $2 Cl^-$(aq) + I_2

5/2/2013

E^o and K: Equilibrium calculations:

When E_{cell} = + the reaction proceeds spontaneously to the right. As the reaction proceeds the $E+_{cell}$ becomes smaller and smaller until eventually it reaches zero. An E_{cell} =0 means that there is no net reaction occurring and that the cell has reached equilibrium. When E_{cell} = 0 The Q term in the Nernst equal equals to K (Q = K):
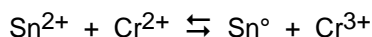
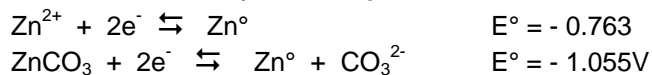$$E = 0 = E° - \boxed{} \log K \qquad \text{Where K = equilbrium constant}$$

and

$$E° = \boxed{} \log K$$

Problems

1. Calculate the K_{eq} for the following reaction:

$$Sn^{2+} + Cr^{2+} \leftrightarrows Sn° + Cr^{3+}$$

2. Calculate the Ksp of $ZnCO_3$ if:

$Zn^{2+} + 2e^- \leftrightarrows Zn°$ $\qquad\qquad$ E° = - 0.763

$ZnCO_3 + 2e^- \leftrightarrows Zn° + CO_3^{2-}$ $\qquad$ E° = - 1.055V

3. Calculate the equilibrium constant for: $\qquad 2\,Fe^{3+} + 2\,I^- \leftrightarrows I_2 + Fe^{2+}$

IV. Cell Potentials and Concentration

Table of standard potentials (at standard conditions)

Standard. conditions:

Solutes at 1 M (solns) { Actually, activity = 1}

Gasses at 1 atm, 760 torr, 760 mm

Metals are pure

$T° = 25 °C$

Table of E° Values	E° (V)
$Fe^{+2} + 2e^- \leftrightarrows Fe°$	+.77
$Cu^{+2} + 2e^- \leftrightarrows Cu°$	+.34
$Zn^{+2} + 2e^- \leftrightarrows Zn°$	-.76
$Na^+ + e^- \leftrightarrows Na$	- 2.71

$°E_{species}$ is measured against: $2H^+ + 2e^- \leftrightarrows H_2$ $°E = 0$

ie. .....all other potentials are measured relative to the H reduction reaction

Nerst equations - E for nonstandard conditions

Use the nerst equation if nonstandard conditions exist....ie [species] $\neq$ 1M
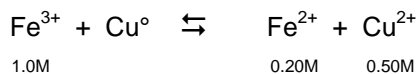
$E = E° - \boxed{} \log Q$ Where: Q = the Reaction Quotient

n = number of electrons

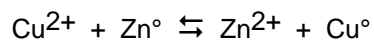0.0592 is a constant

$E = E° - \boxed{} \log \dfrac{[C]^c [D]^d}{[A]^a [B]^b}$
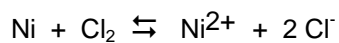
(1) Using the nerst equation

$$Fe^{3+} + Cu° \leftrightarrows Fe^{2+} + Cu^{2+}$$

1.0M   0.20M   0.50M

E calculations:

1. Calculate E for the following if the Cu(II) and Zn^{+2} solutions are both 0.50 M:

$$Cu^{2+} + Zn° \leftrightarrows Zn^{2+} + Cu°$$

2. Determine the cell potential   When the Ni(II) = 0.01M, Cl^- = 0.20 M and the Cl_2 = 1.O atm

$$Ni + Cl_2 \leftrightarrows Ni^{2+} + 2 Cl^-$$
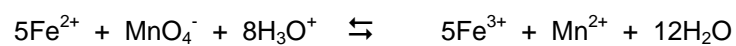
3. What is the E of the cell:

Sn | Sn^{2+}(1.0 M) || Pb^{2+} (0.0010M) |Pb

4. What is the pH in a cell in which Mg^{+2} = 1.00 M and pressure of H_2 = 1.00 atm, if the E of the cell = 2.099 V?

$$Mg\ (s)\ +\ 2\ H^+\ \leftrightarrows\ Mg^{2+}\ (aq)\ +\ H_2\ (g)\quad E^\circ{}_{cell} = 2.363\ V$$
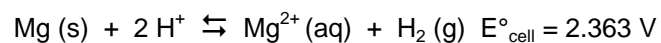
5. Calculate the equilibrium constant from electrode potentials at 25°C for the reaction.

$$2Fe^{3+}\ +\ 2I^-\ \leftrightarrows\ I_2\ +\ 2Fe^{2+}$$
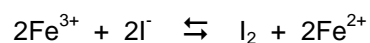
6. What is the potential of the cell represented by the following?

$$5Fe^{2+}\ +\ MnO_4^-\ +\ 8H_3O^+\ \leftrightarrows\quad 5Fe^{3+}\ +\ Mn^{2+}\ +\ 12H_2O$$

When the concentration of each of the solute species is 0.010M and at 25°C?

F. Concentration Cells

Since an electrode potential, E°, depends upon the concentration of the solutions used in the electrode, a cell may be constructed from two half-cells composed of the same materials but differing in concentration of ions. The spontaneous reaction occurs in the direction that tends to make the two ion concentrations equal. In the more concentrated half-cell the Cu(II) ions are reduced to form Zn in order to decrease the Cu(II) concentration. In the more dilute half-cell, more Cu(II) ion will be produced.

Ex.   Calculate the electrode potential for the following:

$$Cu + Cu^{+2} (0.10M) \rightleftarrows Cu^{2+} (0.010 M) + Cu$$
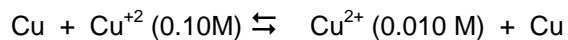
V. Batteries: Using Chemistry to Generate Electricity

Batteries are voltaic cells which can, for a reasonable amount of time, deliver current at a constant potential. This is due to the reactant concentrations remaining reasonably constant.

VI Electrolysis: Driving Nonspontaneous Chemical Reactions with Electricity
Electrolysis occurs in electrolytic cells: Chemical changes occur by applying an electric current to the system
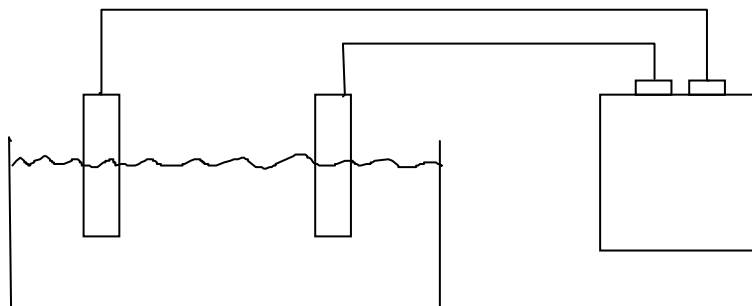
Stoichiometry of Electrolysis
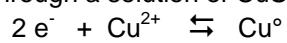
Current = i = amount of q passed per unit time

= ampere, A

=

Calculations

1. Calculate the mass of Al produced in 1.00 Hr by the electrolysis of molten $AlCl_3$ if the electrical current is 10.0 A

2. A current of 0.100 ampere flows through a solution of $CuSO_4$ for 100 seconds. How many grams of copper will be deposited at the cathode? $2 e^- + Cu^{2+} \leftrightarrows Cu°$

VII. Corrosion: Undesirable Redox Reactions

Corrosion is the deterioration of metals due to oxidation

Part III QUANTUM-MECHANICAL MODEL OF THE ATOM

Chapter 7

BACKGROUND

PART I - LIGHT

In 1864 James Maxwell developed a mathematical theory to describe all forms of radiation. Radiation was describe in terms of oscillating or wave-like, electric and magnetic fields in space.

A.   **THE NATURE OF LIGHT**

Electromagnetic Radiation, EM, (Radiant Energy or Electromagnetic energy)

1.

2.

3.

B.   **THE WAVE NATURE OF LIGHT**

1. Wavelength, λ, is the distance between two successive points.

2. Frequency, ν, is the number of complete waves passing through a point in time.

B. The Wave Nature of Light cont'd

3. For all radiation:

$$\text{velocity} = c = \nu \times \lambda$$
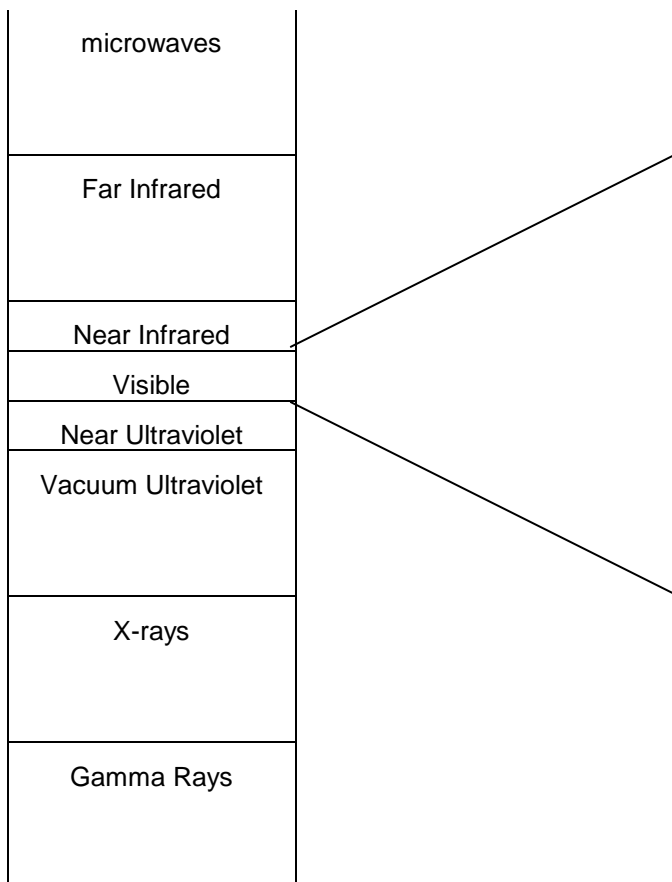
where: $c = 2.998 \times 10^8$ m sec^{-1}

$\nu = $ frequency (sec^{-1} or Hz)

$\lambda = $ wavelength (m)

Problem: If $\lambda = 500.0$ nm, what is the ν ?

C. TheElectromagnetic Spectrum

Radiant energy is characterized by its wavelength

| microwaves |
|---|
| Far Infrared |
| Near Infrared |
| Visible |
| Near Ultraviolet |
| Vacuum Ultraviolet |
| X-rays |
| Gamma Rays |

D. The Particle Nature of Light - Photoelectric Effect

In 1905 Einstein used Planck's quantum theory to explain the photoelectric effect. Experiments had shown that when light shines on metals, electrons could be ejected from the surface of the metals. For each metal there is a minimum frequency of light required to cause an electron to be released. Planck's idea of energy quanta with the notion that light could be described not only as having wave-like properties but also as having particle-like properties. Einstein assumed these *massless* "particles" called **photons** carry energy stated by Planck's law (The energy of a photon is proportional to it's frequency) Essentially, light is behaving is if it was a stream of particles.

$$E = h\nu \qquad where: \quad E = energy$$

h = Planck's constant

radiant
light

meter
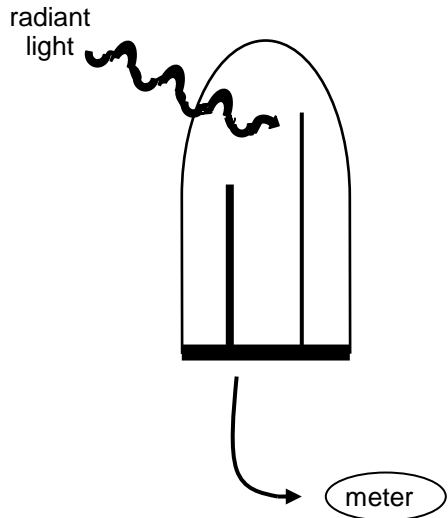
E.Planck's Quantum Theory (1900)

When a piece of metal is heated, it emits electromagnetic radiation, with wavelengths that depend on it's temperature.   Classical physics could not explain the dependence of emitted radiation on the wavelength. According to Planck's quantum theory, radiant energy could not have any arbitrary value; instead, the energy could only be emitted in small discrete amounts he called "quanta" (meaning "fixed amount"). Such energy is said to be "quantized energy"
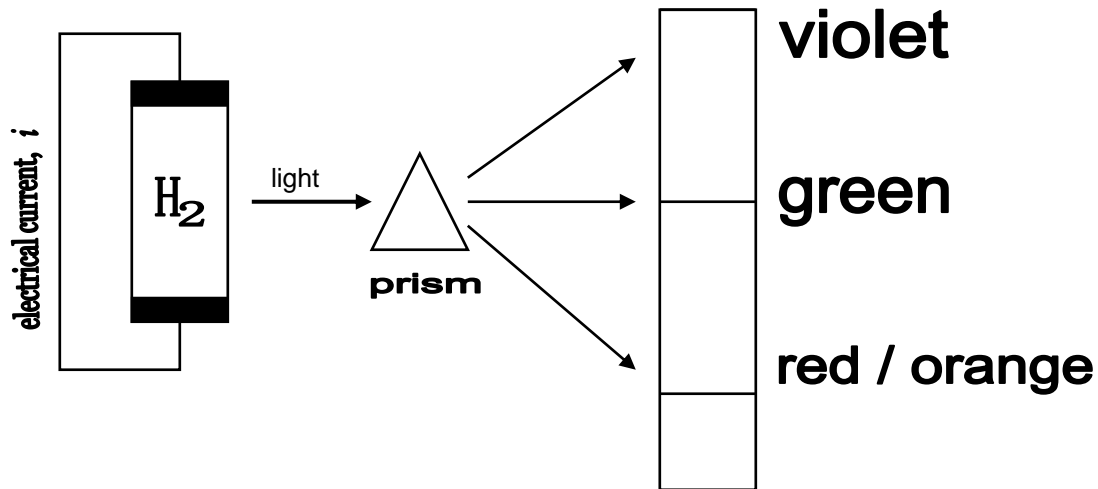
$$E = h\nu$$

where: E = energy

h = Planck's constant

$= 6.63 \times 10^{-34}$ joule sec
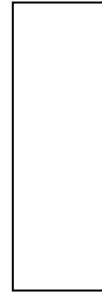
$= 6.63 \times 10^{-27}$ erg sec

F. Atomic Spectra
When an element is vaporize and then heated or an electrical current is passed through it, light (radiation) is emitted. This light when passed through a prism is dispersed and a spectrum is produced

1. Continuous spectrum
    A spectra where continuous range of colors, wavelengths of radiation, are produced

2. Line Spectrum
    A spectrum containing only specific wavelengths, colors, of light, are produced
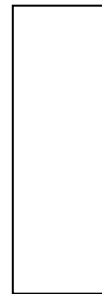
G. The Bohr Model of the Hydrogen atom
In 1913 Niels Bohr offered a theoretical explanation of line spectrum:
    1. Electrons move in circular orbits around the nucleus.

    2. Only orbits of certain radii, corresponding to certain definite energies are permitted.

H. The Wave Behavior of Electrons

In 1925 Louis de Broglie suggested that the electron in its circular path around the nucleus had wave properties with particular wavelengths. He went on to propose that the wavelength of the electron depends on its mass and velocity. De Broglied used the term "matter waves" to describe the wave characteristics of material particles.

$$\lambda = \frac{h}{m\nu}$$

where: m = mass

ν = frequency (sec^{-1} or Hz)

λ = wavelength (meters)

h = Planck's constant)

The quantity $m\nu$ for any object is called its momentum.

I. Uncertainty Principal

In 1927 Werner Heisenberg concluded that it is inherently impossible for us to know simultaneously both the exact position and velocity of a particle.

J. Quantum Mechanics and Atomic Orbitals

In 1926 Erwin Schrodinger proposed an equation ("Schrodinger's wave equation") that describes a tiny particle (e$^-$) that has both wave like and particle like behavior. The equations are complicated (Calculus!) . The solutions to these equations are called wave functions ψ, which are mathematical descriptions of the motion of the electrons in an atom. The wave functions ψ, provides information about an electron's location in allowed energy states. ψ^2 represents the probability of finding an electron in certain regions of space. Therefore, ψ^2 is called the probability density. Electron density is the common way to describe the probability of finding an electron in space.

K. Orbitals and Quantum Numbers
Mathematical solutions to Schrodinger's equation produces wave functions called orbitals. Each orbital describes electron density in space.

    1. Electron structure
    Review: Electron Configuration

Background:
Electrons in the atoms are found in **principal energy levels (n)** also called shells.

In each principal energy level, n, e- move within orbitals.
Principal energy levels are divided into **sublevels** (or subshells), which consists of **orbitals.**
Shapes of orbitals

Quantum Numbers
Each orbital is specified by three quantum numbers:

    1. Principal quantum number,n, can have integral values of 1,2,3, etc.
        a. As n increases the orbital becomes larger and is further away from the nucleus. The electrons in higher n value orbitals will spend more time away from the nucleus and is less tightly bonded.

        b. An increase in n means that the electron in the orbital has a higher energy

    2. Angular momentum /Azimuthal quantum number, l, can have integral values of n-1
        (essentially 0 to n-1)
        a. This quantum number defines the shape of the orbital
        b.

Value of l	0	1	2	3
Orbital	s	p	d	f

    3. Magnetic quantum ,m_l, can have integral values of ± l
        (essentially between -1 to +l, including 0).

        This quantum number describes the orientation in space

    4. Magnetic spin, m_s, can have a value of +1/2 or -1/2 (i.e.±1/2)
        a. An electron acts as if were spinning on its axis like the earth.

        b. Such an electron spin would give rise to a circulating electric charge that would generate a magnetic field.

Permissible Values of Quantum Numbers for Atomic Orbitals

n	l	m_l	m_s	Orbital

Filled and Half Filled Shells " The Story of Cu and Cr "

Problems:

Types of orbitals

1) n = 2   l = 0

   n = 3   l = 2

   n = 4   l = 1

   n = 5   l = 3

n & l values

2)   6s

    5p

    4f

    4d

3)   Are the following sets of quantum number possible or not?

   (4, 0, 0, $\pm$ 1/2)

   (3, 0, +1, $\pm$ 1/2)

   (5, 2, 0, $\pm$ 1/2)

4) Give the quantum numbers to the last electron in S …. In a sulfide ion

5) Give the quantum numbers to the last electron in Co …. In Co (III)

6)   Give the quantum numbers to an electron removed from Cu

6)   Give the quantum numbers to an electron removed from Cu (I)

7)   Give the quantum numbers to an electron removed from Ag

Atomic Spectroscopy Explained

$$E_{photon} = \Delta E = h\nu$$

$$\Delta E = E_{final} - E_{initial} = h\nu$$

The allowed orbits have specific energies, given by: $\mathbf{E_n = -R_H \left(\dfrac{1}{n^2} \right)}$ n = 1,2,3,4....etc.

$$R_H = -2.18 \times 10^{-18} J$$
(Rydberg constant)

$$\mathbf{E_n = -2.18 \times 10^{-18} J \left(\dfrac{1}{n^2_{final}} - \dfrac{1}{n^2_{initial}} \right)}$$

Problems:

1. Calculate the wavelength of light that corresponds to the transition of an electron from n=4 to n=2 state of the hydrogen atom. Is the light absorbed or emitted?

2. Textbook Problem

L.   <u>Orbital Diagrams of atoms</u>

<u>Page 322 in Tro</u>

M.   <u>Hunds Rule</u>
<u>Page 322 in Tro</u>
For a subshell/orbital, the lowest energy is attained when the electrons are placed in separate orbitals of the subshell with the same spin before pairing electrons.

N.   <u>Pauli Exclusion Principle</u>
<u>Page 318 in Tro</u>
No two electrons in an atom can have the **<u>same</u>** set of four quantum numbers (n, l, m_l, and m_s)

## O. <u>Paramagnetic and Diamagnetic substances</u>
Page 441 in Tro

Paramagnetic substances are substances with unpaired electrons. The unpaired electrons are attracted to a magnetic field.

Diamagnetic substances are substances which all of the electrons in the substance being paired and are not attracted to a magnetic field.

Problems

Which are incorrect box diagrams for a ground state atom and why?

a)

↑	↑↑	↑	↑	↑

    3d

b)

↑↓	↑	

    2p

c)

↑↓		↑↓		↑	↑	↑

 1s   2s   sp

d)

↑↓		↑↓	↑↓	↑↓		↑	↑			

 3s   3p   3d
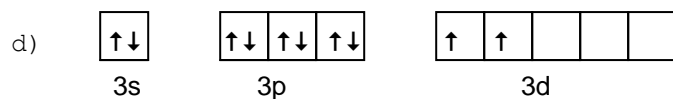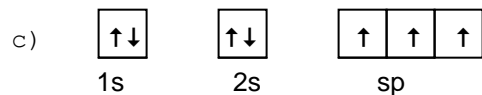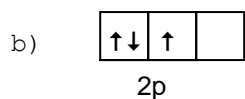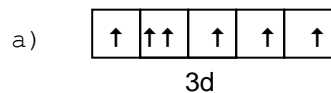
Which are paramagnetic? Diamagnetic?

a)

↑↓		↑↓	↑↓	↑↓

b)

↑↓		↑↓	↑↓	↑↓		↑↓	↑↓	↑↓	↑↓	↑