

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**

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

- **Surrounding/ System**
 - Exothermic rxn:
 - Endothermic rxn:

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.

State Function

“pathway independent”

Nonstate Function

“pathway dependant”

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

$$q = m \times C \times \Delta T$$

$$q = \text{Mass} \times \text{Specific heat capacity (J/g } ^\circ\text{C)} \times \Delta T$$

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

$$w = F \times D$$

$$w = \text{Force} \times \text{Distance}$$

$$w = - P \Delta V$$

$$\text{Internal Energy} = \Delta E = q + w$$

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:

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

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

$$\Delta H_{\text{rxn}} < 0$$

$$\Delta H_{\text{rxn}} > 0$$

$$\Delta H_{\text{rxn}} = 0$$

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 = $0.908 \frac{\text{J}}{\text{g K}}$

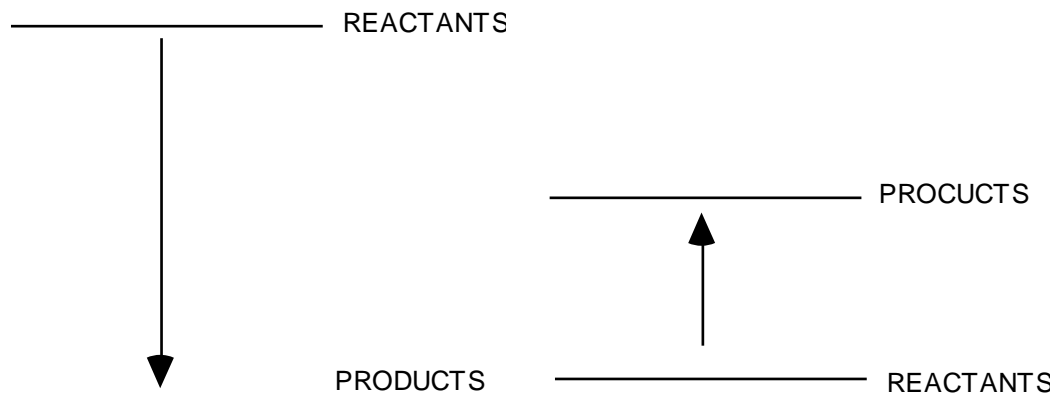
The **Heat Capacity** of a substance is the amount of heat required to change its temperature 1 °

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

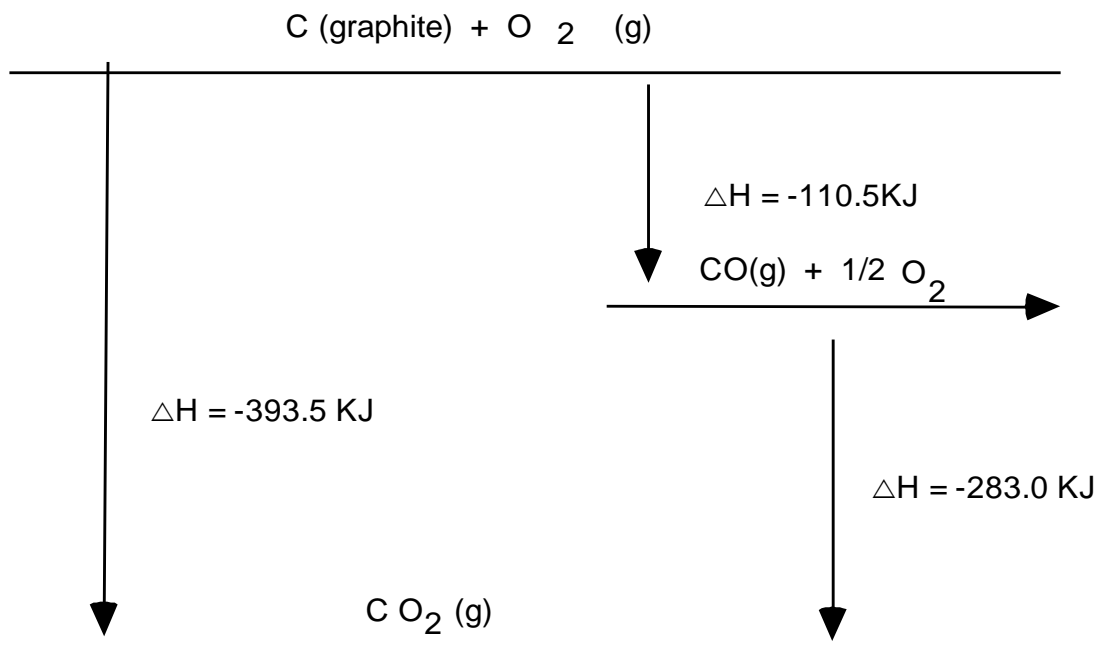
VII. Law of Hess-Law of constant heat summation

A. Enthalpy, ΔH

$$\Delta H_{rxn} = \Delta H_{products} - \Delta H_{reactants}$$

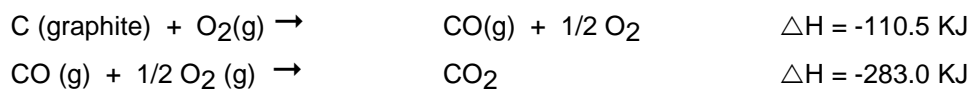


B. Energy diagram

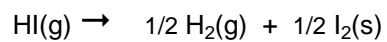


C. Energy Equations:

1. Addition of equations

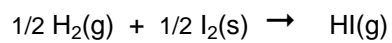


2. Multiplying:



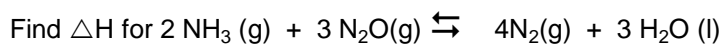
$$\Delta H = -25.9 \text{ KJ}$$

3. Reversing:

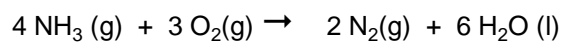


$$\Delta H = +25.9 \text{ KJ}$$

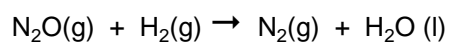
4. Problem:



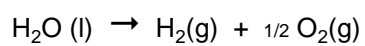
Given:



$$\Delta H = -1531 \text{ KJ}$$



$$\Delta H = -367.4 \text{ KJ}$$



$$\Delta H = +285.9 \text{ KJ}$$

Warning! You need to print out more Exam 1 lecture outline pages!

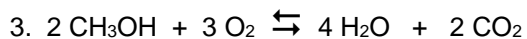
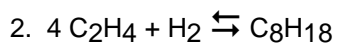
VIII. Bond Energies and Bond Lengths Chapter 9 Pages 409-413

IX Bond Energy Page 410 in Tro

$$\Delta H_{\text{rxn}} = \sum \Delta H_{\text{Bonds broken/reactants}} - \sum \Delta H_{\text{Bonds made/products}}$$

$$\Delta H_{\text{rxn}} = \sum \Delta \text{Bond Energy}_{\text{Bonds broken/reactants}} - \sum \Delta \text{Bond Energy}_{\text{Bonds made/products}}$$

Calculate the the ΔH for the following reactions using bond energies:



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 Thermodynamics: 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

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

B. Second Law of Thermodynamics

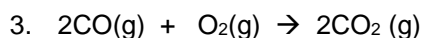
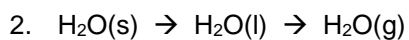
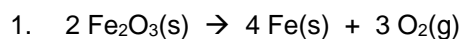
For a spontaneous reaction, total entropy always increases for a system and its surroundings:

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

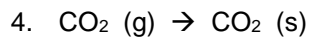
$$S_{\text{universe}} > 0 \text{ for a spontaneous reaction}$$

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

Predicting an entropy change for a reaction:



ΔS	Spontaneous/nonspontaneous



C. Gibbs Free Energy

Background: Reaction Spontaneity: ΔS vs ΔH

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

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

Note: $\Delta G^\circ = 0$ for elements

D. Third Law of Thermodynamics

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

E. Thermodynamics and Equilibrium.

$$\Delta G^\circ = -RT \ln K$$

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

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

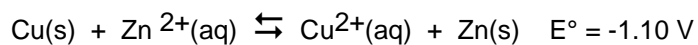
$\Delta G^\circ > 0$ $K < 1$ Reactants are favored at equilibrium

F. Thermodynamics and Standard Potential, E° .

$$\Delta G^\circ_{\text{rxn}} = -nFE^\circ$$

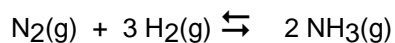
G. Problems:

1. Calculate the ΔG° for the following redox reaction:



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

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



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



4. Given the following ΔG° values:

$$\text{I}^- (\text{aq}) = -51.7 \text{ kJ/mol}$$

$$\text{Cl}^- (\text{aq}) = -131.2 \text{ kJ/mol}$$

Calculate E° for the following reaction: $\text{Cl}_2 + 2 \text{I}^- (\text{aq}) \rightleftharpoons 2 \text{Cl}^- (\text{aq}) + \text{I}_2$

5. Calculate K for the following reaction: $2 \text{SO}_2 + \text{O}_2 \rightleftharpoons 2 \text{SO}_3$

$$\Delta G_f^\circ \text{SO}_2 = -300.8 \text{ kJ/mol}$$

$$\Delta G_f^\circ \text{SO}_3 = -370.4 \text{ kJ/mol}$$

PART I - ELECTROCHEMISTRY

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

Type I- Ions & Atoms

Ion/Atom	Oxidation Number

Type II- Molecules & Polyatomic Ions

Molecule/Polyatomic Ion	Oxidation Number

OXIDATION NUMBERS

1. The oxidation number for oxygen is usually -2.

Exceptions: O₂ and peroxides
(O--O bond → ex. H₂O₂, Na₂O₂, and BaO₂ and etc.)

2. The oxidation number of hydrogen is usually +1.

Exceptions: H₂ and hydrides Ex. NaH, BaH₂, 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. H₂, S₈, Br₂....etc.)

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

<u>ION</u>	<u>OXIDATION NUMBER</u>
K ¹⁺	+1
Ca ²⁺	+2
Fe ³⁺	+3
S ²⁻	-2

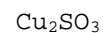
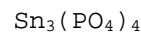
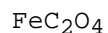
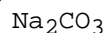
d. The sum of the oxidation numbers of the elements in a compound is equal to zero



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



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



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)
- 3.



Half reactions:

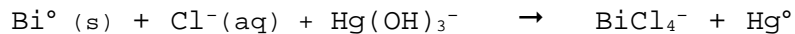
E. Balancing Redox Reaction - Half- Reaction Method:

In Acidic Solution:



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:



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

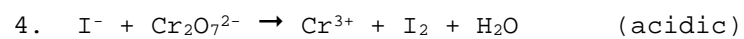
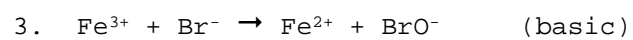
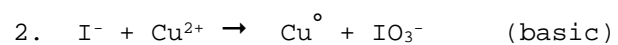
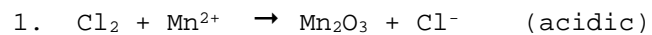
 - d. Use e^{-} to balance positive charges

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:

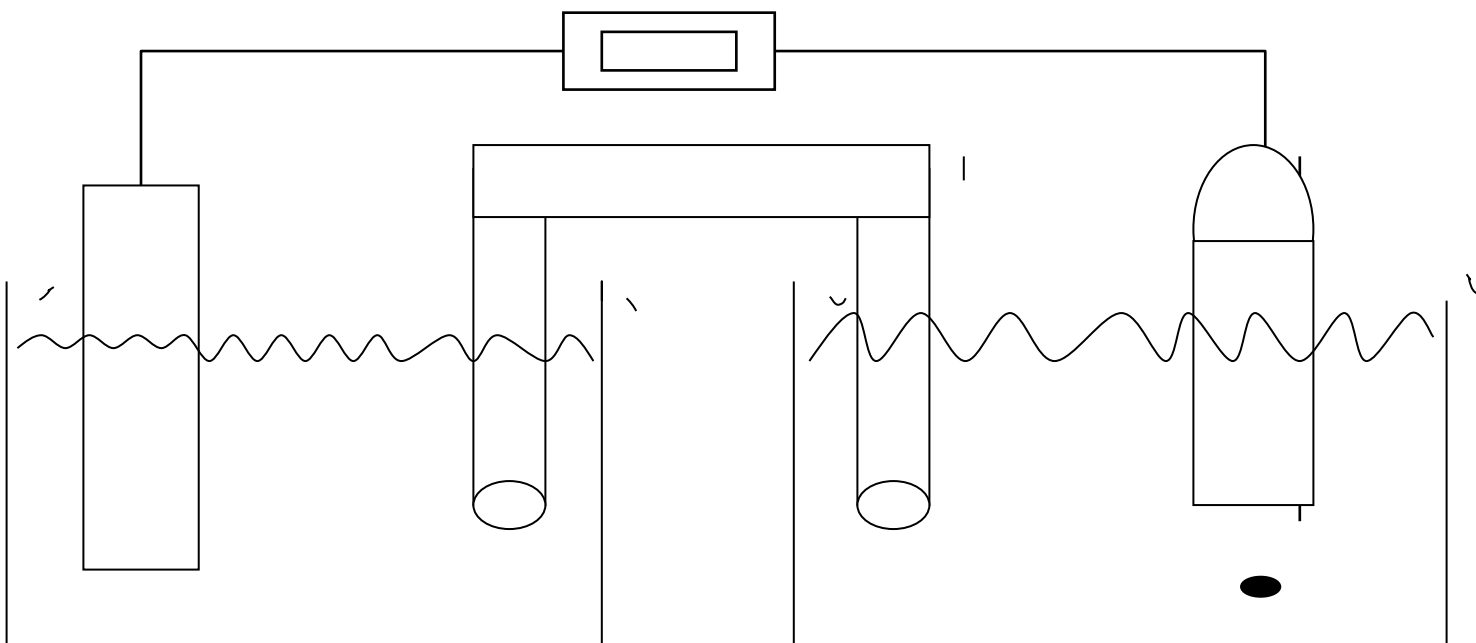


G. Electrochemical Cells

1. **Electrochemical Cells** are systems that allow electrons to flow from a reducing agent to an oxidizing agent.
 - The conversion between chemical energy and electrical energy is carried out in an **electrochemical cell**.
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:

a. Electrochemical cell Diagram:



b. The Balanced Redox 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.

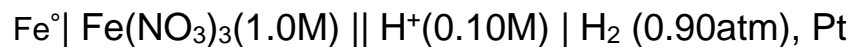
c. Electrochemical Cell Notation:

3. Electrochemical Cell Notation: (Schematic Cell representation)

Oxidation || Reduction



Electrochemical Cell Notation continued:

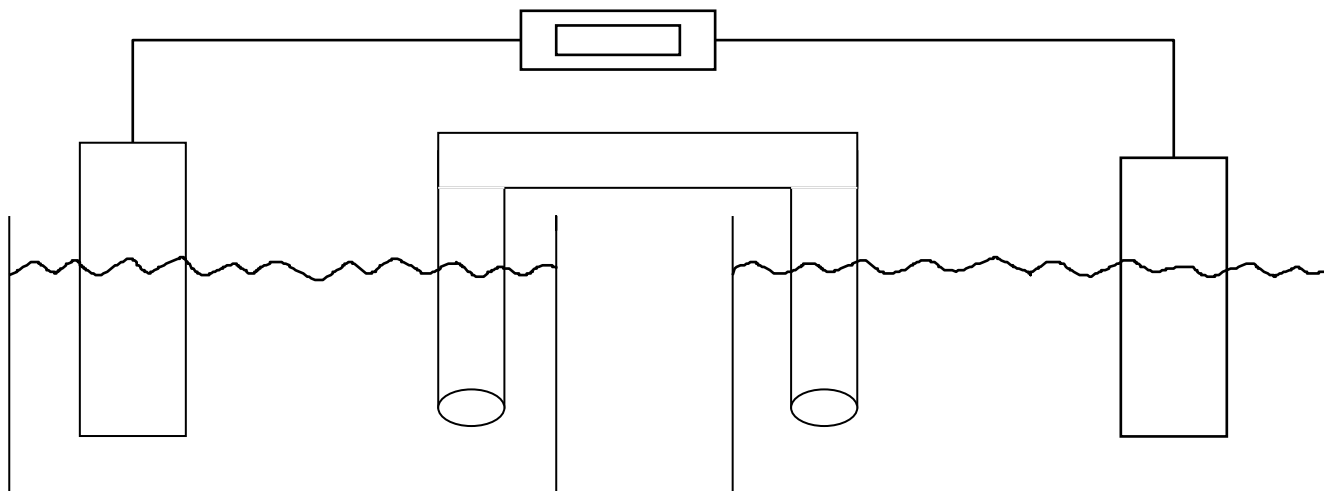
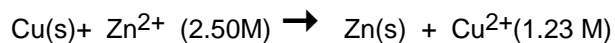


Voltaic Cells:

(also known as galvanic cells)

Danielle cell: John Daniell invented the first battery to generate electricity

a. Cell Diagram

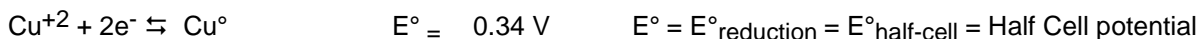


b. Balanced Redox Equation:

c. Cell Notation:

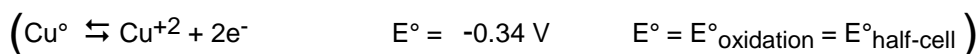
H. Cell Potentials, E, emf

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 electromotive force (emf), An electromotive force is also known as the cell potential (E) and cell voltage

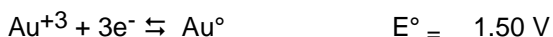


V = Volts

E° = standard cell potential



Some Examples of Standard Cell potentials



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. $E^{\circ}_{\text{species}}$ is measured against: $2\text{H}^{+} + 2\text{e}^{-} \rightleftharpoons \text{H}_2$ $E^{\circ} = 0$
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:

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

$$E^{\circ}_{\text{cell}} = E^{\circ}_{+} - E^{\circ}_{-}$$

species undergoing reduction

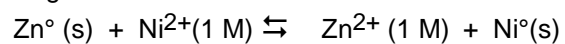
species undergoing oxidation

EXAMPLES

1. $\text{Cu}^{+2} (1 \text{ M}) + \text{H}_2 (1 \text{ atm}) \rightleftharpoons 2\text{H}^+ (1 \text{ M}) + \text{Cu}^0$ $E^\circ_{\text{Cu}} = 0.34 \text{ V}$ Calculate the E°_{cell}

2. $2\text{H}^+(1\text{M}) + \text{Zn}^0 \rightleftharpoons \text{Zn}^{2+}(1\text{M}) + \text{H}_2 (1 \text{ atm})$ $E^\circ_{\text{cell}} = + 0.76 \text{ V}$ Calculate E°_{Zn}

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



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.



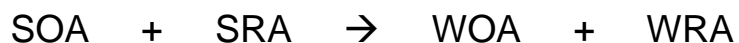
ELECTROCHEMISTRY

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

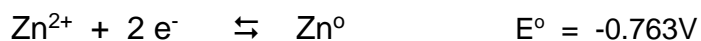
A redox reaction is the sum of two half-reactions, one for oxidation and the other for reduction

Consider the following:

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

Example:

Write a nonspontaneous (electrolytic cell) redox reaction for $\text{Cd}^{2+} / \text{Cd}^0$ with $\text{Zn}^{2+} / \text{Zn}^0$



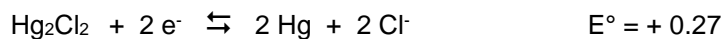
To write Spontaneous Redox Reactions:

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 obtain an overall redox reaction in such a way that the number of electrons cancel from both sides of the equation.

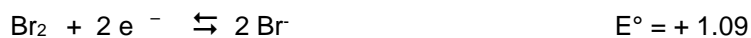
*NOTE: Changing the "balancing" coefficients of a half-rxn does **NOT** change the E° value. An electrode potential, E° is an intensive property, one that does not depend on the amount of substance present. The potential is the ratio of energy to charge, when the coefficients are changed (increasing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

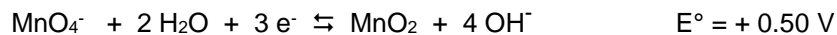
1. Give a Galvanic cell redox reaction using:



2. Give an electrolytic cell redox reaction using:



3. Give a nonspontaneous cell redox reaction using:



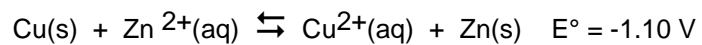
III. Cell Potential, E°, and Free Energy, G°.

G° and E° :

$$\Delta G^\circ_{\text{rxn}} = -nFE^\circ$$

Problems:

1. Calculate the ΔG° for the following redox reaction:



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

2. Given the following ΔG° values:

$$\text{I}^- (\text{aq}) = -51.7 \text{ kJ/mol}$$

$$\text{Cl}^- (\text{aq}) = -131.2 \text{ kJ/mol}$$

Calculate E° for the following reaction: $\text{Cl}_2 + 2 \text{I}^- (\text{aq}) \rightleftharpoons 2 \text{Cl}^- (\text{aq}) + \text{I}_2$

E° and K: Equilibrium calculations:

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

$$E = 0 = E^\circ - \log K$$

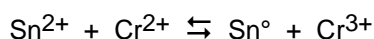
and

Where K = equilibrium constant

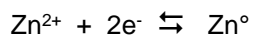
$$E^\circ = \frac{0.0592}{n} \log K$$

Problems

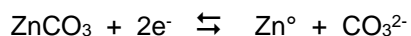
1. Calculate the K_{eq} for the following reaction:



2. Calculate the K_{sp} of ZnCO_3 if:

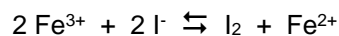


$$E^\circ = -0.763$$



$$E^\circ = -1.055\text{V}$$

3. Calculate the equilibrium constant for:



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

<u>Table of E° Values</u>	<u>E° (V)</u>
$\text{Fe}^{+2} + 2\text{e}^- \rightleftharpoons \text{Fe}^\circ$	+ .77
$\text{Cu}^{+2} + 2\text{e}^- \rightleftharpoons \text{Cu}^\circ$	+ .34
$\text{Zn}^{+2} + 2\text{e}^- \rightleftharpoons \text{Zn}^\circ$	- .76
$\text{Na}^+ + \text{e}^- \rightleftharpoons \text{Na}$	- 2.71

°E species is measured against: $2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$ °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] ≠ 1M

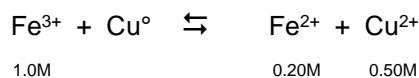
$$E = E^\circ - \frac{0.0592}{n} \log Q \quad \text{Where:} \quad Q = \text{the Reaction Quotient}$$

n = number of electrons

0.0592 is a constant

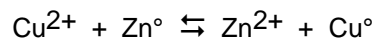
$$E = E^\circ - \frac{0.0592}{n} \log \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

(1) Using the nerst equation

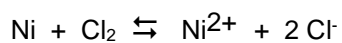


E calculations:

1. Calculate E for the following if the Cu(II) and Zn²⁺ solutions are both 0.50 M:



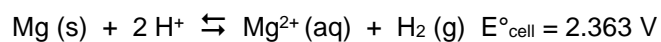
2. Determine the cell potential When the Ni(II) = 0.01M, Cl⁻ = 0.20 M and the Cl₂ = 1.0 atm



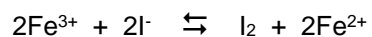
3. What is the E of the cell:



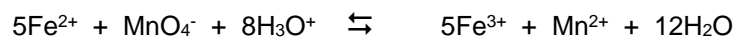
4. What is the pH in a cell in which $Mg^{+2} = 1.00 \text{ M}$ and pressure of $H_2 = 1.00 \text{ atm}$, if the E of the cell = 2.099 V ?



5. Calculate the equilibrium constant from electrode potentials at 25°C for the reaction.



6. What is the potential of the cell represented by the following?

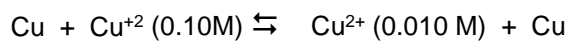


When the concentration of each of the solute species is 0.010M and at 25°C ?

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:



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.

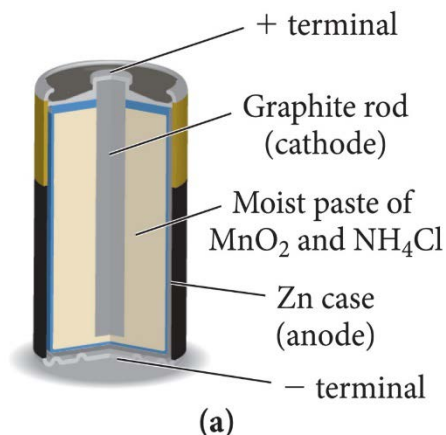
- Redox reactions involve the transfer of electrons from one substance to another.
- Therefore, redox reactions have the potential to generate an electric current.
- To use that current, we need to separate the place where oxidation is occurring from the place where reduction is occurring.
- Batteries are:
 - Voltaic cells
 - Galvanic cells
 - Spontaneous $E_{\text{cell}} > 0$
 - Batteries delivers a relatively constant current, i.
 $E_{\text{cell}} = 0$

Types

- See textbook for battery examples

Leclanché Acidic Dry Cell

- Electrolyte in paste form
 - $\text{ZnCl}_2 + \text{NH}_4\text{Cl}$
(or MgBr_2)
 - Anode = Zn (or Mg)
- $$\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2 \text{e}^-$$
- Cathode = graphite rod
 - MnO_2 is reduced.
- $$2 \text{MnO}_2(\text{s}) + 2 \text{NH}_4^+(\text{aq}) + 2 \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \rightarrow 2 \text{NH}_4\text{OH}(\text{aq}) + 2 \text{Mn}(\text{O})\text{OH}(\text{s})$$
- Cell voltage = 1.5 V
 - Expensive, nonrechargeable, heavy, easily corroded



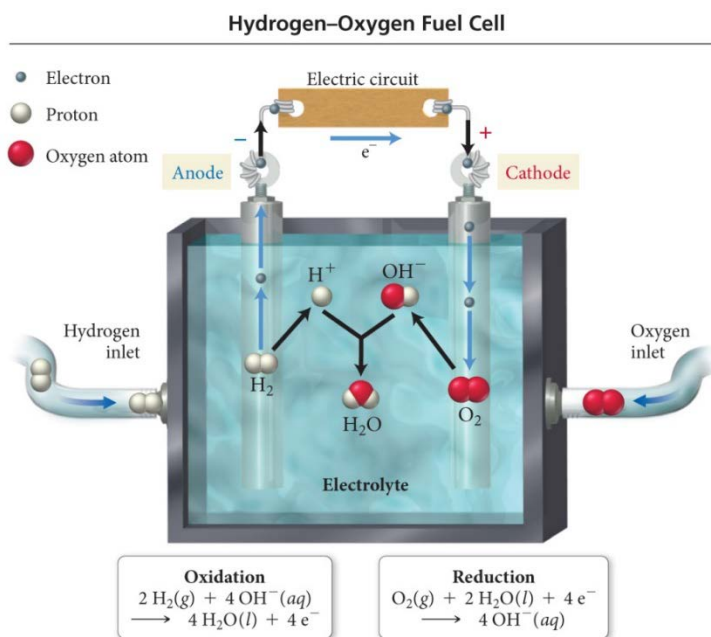
Ref: Chemistry: A Molecular Approach, 3e Tro

VI. Fuel Cells

- Like batteries in which reactants are constantly being added
 - So it never runs down!
- Anode and cathode both Pt coated metal
- Electrolyte is OH^- solution.
- Anode reaction

$$2 \text{H}_2 + 4 \text{OH}^- \rightarrow 4 \text{H}_2\text{O}(\text{l}) + 4 \text{e}^-$$
- Cathode reaction

$$\text{O}_2 + 4 \text{H}_2\text{O} + 4 \text{e}^- \rightarrow 4 \text{OH}^-$$

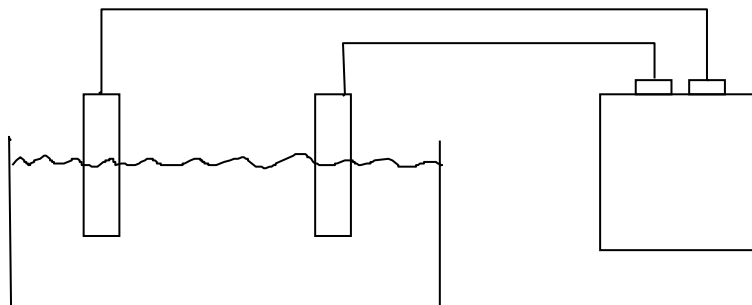


Ref: Chemistry: A Molecular Approach, 3e Tro

VI Electrolysis: Driving Nonspontaneous Chemical Reactions with Electricity

Electrolysis occurs in electrolytic cells: Chemical changes occur by applying an electric current to the system

- Electrons are drawn off the anode, so it must have a place to release the electrons—the positive terminal of the battery.
- Electrons are forced toward the anode, so it must have a source of electrons—the negative terminal of the battery



Anode:

Cathode: _____

Redox:

Stoichiometry of Electrolysis

Current = i = amount of q passed per unit time

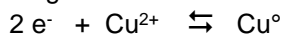
= ampere, A

=

Calculations

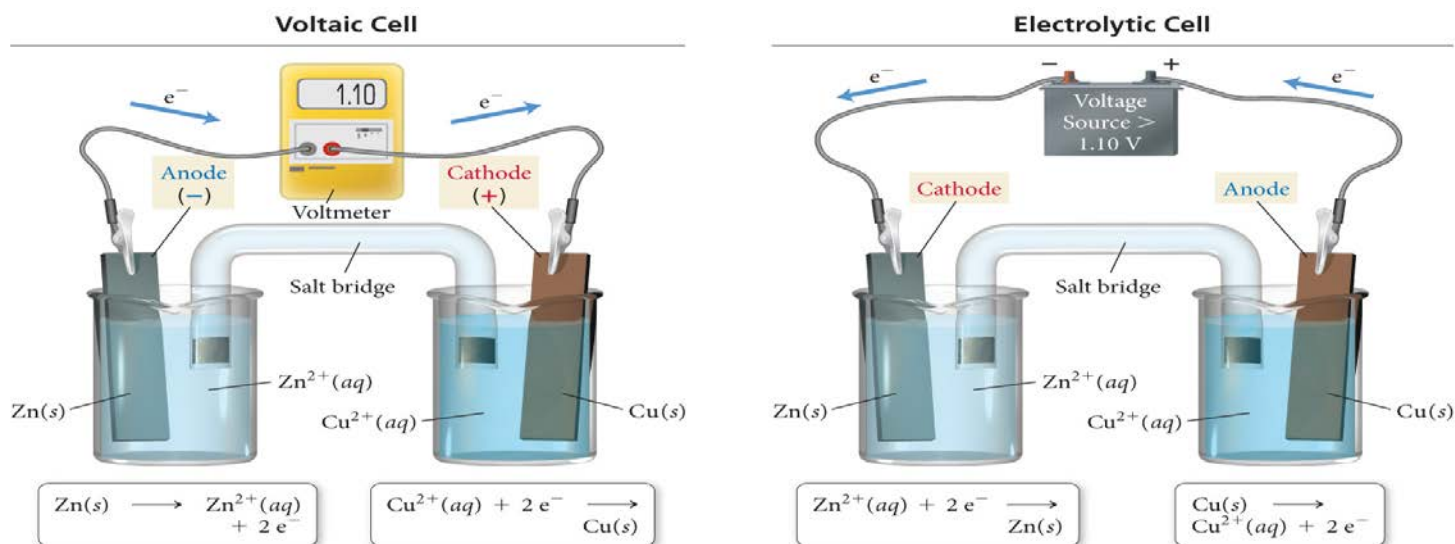
1. Calculate the mass of Al produced in 1.00 Hr by the electrolysis of molten AlCl_3 if the electrical current is 10.0 A

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?



Electrochemical Cells, Summary:

- In all electrochemical cells, oxidation occurs at the anode, reduction occurs at the cathode.
- In voltaic cells
 - Anode is the source of electrons and has a (-) charge.
 - Cathode draws electrons and has a (+) charge.
- In electrolytic cells
 - Electrons are drawn off the anode, so it must have a place to release the electrons—the positive terminal of the battery.
 - Electrons are forced toward the anode, so it must have a source of electrons—the negative terminal of the battery.



Ref: Chemistry: A Molecular Approach, 3e Tro

VII. Corrosion: Undesirable Redox Reactions

Corrosion is the deterioration of metals due to oxidation

- Corrosion is the spontaneous oxidation of a metal by chemicals in the environment.
 - Mainly O₂
- Because many materials we use are active metals, corrosion can be a very big problem.
 - Metals are often used for their strength and malleability, but these properties are lost when the metal corrodes.
 - For many metals, the product of corrosion also does not adhere to the metal,

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:

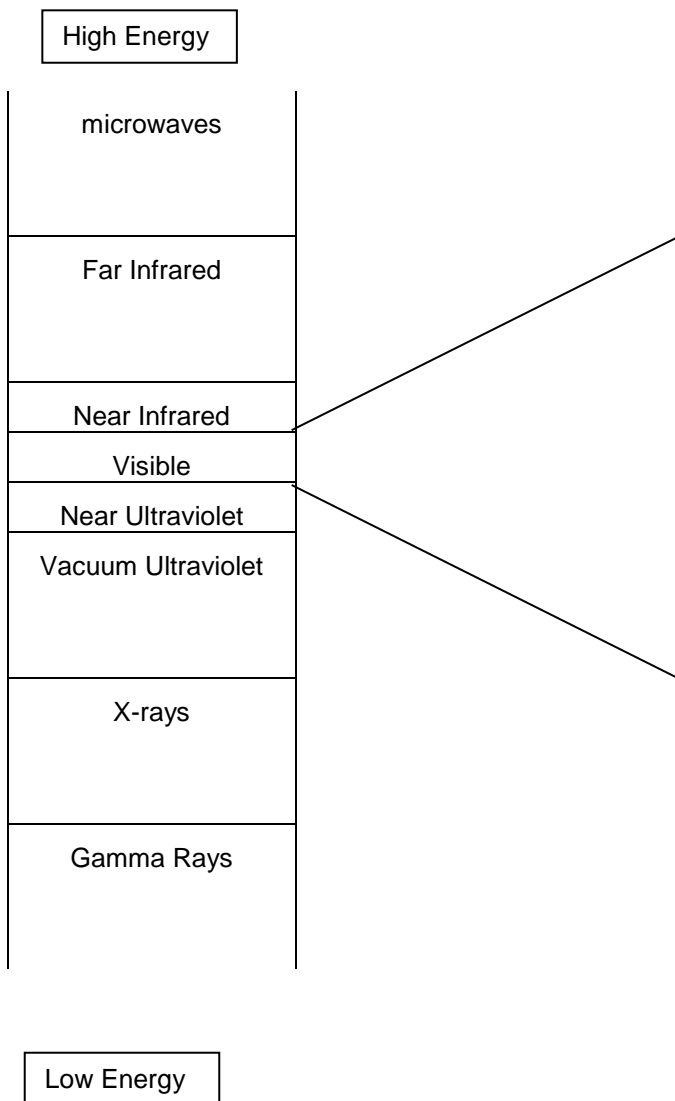
$$\text{velocity} = c = v \times \lambda$$

where: $c = 2.998 \times 10^8 \text{ m sec}^{-1}$
 $v = \text{frequency (sec}^{-1} \text{ or Hz)}$
 $\lambda = \text{wavelength (m)}$

Problem: If $\lambda = 500.0 \text{ nm}$, what is the v ?

C. The Electromagnetic Spectrum

Radiant energy is characterized by its wavelength



D. Planck's Quantum Theory (1900)

When a piece of metal is heated, it emits electromagnetic radiation, with wavelengths that depend on its 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:

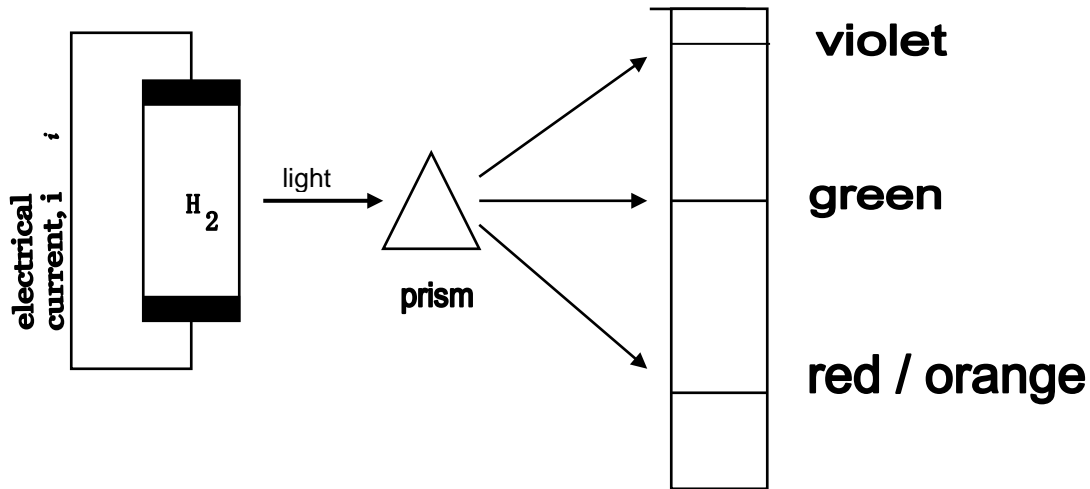
E = energy

h = Planck's constant

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

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

I. Experiment



II Explanation of the Experimental Results

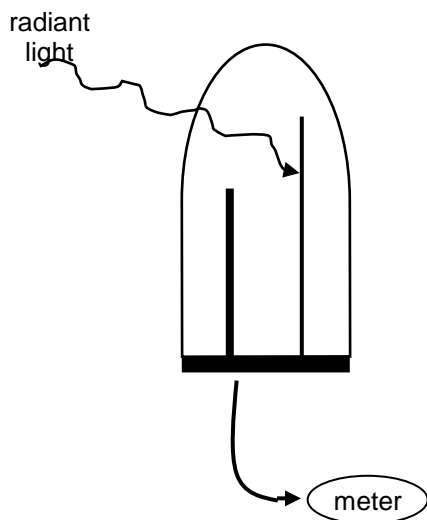
III Theory

E. 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.

$$E = h\nu \quad \text{where:} \quad E = \text{energy and } h = \text{Planck's constant}$$

I. Experiment



II Explanation of the Experimental Results

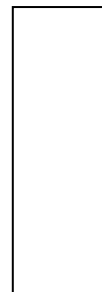
III Theory

F. Atomic Spectra

When an element is vaporized 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

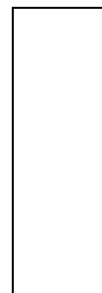
1. Continuous spectrum

A spectrum 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 Broglie used the term "matter waves" to describe the wave characteristics of material particles.

$$\lambda = \frac{h}{mV}$$

where:

m = mass

V = velocity

λ = wavelength (meters)

h = Planck's constant)

The quantity mV 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 $\pm l$ (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. $\pm 1/2$)
 - 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) $n = 2 \quad l = 0$
 $n = 3 \quad l = 2$
 $n = 4 \quad l = 1$
 $n = 5 \quad l = 3$

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

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

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

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

$$R_H = -2.18 \times 10^{-18} \text{J}$$

(Rydberg constant)

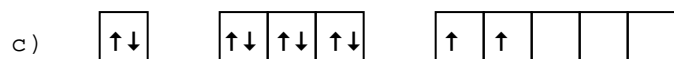
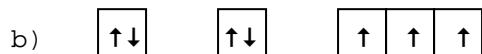
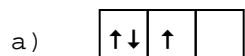
$$E_n = -2.18 \times 10^{-18} \text{J} \left(\frac{1}{n_{\text{final}}^2} - \frac{1}{n_{\text{initial}}^2} \right)$$

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?

L. Orbital Diagrams of atoms

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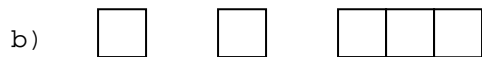
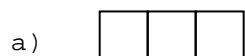
M. Hunds Rule

Page 322 in Tro

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.

Ground State-Obeys's Hunds's Rule

Not Ground State- Disobey's Hunds's Rule



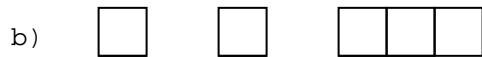
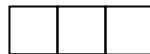
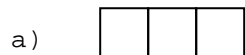
N. Pauli Exclusion Principle

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No two electrons in an atom can have the same set of four quantum numbers (n, l, m_l , and m_s)

Obeys Pauli Exclusion Theorem

Violates Pauli Exclusion Theorem

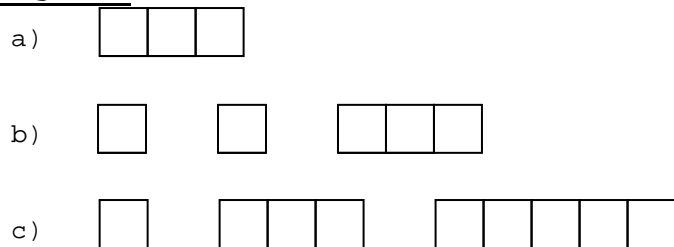


O. Paramagnetic and Diamagnetic substances

Page 441 in Tro

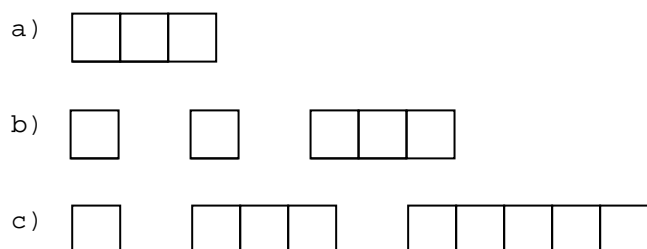
Paramagnetic substances are substances with unpaired electrons. The unpaired electrons are attracted to a magnetic field.

Paramagnetic



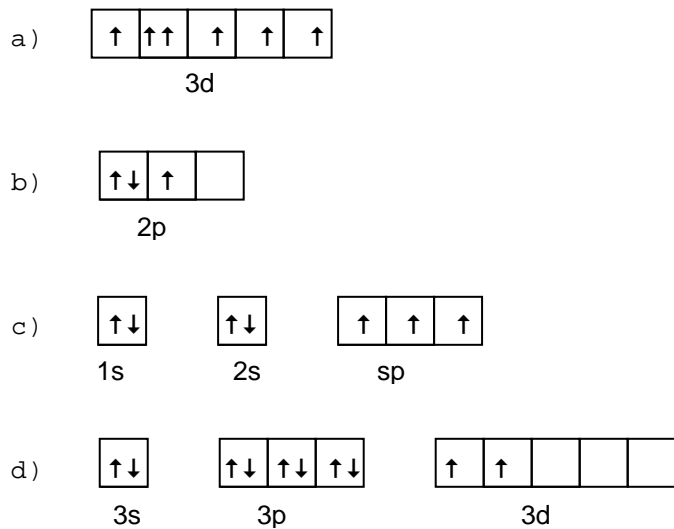
Diamagnetic substances are substances which all of the electrons in the substance being paired and are not attracted to a magnetic field.

Diamagnetic



Problems

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



Which are paramagnetic? Diamagnetic?

