

# Physical Chemistry Rapid Learning Series

## Course Content Study Guide



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- Rotational Transition Selection Rules

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- Method
- Results
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## COURSE FEATURES

This tutorial series is a carefully selected collection of core concept topics that cover the essential concepts. It consists of three parts:

1. Concept Tutorials – 24 essential topics
2. Problem-Solving Drills – 24 practice sets
3. Super Condense Cheat Sheets – 24 super review sheets

### **Core Tutorials**

- Self-contained tutorials, not an outline of information which would need to be supplemented
- by an instructor.
- Concept map showing inter-connections of new concepts in this tutorial and those previously introduced.
- Definition slides introduce terms as they are needed.
- Visual representation of concepts.
- Conceptual explanation of important properties and problem solving techniques
- A concise summary is given at the conclusion of the tutorial.

### **Problem Solving Drills**

- Each tutorial has an accompanying Problem Set with 10 problems covering the material presented in the tutorial. The problem set affords the opportunity to practice what has been learned.

### **Condensed Cheat Sheet**

- Each tutorial has a one-page cheat sheet that summarizes the key concepts and vocabularies and structures presented in the tutorial. Use the cheat sheet as a study guide after completing the tutorial to re-enforce concepts and again before an exam.

## CHAPTER BY CHAPTER DETAILED CONTENT DESCRIPTIONS

### 01: Chemistry and Physics Review for Physical Chemistry

#### Chapter Summary

This chapter reviews the basic physical and chemical concepts used in Physical Chemistry.

#### Tutorial Features

- Concept map showing inter-connections of concepts.
- Definition slides introduce terms as they are needed.
- Examples given throughout to illustrate how the concepts apply.
- A concise summary is given at the conclusion of the tutorial.

#### Core Issues of Basic Chemistry and Physics

- Energy
- Classical Mechanics
- Waves
- Chemical Bonding
- Intermolecular Forces
- Phases
- Chemical Reaction
- Chemical Equilibrium
- Chemical Kinetics

#### Chapter Review

- There are two types of energy: Kinetic and Potential. Kinetic Energy is associated with motion and is calculated as one-half the mass of an object multiplied by velocity squared.
- **Potential Energy** is the force acting on an object multiplied by the distance over which the force acts. The force on an object is associated with location. As a result potential energy is associated with location.
- **Classical Mechanics** predicts that if the initial position and momentum of an object free from outside forces are known, all future positions and momenta may be calculated.
- Disturbances that travel through space are Waves.
- Disturbances (waves) in Electromagnetic Radiation are oscillating Electric and Magnetic Fields.
- **Chemical bonds** are the forces that hold atoms together in molecules and ionic solids and liquids. Chemical bonds are strong forces between atoms referred to as Covalent Bonds or Ionic Bonds.
- Intermolecular forces (forces between molecules) are weaker forces than chemical bonds and are referred to as Van der Waals forces in honor of Johannes Van der Waals.
- Most chemicals may exist in solid phases, liquid phases or a gas phase depending on the temperature, pressure and presence of other chemicals.
- A chemical reaction takes place when one set of chemicals (reactants) interact and change into another set of chemicals (products).

- A chemical reaction is at equilibrium when the forward reaction rate, from left to right, is equal to the reverse reaction rate, from right to left.
- The rate or speed of a chemical reaction is expressed in terms of the rate of formation of a product or the rate of use of a reactant.
- The rate or speed of a chemical reaction is determined by the activities/concentrations of the reactant species and temperature.
- Chemical reactions take place as a result of random collisions of chemical species.
- Most chemical reactions require a series of collision processes, steps, and often one of the steps is much slower and determines the rate of the reaction.



### Chapter Summary

Physical-Chemical principles and related insights result from mathematical analysis of Chemical data. Clear understanding of Mathematics is essential to understanding Physical Chemistry. This chapter is a review of much of the mathematics of Physical Chemistry.

### Tutorial Features

- Concept map showing inter-connections of concepts.
- Definition slides introduce terms as they are needed.
- Examples given throughout to illustrate how the concepts apply.
- A concise summary is given at the conclusion of the tutorial.

### Core Issues of Math for Physical Chemistry

- Basic Mathematical Procedures
  - Logarithms
  - Exponentials
  - Complex Numbers
  - Vectors
- Calculus
  - Differentiation
  - Integration
  - Partial Derivatives
  - Differential Equations
- Statistics and Probability
  - Random Selection
  - Mean Value of a Variable
  - Mean Value of a Function
- Matrix Algebra
  - Matrix addition
  - Matrix Multiplication
  - Simultaneous Equations

### Chapter Review

- The **Common Logarithm** of a number  $x$  is the power to which 10 must be raised to have the value  $x$ .
- The **Natural logarithm** of a number  $x$  is the power to which  $e$  must be raised to have the value  $x$ .
- Exponential functions occur often in chemical calculations.
- An Exponential Function includes a base raised to a power.
- A product of Exponential Functions is the base raised to the power of the sum of the exponents of the Exponential Functions.
- A quotient of Exponential Functions is the base raised to the sum of the exponents of the Exponential Functions in the numerator minus the sum of the exponents of the Exponential Functions in the denominator.
- An Exponential Function raised to a power is the base raised to the product of the powers.

- **Complex Numbers** include the square root of -1 as a factor. The general format for a complex number is factored into a real part and an imaginary part.
- A Vector is a quantity that has both direction and magnitude.
- Unit Vectors  $i$ ,  $j$ , and  $k$  have a magnitude of 1 and convert magnitudes into vector components along their respective directions:  $x$ ,  $y$ , and  $z$ .
- **Vectors** may be added and/or subtracted by adding and/or subtracting their component;  $x$ ,  $y$ , and  $z$ , magnitudes.
- Vectors may be multiplied as either cross-products or scalar-products.
- The slope of a function at a point is the derivative of the function at that point.
- A ratio of differentials is a derivative.
- An infinitesimal change in a function or variable is a differential.
- The process of obtaining a derivative is differentiation.
- Derivatives of functions are obtained by referring to Tables of Derivatives available in calculus texts, math reference books and on the internet.
- Determining the derivative of a function having more than one independent variable, when all but one independent variable is held constant is partial differentiation.
- A **partial derivative** is obtained using the same process as an ordinary derivative, except that all but one of the independent variables is held constant.
- Notation for a partial derivative list all variables held constant in a right-hand subscript.
- Adding together, summing, an infinite number of differentials is Integration.
- A **Table of Integrals** is used to obtain integrals of common functions.
- Integration between limits, from A to B, is a definite integral.
- A **differential equation** is an algebraic equation that includes derivatives.
- Problems in Chemistry and Physics are commonly able to be expressed in terms of Differential Equations.
- Solving a differential equation means finding the function or functions that fit the equation.
- The most probable behavior of a system of molecules is determined by calculating the number of ways that a particular distribution of the molecules, among the quantum states of the system, may occur.
- The number of ways that a particular distribution of the molecules, among the quantum states of a system, may occur is  $W$ .
- The mean value of a variable is calculated from the probabilities of occurrence of the possible values of the variable.
- A **Matrix** is a rectangular array of numbers, Elements of the matrix.
- Matrix-Element symbols give the row number followed by the column number as a right-hand subscript.
- Matrices are added to give a sum matrix  $C$  by adding the corresponding elements of the summed matrices  $A$  and  $B$ .
- Two Matrices may be multiplied if the number of rows in the first matrix is equal to the number of columns in the second matrix.
- Matrices are multiplied to give a product matrix  $C$  by multiplying corresponding elements of a row of the matrix  $A$  by the elements of the corresponding column of matrix  $B$  and summing these to give product matrix elements.
- When the conditions for a set of equations are met simultaneously, the equations are called Simultaneous Equations.

## Chapter Summary

The Zeroth Law of thermodynamics is the basis for the design and use of thermometers. The first law of thermodynamics makes possible the combination of heat flow and mechanical work to give the total internal energy change for a process.

## Tutorial Features

- Concept map showing inter-connections of concepts.
- Definition slides introduce terms as they are needed.
- Examples given throughout to illustrate how the concepts apply.
- A concise summary is given at the conclusion of the tutorial.

## Key Concepts

- Zeroth Law
- Work
- Heat
- Energy
- First Law
- Internal Energy
- Expansion Work
- Enthalpy
- Adiabatic Processes
- Standard Enthalpy Changes
- Reaction Enthalpy and Temperature
- Exact and Inexact Differentials
- Joule-Thompson Effect

## Chapter Review

- The **Zeroth Law** of Thermodynamics states that if systems in a physical-chain of systems are in thermal equilibrium with their neighboring systems then they are in thermal equilibrium with all members of the chain of systems.
- **Heat** is energy flow from a hotter object to a cooler object when the two are in thermal contact.
- **Work**,  $w$ , is done on a system when a force is exerted on a system, as by steam on the piston of the steam engine below, causing a displacement.
- Work,  $w$ , and Heat Flow,  $q$ , are energy transfer processes.
- A system has an amount of energy, not an amount of work or heat.
- Heat flow for a system,  $q$ , is calculated by multiplying the heat capacity,  $C$ , for the system by its temperature change,  $\Delta T$ .
- Work is calculated by multiplying a driving force,  $F$ , by distance driven,  $d$ , Force x Distance,  $F \times d$ , or other equivalent products such as Pressure x Volume Change,  $P \times \Delta V$ .
- The Internal Energy of a system is stored in a number of forms: molecular electronic, vibrational, rotational and translational energy.
- **Internal Energy**,  $U$ , does not include energy of motion through space of a whole system.
- The **First Law** of Thermodynamics states that Internal Energy change for a system is the sum of work and heat flow for the system.
- A gas flowing into a vacuum such as gases leaking, expanding, into the vacuum of Space, a Free Expansion does not perform any work, because there is no resisting pressure.

- Work done by reversible expansion with higher, equilibrium, gas pressures leads to a larger amount of work.
- A very slow expansion/contraction process will be at equilibrium (reversible) at all times.
- The work done by reversible/equilibrium expansion of a system is the greatest amount of work possible for that expansion.
- The **Ice Calorimeter** is one of several types of Calorimeters used for measuring Heat Flow.
- An **Adiabatic Bomb Calorimeter** has a very strong container, Bomb, inside of which a heat-flow process, such as a chemical reaction, takes place at constant Volume.
- **Enthalpy** ( $H$ ) is the sum of Internal Energy  $U$  and Pressure times Volume:  $H=U +PV$ .
- Enthalpy, pressure, volume and Internal Energy are all State Functions.
- A **State Function** depends only on the State/Condition of a System and not on the processes which lead to the state.
- An Adiabatic process has no heat flow between system and surroundings.
- Enthalpies of Standard formation Reactions are available in reference sources.
- **Hess's Law** is applied to Standard Formation Reactions to obtain Standard Reaction Enthalpies.
- The Chemical Product in a Standard Formation Reaction is one mole of the chemical being formed.
- Reactants in Standard Formation Reactions are elements in their most stable form at the reference temperature.
- Variables that depend only on the condition/state of a system and not on the path/manner by which the state was created are State Functions and have exact differentials.
- **Exact differentials** may be integrated along any path between two states with the same result for each path.
- The **Joule-Thompson Effect** is the cooling of gases when they expanded at constant Enthalpy,  $H$ .



### Chapter Summary

The Second Law of Thermodynamics Introduces the State Function Entropy ( $S$ ). Entropy is a measure of the degree to which energy is dispersed. Entropy increases as energy is more widely distributed/dispersed. The Third Law of Thermodynamics describes what happens to Entropy when the Absolute Zero of Temperature is reached. In the case of a perfect crystalline material the entropy becomes zero.

### Tutorial Features

- Concept map showing inter-connections of concepts.
- Definition slides introduce terms as they are needed.
- Examples given throughout to illustrate how the concepts apply.
- A concise summary is given at the conclusion of the tutorial.

### Key Concepts

- Dispersal of Energy
- Entropy and Second Law
- Entropy Change
- Third Law
- Helmholtz and Gibbs Energies
- Standard Gibbs Energies
- Internal Energy
- Gibbs Energy

### Chapter Review:

- Analysis of spontaneous processes in Isolated Regions of the Universe yield a simple fact: all spontaneous processes lead to great dispersal of energy and/or matter within an Isolated Region.
- An **Isolated Region Isolated** (System + Surroundings) does not exchange energy or material with the remainder of the Universe.
- Processes, such as phase transitions or chemical reactions that lead to more even/random distribution of material and/or energy within an Isolated Region of Universe tend to be spontaneous.
- Mathematical analysis of Spontaneous Processes leads to a new Thermodynamic Function, Entropy, and the Second Law of Thermodynamics.
- Solid or liquid phases evaporating to gases or transfer of energy from high temperature regions to lower temperature regions are examples of spontaneous processes in isolated regions of the Universe.
- The **Second Law** of Thermodynamics formalizes the understanding of spontaneous processes with the definition of a thermodynamic quantity called Entropy,  $S$ .
- **Entropy** change is defined in terms of a differential, infinitesimal, change in Entropy.
- To determine an Entropy change it is necessary to find a reversible path between the initial and final states for the process and to integrate,  $dS$ , along that path.
- A Thermodynamic Temperature Scale, **Kelvin**, was defined by Lord Kelvin of Scotland in terms of the efficiency of an ideal reversible heat engine.
- The **Third Law** of Thermodynamics: The entropy of all perfect crystalline substances is zero at 0K.
- The Kelvin temperature scale defines a zero of temperature as the temperature at which the efficiency of an ideal heat engine is unity. Nernst Theorem: the entropy change



accompanying any physical or chemical process approaches zero as the temperature approaches 0K provided all the substances involved are perfectly crystalline.

- Entropy is shown to be a state function by demonstrating that it has zero change over any cyclic path, beginning and ending with the same arbitrary state.
- Helmholtz and Gibbs Energies are state functions defined for the purpose of determining process spontaneity solely on the states of a system, rather than on both system and surroundings.
- In words, the Gibbs Energy change for a process at constant temperature and pressure is negative for spontaneous processes.
- Gibbs Energy changes for combustion and formation reactions under standard conditions are available in text books and in the NIST Chemistry Web-book:  
<http://webbook.nist.gov/chemistry>.
- Standard Conditions, Standard State, for reactants and products is a pure chemical at 1 bar pressure and, most commonly, a temperature of 298 K.
- It is common to ignore the small effect of pressure on molar Gibbs energy for condensed phases unless pressure changes are large as in some Geological environments.
- $\Delta G$  values for solids and liquids caused by pressure changes are small due to the small molar volumes of these Condensed Phases.
- $\Delta G$  values for solids and liquids caused by pressure changes are small due to the small molar volumes of these Condensed Phases.

### Chapter Summary

The equilibrium position of a chemical reaction is located by determining the balance of reactant and product chemical composition that has the lowest/minimum value of Gibbs Energy. Gibbs Reaction Energy is the slope of a plot of Gibbs Energy of Reaction versus the Extent of Reaction,  $\xi$ , at constant pressure and Temperature. Gibbs Energy of Reaction is negative when reactants convert spontaneously to products. Gibbs Energy of Reaction is positive when products convert spontaneously to reactants. Gibbs Energy of Reaction is zero when a reaction is at equilibrium, which occurs when Gibbs energy is at a minimum.

### Tutorial Features

- Concept map showing inter-connections of concepts.
- Definition slides introduce terms as they are needed.
- Examples given throughout to illustrate how the concepts apply.
- A concise summary is given at the conclusion of the tutorial.

### Key Concepts

- Gibbs Energy Minimum
- Equilibrium and Gibbs Energy Minimum
- Equilibrium and Pressure Change
- Equilibrium and Temperature Change

### Chapter Review

- The equilibrium position of a chemical reaction is located by determining the balance of reactant and product chemical composition that has the lowest/minimum value of Gibbs Energy,  $G$ .
- Gibbs Reaction Energy is the slope of a plot of Gibbs Energy of Reaction,  $G$ , versus the Extent of Reaction,  $\xi$ , at constant pressure and Temperature.
- In words, **Chemical Potential** is the rate at which Gibbs Energy Changes in a mixture of chemicals as the moles of one chemical is changed by an infinitesimal amount at constant pressure, Temperature and moles of other components of the mixture.
- The Gibbs Energy of Reaction is not only the slope of a plot of  $G$  versus  $\xi$ , but is also the difference between the Chemical Potentials of the products and reactants. Gibbs Energy of Reaction is negative when reactants convert spontaneously to products.
- Gibbs Energy of Reaction is positive when products convert spontaneously to reactants. Gibbs Energy of Reaction is zero when a reaction is at equilibrium, which occurs when Gibbs energy is at a minimum.
- When Gibbs Energy of Reaction is negative, the reaction is Exergonic because it can drive another reaction or do non- $pV$  work.
- The **Equilibrium Constant** for a chemical reaction is independent of pressure, however pressure may affect equilibrium composition.
- If pressure is changed by adding or removing an inert gas equilibrium concentrations are not changed when gases are behaving ideally.
- If pressure is changed by adding or removing one of the reactant or product gases, the reaction equilibrium will shift in the direction that reduces the affect of that change.
- If pressure is changed by increasing or decreasing the volume of the reaction container, the reaction equilibrium will shift in the direction that reduces the affect of that change.

- If a reaction container is reduced in volume, increasing the total pressure, the reaction equilibrium will shift in a direction that reduces the total amount of gas, thus decreasing the total pressure.
- If temperature is increased a reaction will shift in the Endothermic Direction, energy absorbing direction, thus decreasing the temperature.
- If temperature is decreased a reaction will shift in the Exothermic Direction, energy-releasing direction, thus increasing the temperature.
- A **Hess's Law** sum of standard enthalpies is the standard reaction enthalpy of the overall reaction.

### Chapter Summary

A phase diagram displays the regions of stability of each phase available to the system under a particular set of conditions. Most pure substances have similar phase diagrams, but each with its own unique set of phase diagrams. Phase boundary lines that separate regions are points at which adjacent phases may be present together at equilibrium.

### Tutorial Features

- Concept map showing inter-connections of concepts.
- Definition slides introduce terms as they are needed.
- Examples given throughout to illustrate how the concepts apply.
- A concise summary is given at the conclusion of the tutorial.

### Key Concepts

- Stabilities of Phases
- Phase Boundaries
- Phase Diagrams
- Thermodynamic Equilibrium
- Gibbs Phase Rule
- Experimental Procedures
- Vapor Pressure Diagrams
- Temperature Composition Diagrams
- Liquid-Liquid Phase Diagrams
- Liquid-Solid Phase Diagrams

### Chapter Review:

- A **pressure versus Temperature phase diagram** displays the regions of stability of each phase available to the system at a particular temperature and pressure.
- Most pure substances have similar phase diagrams, but each with its own unique pressure-temperature ranges.
- **Phase boundary lines** that separate regions are points at which adjacent phases may be present together at equilibrium.
- **Phase diagrams** commonly have a unique solid-liquid-vapor triple point at which the three phases exist together.
- Phase diagrams commonly have a unique liquid-vapor critical point, the highest temperature at which a liquid phase exists.
- The vapor pressure at the critical temperature is the critical pressure.
- A single **Super-Critical Fluid phase** exists at or above the Critical Point.
- The Chemical Potential of a substance has the same value throughout a system at equilibrium.
- Along the Phase Boundary lines the chemical potential of the substance is the same in the two phases: solid and liquid, solid and vapor, and liquid and vapor.
- At the **Triple Point**, the Chemical Potential of a substance has the same value in the three phases: Solid, Liquid and Vapor.
- For a pure substance the chemical potential is the Molar Gibbs Energy.
- For a pure substance the Gibbs energy is not affected by the moles of substance, just more of the same.
- The negative of the entropy of a substance gives the temperature dependence of Gibbs Energy.
- The entropy of the phases increases from solid  $\rightarrow$  liquid  $\rightarrow$  vapor, and the negative slope of a plot of chemical potential versus temperature will increase in the same order.



- Increased pressure causes most substances to melt at higher temperatures and a few substances such as water to melt at lower temperatures.
- This is explained by considering the rate of change of chemical potential with respect to pressure at constant temperature.
- The chemical potential of a condensed phase increases with increased applied pressure. Increasing pressure on a solid or liquid phase, by adding an inert gas to the vapor, increases the vapor pressure since increased pressure for a vapor/gas corresponds to increased chemical potential.
- **Chemical potential** for a gas is proportional to pressure, so increased gas/vapor pressure corresponds to increased chemical potential.
- For two phases to be in equilibrium they must have the same chemical potential.
- As chemical potential for a condensed phase increases, due to an increase in applied pressure, its vapor pressure increases.
- **Gibbs' Phase Rule** is central to analyzing multi-component phase equilibria.
- In the Gibbs Phase Rule,  $F=C-P+2$ ,  $P$  is the number of phases present at equilibrium.  $C$  is the number of chemically independent constituents present at equilibrium.  $F$  is the number of independently variable intensive variables or Degrees of Freedom for the system. Experimental techniques such as Thermal Analysis and Differential Scanning Calorimetry have been developed to identify phase transitions and make it possible to obtain data for phase diagrams.
- Two liquid phases from the same two components may coexist at equilibrium.
- An upper critical solution temperature may exist, above which there is only one liquid phase. A Eutectic Point is the lowest temperature equilibrium liquid phase possible for a particular pair of solids.



### Chapter Summary

This tutorial reviews Thermodynamics and applies thermodynamics to Electrochemistry. Electrochemical cells may do electrical work, galvanic cells, or have electrical work done on them, electrolytic cells. Electrochemical Cells all have in common: (1) an anode where oxidation takes place, (2) a cathode where reduction takes place. Chemical process taking place at electrodes, anodes or cathodes, are only  $\frac{1}{2}$  of a chemical reaction and are called  $\frac{1}{2}$  reactions.

### Tutorial Features

- Concept map showing inter-connections of concepts.
- Definition slides introduce terms as they are needed.
- Examples given throughout to illustrate how the concepts apply.
- A concise summary is given at the conclusion of the tutorial.

### Key Concepts

- Zeroth Law: thermometers
- First Law: conservation of Energy
- Second Law: spontaneity and maximum disorder
- Gibbs Energy: spontaneity, chemical equilibrium and maximum non-pV work
- Ionic Activity
- Biological Standard State
- Electrochemical Cells
- Half-Reactions and Electrodes
- Electrochemical Cells
- Electromotive Force
- Applications of Standard Potentials

### Chapter Review

- The **Zeroth Law** allows for objects in thermal contact to be used as a thermometer.
- Work,  $w$ , and Heat Flow,  $q$ , are energy transfer processes.
- A system has an amount of energy, not an amount of work or heat.
- A system does not have heat or work; rather it has an amount of Energy that may be altered by these processes. Heat and work are not different forms of energy; they are different energy transfer processes.
- Work,  $w$ , and Heat,  $q$ , are not State Functions, and  $dw$  and  $dq$  are inexact differentials. Integrals of  $dw$  and  $dq$  are path dependent, therefore  $w$  and  $q$  are Path Functions.
- The **First Law of Thermodynamics** states that Internal Energy change for a system is the sum of work and heat flow for the system.
- Energy flow is positive for a portion of the Universe, system or surroundings, if energy is flowing to that portion, system or surroundings, and negative if energy is flowing away. Enthalpy is defined as  $H = U + PV$ . Temperature, Pressure, Volume, Internal Energy, and Enthalpy are all State Functions and have exact differentials:  $dT$ ,  $dP$ ,  $dV$ ,  $dU$ ,  $dH$ . Analyses of changes of state for systems, such as the expansion of gases, rely heavily on the properties of exact differentials.
- Processes, such as phase transitions or chemical reactions that lead to more even/random distribution of material and/or energy within an Isolated Region of Universe, tend to be spontaneous.
- Mathematical analysis of Spontaneous Processes leads to a new Thermodynamic Function, Entropy, and the Second Law of Thermodynamics.

- The **Second Law of Thermodynamics** formalizes the understanding of spontaneous processes with the definition of a thermodynamic quantity called Entropy,  $S$ .
- To determine an Entropy change it is necessary to find a reversible path between the initial and final states for the process and to integrate,  $dS$ , along that path.
- **Entropy** is shown to be a state function by demonstrating that it has zero change over any cyclic path, beginning and ending with the same arbitrary state.
- The Entropy for a system in a particular state is given relative to its entropy as pure-perfect-crystalline materials at 0K.
- All elements and compounds are solid at 0K. Standard Reaction Entropy Changes are calculated from Standard molar entropies.
- The Gibbs Energy change for a process at constant temperature and pressure is the negative of the maximum non-pV work the process can perform. Gibbs Energy changes for combustion and formation reactions under standard conditions are available in the NIST Chemistry Web-book: <http://webbook.nist.gov/chemistry>.
- Standard Conditions, Standard State, for reactants and products is a pure chemical at 1 bar pressure and, most commonly, a temperature of 298 K.
- The equilibrium position of a chemical reaction is located by determining the balance of reactant and product chemical composition that has the lowest/minimum value of Gibbs Energy,  $G$ .
- **Gibbs Energy of Reaction** is negative when reactants convert spontaneously to products. Gibbs Energy of Reaction is zero when a reaction is at equilibrium, which occurs when Gibbs energy is at a minimum.
- Solids in a reaction environment are often pure and are assigned an activity of 1, meaning that the pure solid is the standard state.
- Activities of ionic solutes are expressed in term of dimensionless mean-ionic activity coefficients and dimensionless concentration ratios in order to retain the relationship between activity and chemical potential.
- The mean ionic activity coefficient expresses all deviations from ideal behavior of ions and distributes that deviation between cations and the anions.
- Protons are involved in many biochemical reactions and in vivo biological conditions most commonly have pH's close to neutral,  $\text{pH} = 7.0$ .
- **Electrochemical cells** may do electrical work, galvanic cells, or have electrical work done on them, electrolytic cells.
- Electrochemical Cells all have in common: (1) an anode where oxidation takes place, (2) a cathode where reduction takes place.
- Chemical process taking place at electrodes, anodes or cathodes, are only  $\frac{1}{2}$  of a chemical reaction and are called  $\frac{1}{2}$  reactions.
- **Electrode Half-Reactions** are of several types: Metal/metal ion, Gas at Inert Electrode, Metal/Insoluble salt, Redox at Inert Electrode.
- Metals involved in electrode  $\frac{1}{2}$  reactions usually are the electrode material. Platinum, Pt, is the usual inert electrode material.
- Most cells require separate anode and cathode electrolyte solutions.
- Commonly this is accomplished by connecting the two solutions by a salt bridge, permitting anions to flow to the anode and cations to flow to the cathode without allowing the anode and cathode solutions to mix.
- A **cell** has an electromotive force, Voltage, produced by combination of the anode half-reaction's tendency to undergo oxidation and the cathode half-reaction's tendency to undergo reduction.
- **Voltage** is a measure of joules of energy available per coulomb of electron flow.
- The chemical reaction for a cell is obtained by adding the anode  $\frac{1}{2}$  reaction to the cathode  $\frac{1}{2}$  reaction and the standard emf of the cell may be determined using Standard Reduction Potentials for the electrodes.
- The **Nernst Equation** relates Standard Cell Potential to equilibrium and equilibrium constants. Standard Electrode Reduction Potentials in aqueous solution, when placed in order of decreasing voltage, form an electrochemical series.

- In this series the standard hydrogen electrode is assigned a voltage of zero.
- In theory and often in practice, any two electrodes may be used to form an electrochemical cell.
- A Standard Cell emf, voltage, is obtained by adding the more positive standard electrode reduction potential, the cathode, to the negative of the less positive standard electrode reduction potential, the anode.



## Chapter Summary

This tutorial reviews Thermodynamics and applies thermodynamics to life processes.

## Tutorial Features

- Concept map showing inter-connections of concepts.
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## Key Concepts

- Zeroth Law: thermometers
- First Law: conservation of Energy
- Second Law: spontaneity and maximum disorder
- Gibbs Energy: spontaneity, chemical equilibrium and maximum non-pV work
- Ionic Activity
- Biological Standard State
- Life Transport
- Energy Conversion

## Chapter Review

- The **Zeroth Law** allows for objects in thermal contact to be used as a thermometer.
- Work,  $w$ , and Heat Flow,  $q$ , are energy transfer processes.
- A system has an amount of energy, not an amount of work or heat.
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- Work,  $w$ , and Heat,  $q$ , are not State Functions, and  $dw$  and  $dq$  are inexact differentials. Integrals of  $dw$  and  $dq$  are path dependent, therefore  $w$  and  $q$  are Path Functions.
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- Processes, such as phase transitions or chemical reactions that lead to more even/random distribution of material and/or energy within an Isolated Region of Universe, tend to be spontaneous.
- Mathematical analysis of Spontaneous Processes leads to a new Thermodynamic Function, Entropy, and the Second Law of Thermodynamics.
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- To determine an Entropy change it is necessary to find a reversible path between the initial and final states for the process and to integrate,  $dS$ , along that path.
- **Entropy** is shown to be a state function by demonstrating that it has zero change over any cyclic path, beginning and ending with the same arbitrary state.
- The Entropy for a system in a particular state is given relative to its entropy as pure-perfect-crystalline materials at 0K.
- All elements and compounds are solid at 0K. Standard Reaction Entropy Changes are calculated from Standard molar entropies.

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- Standard Conditions, Standard State, for reactants and products is a pure chemical at 1 bar pressure and, most commonly, a temperature of 298 K.
- The equilibrium position of a chemical reaction is located by determining the balance of reactant and product chemical composition that has the lowest/minimum value of Gibbs Energy, G.
- Solids in a reaction environment are often pure and are assigned an activity of 1, meaning that the pure solid is the standard state.
- Activities of ionic solutes are expressed in term of dimensionless mean-ionic activity coefficients and dimensionless concentration ratios in order to retain the relationship between activity and chemical potential.
- The **mean ionic activity coefficient** expresses all deviations from ideal behavior of ions and distributes that deviation between cations and the anions.
- Protons are involved in many biochemical reactions and in vivo biological conditions most commonly have pH's close to neutral,  $\text{pH} = 7.0$ .
- **Chemical Standard State** thermodynamic quantities have a right-hand superscript indicating the standard state.
- **Biological Standard State** thermodynamic quantities are distinguished by adding a feature to the superscript.
- The energy and material difference between Nutrient molecules and Waste molecules provides the energy and substance for building, maintaining and running the biochemistry of life forms.
- **Plasma**, lipid-bilayer, membranes surrounding cells have the ability to maintain different concentrations of ions on the two sides of these membranes, inside versus outside. Ion channels, ion pumps and ion transporters embedded in the lipid bilayer membranes produce concentration differences in  $\text{H}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$  and  $\text{Ca}^{2+}$  ions.
- Concentration differences in  $\text{H}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$  and  $\text{Ca}^{2+}$  ions between the two sides of membranes generate electrochemical potentials, Trans-Membrane Potentials.
- **Glycolysis** takes a mole of glucose, 2 moles of  $\text{NAD}^+$ , 2 moles of ADP and in 11 steps converts them to two moles of pyruvate, 2 moles of NADH and 2 moles of ATP with a Standard Gibbs Energy of reaction of  $-85 \text{ kJ/mol}$ .
- Each step in Glycolysis is enzyme catalyzed. Cell fluid, cytosol, conditions are not standard conditions. Standard conditions are  $\text{pH} = 7$ , and every other reactant and product at unit activity.
- The **Citric Acid Cycle** takes 2 moles of pyruvate, 8 moles of  $\text{NAD}^+$ , 2 moles of FAD, 2 moles of ADP and converts them to 6 moles of  $\text{CO}_2$ , 8 moles of NADH and 2 moles of ATP, 2 moles of  $\text{FADH}_2$ .
- If temperature is decreased a reaction will shift in the Exothermic Direction, energy releasing direction, thus increasing the temperature.
- The Respiratory Chain involves reactions at four membrane protein-bound protein complexes: Complexes I, II, III, and IV.
- **Oxidative Phosphorylation** receives energy from the respiratory chain and uses it to convert ADP into ATP. Oxidative Phosphorylation and the chemistry of the Respiratory chain take place inside of Mitochondria in association with mitochondrial membranes.
- Energy from the Respiratory Chain is stored in a Transmembrane Proton Gradient and a Membrane Potential.



### Chapter Summary

Classical mechanics is unable to explain blackbody radiation or the photoelectric effect. Quantum Mechanics is able to explain these and other important concerns such as the structures of atoms and molecules. Classical mechanics is unable to explain the photoelectric effect. Quantum Mechanics is able to explain the photoelectric effect. The methods and results of quantum mechanics are introduced in this chapter.

### Tutorial Features

- Concept map showing inter-connections of concepts.
- Definition slides introduce terms as they are needed.
- Examples given throughout to illustrate how the concepts apply.
- A concise summary is given at the conclusion of the tutorial.

### Key Concepts

- Need for Quantum Mechanics
- Wave-Particle Duality
- Schrodinger Equation
- Operators
- Eigenfunctions
- Eigenvalues
- Hermitian Operators
- Uncertainty Principle

### Chapter Review

- **Classical mechanics** is unable to explain blackbody radiation or the photoelectric effect.
- **Quantum Mechanics** is able to explain these and other important concerns such as the structures of atoms and molecules.
- Classical mechanics is unable to explain the photoelectric effect.
- Quantum Mechanics is able to explain the photoelectric effect.
- Light has properties of waves, electric and magnetic waves, and particles of energy, photons.
- **Light** is the first example of what is call the Wave-Particle Duality of Matter.
- Particles of light, quanta of light energy are photons which travel at the speed of light.
- The photoelectric effect is that when light shines on a metal surface, such as tin, electrons may be emitted.
- **Photoelectrons** are not ejected unless the energy of a photon exceeds the work function of the metal.
- Photoelectrons are not ejected unless the energy of the photons exceeds the work function of the metal.
- The kinetic energy of ejected electrons depends only on the photon energy, not photon intensity.
- The **photoelectric effect** strongly suggests that light is composed of particles of energy, contrary to Classical Physics and consistent with Quantum Mechanics.
- The **Bohr hydrogen atom** is a major improvement on Classical Physics since it correctly identifies quantized energy states for hydrogen, but fails by placing electrons in well defined orbits around a nucleus.
- **De Broglie** said that all matter has both wave and particle behavior.
- When the **wave-particle duality** was applied to electrons it was found to be true, and this is the basis for the electron microscope.

- Classical Physics describes the dynamical behavior of a particle in terms of its location and momentum.
- Quantum Mechanics uses a wavefunction to describe the dynamical behavior of a particle.
- A wavefunction is the solution to a Schrodinger Equation.
- The **Schrodinger equation** describes the wave nature of a particle.
- The Schrodinger Equation is an Eigenvalue equation containing the Hamiltonian operator and the Energy Eigenvalue.
- Time-Independent Wavefunctions,  $\psi(x,y,z)$ , are obtained by solving a time-independent Schrodinger equation.
- Time-Dependent Wavefunctions,  $\psi(x,y,z,t)$ , are obtained by solving a time-dependent Schrodinger equation.
- Quantum mechanics limits our knowledge of Position and Momentum of a particle at a point in time, as is quantified in the Uncertainty Principle.

### Chapter Summary

Application of Quantum Mechanics to atoms and molecules requires approximations. Those techniques are discussed and applied in this chapter.

### Tutorial Features

- Concept map showing inter-connections of concepts.
- Definition slides introduce terms as they are needed.
- Examples given throughout to illustrate how the concepts apply.
- A concise summary is given at the conclusion of the tutorial.

### Key Concepts

- Acceptable Solutions to a Wave Equation
- Quantization of Translational Motion
- Quantum-Mechanical Tunnelling
- Quantization of Vibrational Motion
- Quantization of Rotational Motion
- Time-Independent Perturbation Theory
- Time-Dependent Perturbation Theory

### Chapter Review

- A particle confined between two infinitely high barriers and constrained to move in only the  $x$  direction it is called a Particle in a One-Dimensional Box.
- A particle moving in a one-dimensional box has Quantized Translational Motion.
- Quantum Mechanics allows a particle in a box to have only certain amounts of energy, its Energy is Quantized.
- **Tunnelling** describes the entry of a particle into a region of space in which the potential energy is greater than the total energy of the particle.
- Using appropriate boundary conditions, solving the Schrodinger equation gives Normalized Wave Functions and associated Eigenvalues.
- **Particle in a box** wavefunctions and hydrogen atomic orbital wavefunctions are Orthonormal sets of wavefunctions.
- Separation of Variables is a technique used to solve for multidimensional Wavefunctions and is used to obtain Wavefunctions and Eigenvalues for the three-dimensional Atomic Orbitals and for a particle in a multi-dimensional box.
- An object that experiences a restoring force  $F$  that is proportion to displacement  $x$  has Harmonic Motion, and is a Harmonic Oscillator.
- A **chemical bond** is approximated as a Quantum Harmonic Oscillator.
- Rotational motion is quantized due to the wave nature of matter.
- A rotating particle's wave must fit evenly on the path of a rotational state in order to not have wave interference and to be single valued.
- **Time-Independent Perturbation theory** represents a real Hamiltonian Operator by a sum of a Model System Hamiltonian Operator and a Perturbation Operator.
- In **Time-Independent Perturbation Theory**, the perturbation is constant and does not change with time.
- In Time-Dependent Perturbation Theory, the perturbation is not constant and does change with time.
- **Wavefunctions** for a model system are use to obtain approximate Wavefunctions for a real system.

- First-order-corrections to model wavefunctions are linear combinations of model system wavefunctions with coefficients calculated using a first-order-Perturbation Hamiltonian term and model wavefunctions and Eigenvalues.
- **Coefficients** in the linear combination of model wavefunctions are calculated using a first-order-Perturbation Hamiltonian term and model wavefunctions and Eigenvalues.
- A first-order correction to the ground state energy level is calculated using a zero-order model ground state wavefunction and the first-order-Perturbation Hamiltonian Operator.
- The second-order correction to the ground state energy level is calculated using a complete set of Model wavefunctions and the first-order-Perturbation Hamiltonian Operator.
- An important example of a Time-Dependent Perturbation is encountered when electromagnetic radiation interacts with atoms and molecules.



### Chapter Summary

This chapter is an introduction to the application of Quantum Mechanics to atomic structure and atomic spectra.

### Tutorial Features

- Concept map showing inter-connections of concepts.
- Definition slides introduce terms as they are needed.
- Examples given throughout to illustrate how the concepts apply.
- A concise summary is given at the conclusion of the tutorial.

### Key Concepts

- Structure of Hydrogenic Atoms
- Atomic Orbitals and Energies
- Spectroscopic Transitions
- Selection Rules
- The Orbital Approximation
- Self-Consistent Field Orbitals
- Quantum Defects and Ionization Limits
- Singlet States and Triplet States
- Spin-Orbit Coupling
- Term Symbols and Selection Rules

### Chapter Review

- The fact that only certain frequencies of light are absorbed or emitted by atoms strongly suggests that energy states of atoms are quantized.
- **Separation of variables** factors a wavefunction into terms, each dependent on only a portion of the systems variables.
- **Atomic symmetry** suggests separating atomic wavefunctions into a radial function and an angular function.
- One-electron atom wavefunctions are factored into radial wavefunctions of the form and a set of Spherical Harmonic wavefunctions.
- **One-Electron Atomic Orbitals** are One-Electron Wavefunctions.
- One-Electron Atomic-Orbital Wavefunctions are identified by three Quantum Numbers.
- One-Electron One-Electron-Orbital Energies depend only on the principle quantum number.
- Spectroscopic transitions may only occur between certain Quantum States.
- **Angular Momentum** must be conserved in a Spectroscopic Transition.
- A Spectroscopic Transition must compensate for the gain or loss of a photon and its intrinsic 1 unit of angular momentum.
- An approximation of some sort is required because a direct analytic solution for a Many-Electron atom is not possible due to electron-electron interactions.
- The **Pauli-Exclusion Principle** requires that these two electrons must have opposite spin quantum numbers in order to be in the same orbital.
- A general statement of the Pauli-Exclusion Principle requires that when the labels of two electrons are exchanged the sign of the Total Wavefunction must change.
- **Nuclear Charge** experienced by an electron is reduced by the presence of other electrons between it and the nucleus.
- Electrons that are on average closer to the nucleus have greater Penetration and are less Shielded from the nuclear charge.
- Electrons in orbitals with lower shell numbers are on average closer to the nucleus and thus lower in energy.

- The **Aufbau or Building-Up Principle** combines the various energy lowering factors to give rules for predicting ground-state electron configurations.
- The amount of energy required to remove one electron from a neutral gaseous atom is the first ionization energy for that element.
- The amount of energy released when an electron adds to a neutral gaseous atom is the electron affinity for that element.
- The **Hartree-Fock Self-Consistent Field procedure**, HF-SCF, for calculating wavefunctions and energies for many-electron atoms is one of several numerical procedures available.
- Guessed approximate wavefunctions provide an approximate electronic environment for the one orbital being determined by computerized numerical analysis.
- Wavefunctions and energy values obtained by HF-SCF calculations correlate well with experimental observations.
- An electron's spin angular momentum and orbital angular momentum interact in Spin-Orbit Coupling giving a total angular momentum quantum number  $J$ .
- **Term Symbols** summarize the important quantum parameters of a spectroscopic state.
- **Selection Rules** identify Allowed Transitions.

### Chapter Summary

This chapter is an introduction to the application of Quantum Mechanics to molecular structure and bonding.

### Tutorial Features

- Concept map showing inter-connections of concepts.
- Definition slides introduce terms as they are needed.
- Examples given throughout to illustrate how the concepts apply.
- A concise summary is given at the conclusion of the tutorial.

### Key Concepts

- Born-Oppenheimer Approximation
- Homonuclear Diatomic Molecules
- Polyatomic Molecules
- Hydrogen Molecule-ion
- Homonuclear Diatomic Molecules
- Heteronuclear Diatomic Molecules
- Huckel Approximation
- Computational Chemistry
- Prediction of Molecular Properties

### Chapter Review:

- The **Born-Oppenheimer Approximation** states that bonding forces adjust so rapidly that bonded atoms may be treated as being stationary in some calculations.
- **Valence-Bond Theory**, VB Theory, describes a bond between two atoms in terms of two atoms coming together, each with one electron in an atomic orbital.
- A Valence Bond, VB, is formed when atomic orbitals overlap and spins of the two electrons interact by pairing.
- **Molecular Orbitals** are written as Linear Combinations of Atomic Orbitals, a technique with the acronym, LCAO-MO.
- Solutions to the Schrodinger equation for multi-electron molecular orbitals cannot be obtained by analytical solutions.
- Approximate methods such as LCAO-MO must be used to obtain wavefunctions for multi-electron molecules.
- Molecular Orbitals are written as Linear Combinations of Atomic Orbitals, with the acronym, LCAO-MO.
- Theory predicts that a LCAO-MO has linear contributions from all atomic orbitals with proper symmetry.
- A common simplification is to limit LCAO-MO's to valence atomic orbitals with appropriate symmetries.
- A **pi bond**  $\pi$  bond is formed from atomic orbitals having axes perpendicular to the axis of the bond they form.
- **Trial LCAO-MO wavefunctions** are modified by adjusting the basis set and coefficients until the energy expectation value is minimized.
- Coefficients in the simple LCAO-MO trial wavefunction are optimized by minimizing the expectation value for the Energy.
- **Huckel approximations** are used to obtain approximate energy level diagrams for pi molecular-orbitals.
- The Highest-energy Occupied Molecular Orbital, HOMO, and the Lowest -energy Unoccupied Molecular Orbital, LUMO, are Frontier Orbitals.

- Frontier Orbitals are responsible for many of the chemical and spectroscopic properties of molecules.
- The **Hartree-Fock Self-Consistent Field procedure**, HF-SCF, for calculating wavefunctions and energies for Polyatomic Molecules is one of several computational procedures available.
- The Hartree-Fock Self-Consistent Field procedure begins with guessed one-electron LCAO-MO wavefunctions.
- **Ab Initio Methods** attempt to calculate all of the integrals in the Hartree-Fock Equations and require tremendous amounts of computation.
- Semi-Empirical Methods estimate many of the Hartree-Fock integrals using experimental data and setting some integrals to zero.
- **Density Functional Theory** based calculations require less computation than Hartree-Fock calculations.
- DFT is widely used to calculate molecular structure and in some cases is in better agreement with experiment than Hartree-Fock .
- **Optimized LCAO-MO wavefunctions** and eigenvalues are particularly useful for suggesting trends in molecular properties.



### Chapter Summary

Orbital overlap is required for bond formation and is determined using Group Theory. Orbitals must have the same symmetry species in order to have a nonzero overlap integral. The best Basis atomic orbitals for a LCAO-MO may be determined in part by evaluating the symmetry species of candidate orbitals. Symmetry-adapted Linear Combinations (SALC) Basis Atomic Orbitals are symmetry-selected linear combinations of atomic orbitals. Selection Rules for spectroscopic transitions are determined by the Transition Dipole Moment. The criterion for an allowed transition is that the integrand in the Transition-Dipole-Moment Integral must have symmetry species  $A_1$  and thus be nonzero.

### Tutorial Features

- Concept map showing inter-connections of concepts.
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### Key Concepts

- Symmetry Operations and Elements
- Symmetry Classification of Molecules
- Character Tables and Symmetry Labels
- Vanishing Integrals and Orbital Overlap
- Vanishing Integrals and Selection Rules

### Chapter Review

- **Molecular shapes** are classified by Symmetry Operations and associated Symmetry Elements.
- A benzene molecule may be rotated in steps of  $60^\circ$  around the center of the molecule and look the same after each step.
- The shapes of molecules are described in terms of the set of corresponding symmetry elements.
- **Unique sets of symmetry elements** are called Point Groups.
- A Character Table relates the symmetry operations associated with a symmetry group to the symmetry species for the group.
- **Optimum LCAO-MO Bases** are composed of atomic orbitals having appropriate symmetry, which may be determined using Character Table data and Group Theory.
- **Orbital overlap** is required for bond formation and may be determined using Group Theory.
- Orbital overlap is determined in LCAO-MO calculations by evaluating overlap integrals.
- **Orbitals Symmetry-adapted Linear Combinations (SALC) Bases** are symmetry-selected linear combinations of atomic orbitals tailored to specific molecules.
- **Selection Rules** for spectroscopic transitions are determined by the Transition Dipole Moment.

## Chapter Summary

Thermodynamic functions are represented in Statistical Thermodynamics in terms of a Canonical Ensemble Partition Function. A Canonical Ensemble is a large number of closed Systems in thermal contact all having the same values of the three macroscopic variables:  $N$ ,  $V$  and  $T$ .

## Tutorial Features

- Concept map showing inter-connections of concepts.
- Definition slides introduce terms as they are needed.
- Examples given throughout to illustrate how the concepts apply.
- A concise summary is given at the conclusion of the tutorial.

## Key Concepts

- Configurations and Configuration Weights
- Molecular Partition Function
- Internal Energy
- Statistical Entropy
- Canonical Ensemble
- Thermodynamic Information in Partition Function

## Chapter Review

- **Statistical Thermodynamics** calculates macroscopic thermodynamic variables such as  $T$ ,  $P$  and  $E$  from molecular properties.
- Statistical Thermodynamics assumes that each molecular energy state has equal probability of having a portion of that system's total energy based on energy level and temperature.
- Statistical Thermodynamics assumes that molecules are constantly transferring energy between themselves due to molecular collisions.
- An **instantaneous distribution** of total energy  $E$  among the  $N$  molecules in the molecular energy states,  $e_0, e_1, \dots$ , has  $n_0, n_1, \dots$ , of the  $N$  molecules in the energy states, and is a configuration of the system.
- $W$  is the configuration weight or likelihood of a distribution occurring. 
$$W = \frac{N!}{n_0!n_1!\dots}$$
- When **configuration weight**  $W$  is determined for the most probable configuration in a macroscopic system, it is found to have a much, much greater probability than the next most probable distribution.
- $W$  for the most probable configuration is so much greater than  $W$  for the next most probable configuration, that thermodynamic calculations are based on the most-probable distribution.
- Focusing all attention on the most probable configuration, yields the Boltzmann Distribution which is a function of temperature  $T$  and energy level.
- The **Boltzmann Distribution** gives the fraction of molecules that are in energy state  $e_i$  at temperature  $T$ .
- The denominator in the Boltzmann Distribution equation is the molecular partition function  $q$ .
- At  $0K$  only the ground state is accessible and the value of  $q$  is the degeneracy of the ground state.
- As  $T$  gets large  $q$  gets large and many states are accessible. As  $T$  gets very large, as on the Sun,  $q$  gets very large and all states are equally accessible.
- In most cases exact analytical expressions for partition functions are not obtainable.

- Exact analytical expressions are available in some cases, for example for a particle of mass  $m$  free to move in one-dimensional container of length  $X$ .
- The lowest available energy state is arbitrarily giving zero energy in statistical calculations.
- To obtain the **Internal Energy**  $U$ , the energy of the lowest available state at  $T=0$ ,  $U(0)$ , must be added to the energy from statistical calculations.
- The Boltzmann Distribution is used to calculate populations of the energy states.
- **Internal Energy** is expressed in terms of partial derivatives of the partition function  $q$ .

$$U = U(0) + E = U(0) - \frac{N}{q} \left( \frac{\partial q}{\partial \beta} \right)_V = U(0) - N \left( \frac{\partial \ln q}{\partial \beta} \right)_V.$$

- **A Canonical Ensemble** is a large number of closed Systems in thermal contact having the same values of the three macroscopic variables:  $N$ ,  $V$  and  $T$ .
- Fluctuations around the configuration of Greatest Weight are very small.
- The configuration of Greatest Statistical Weight has the average energy of the members of the ensemble.

- **The configuration of Greatest Weight** of a member of an ensemble of systems  $\bar{n}_i = \frac{e^{-\beta E_i}}{Q}$

$$Q = \sum_i e^{-\beta E_i}$$

is the Canonical Partition Function.

- **Entropy** in terms of the Canonical Partition Function is:  $S = \frac{U - U(0)}{T} + k \ln Q$ .

- **Internal Energy** in terms of the Canonical Partition Function is:

$$U = U(0) - \frac{1}{Q} \left( \frac{\partial Q}{\partial \beta} \right)_V = U(0) - \left( \frac{\partial \ln Q}{\partial \beta} \right)_V.$$

- **Helmholtz Energy** in terms of the Canonical Ensemble Partition Function is:

$$A - A(0) = -kT \ln Q.$$

- **Pressure** in terms of the Canonical Ensemble Partition Function is:  $p = kT \left( \frac{\partial \ln Q}{\partial V} \right)_T$ .

- **Enthalpy** in terms of the Canonical Ensemble Partition Function is:

$$H - H(0) = - \left( \frac{\partial \ln Q}{\partial \beta} \right)_V + kTV \left( \frac{\partial \ln Q}{\partial V} \right)_T.$$

- **Gibbs energy** in terms of the Canonical Ensemble Partition Function is:

$$G - G(0) = -kT \ln Q + kTV \left( \frac{\partial \ln Q}{\partial V} \right)_T.$$

### Chapter Summary

This chapter introduces the fundamentals of Molecular Spectroscopy with a focus on Vibrational and Rotational Spectroscopy. Molecular spectroscopy is a primary source of information regarding the structures of molecules.

### Tutorial Features

- Concept map showing inter-connections of concepts.
- Definition slides introduce terms as they are needed.
- Examples given throughout to illustrate how the concepts apply.
- A concise summary is given at the conclusion of the tutorial.

### Key Concepts

- What is the electromagnetic spectrum?
  - Classical view
  - Quantum mechanical view
- Factors affecting spectral-line intensities
- Factors affecting spectral-line widths

### Chapter Review

- **Molecular spectroscopy** is a primary source of information regarding the structures of molecules.
- Molecular spectroscopy is the study of absorption or emission of light by molecules.
- A **spectrophotometer** measures and records light intensity over a range of colors.
- **Light** is a form of energy called electromagnetic radiation.
- The modern, quantum mechanical, view of light is as rapidly moving particles of energy called photons with associated oscillating electric and magnetic fields.
- The transition dipole moment is the primary source of information regarding spectral intensities.
- **Spectral line widths** are increased by factors which cause the energies/frequencies of photons emitted or absorbed to vary.
- If an atom or molecule is moving as it emits or absorbs a photon, the photon's energy is altered due to the Doppler Effect, leading to wider spectral lines.
- When atoms or molecules are excited by an energy source they may emit light in order to release that energy.
- **Raman spectra** involve the measurement and analysis of scattered light which has first interacted with a sample and gained or lost energy.
- **Moments of inertia** are key to the analysis of rotational energy states.
- The rigid rotor approximation assumes that molecules are rigid and do not stretch as they rotate.
- **Degeneracy** is the number of states having the same energy level.
- The degeneracy of an energy level is an important piece of information.
- Molecules which have anisotropic polarizabilities are rotationally Raman active.
- Simple models such as the harmonic oscillator and the Morse potential help us to understand complex processes such as molecular vibration.
- Heteronuclear and homonuclear diatomic molecules are Raman active.
- Normal modes of vibration are selected to be independent of one another.



### Chapter Summary:

This chapter expands on the fundamentals of Molecular Spectroscopy with a focus on Electronic Spectroscopy. Molecular spectroscopy is a primary source of information regarding the structures of molecules.

### Tutorial Features

- Concept map showing inter-connections of concepts.
- Definition slides introduce terms as they are needed.
- Examples given throughout to illustrate how the concepts apply.
- A concise summary is given at the conclusion of the tutorial.

### Key Concepts

- Spectral-line intensity
- Spectra of Diatomic Molecules
- Spectra of Polyatomic Molecules
- Energy Loss by Electronic Excited States
- Fluorescence
- Phosphorescence
- Dissociation and Predissociation

### Chapter Review

- The **Beer-Lambert Law** relates Absorbance to the concentration of a light-absorbing chemical, the light path length through the chemical and the nature of the chemical.
- Absorbance is proportional to Molar Concentration.
- Molecules absorb light at wavelengths and with intensities which are unique to their structures.
- The **Vibrational and Rotational Structures** of molecular electronic absorption bands in liquids and solids usually are not resolved and lead to wide bands.
- A **molecular electronic transition** typically includes a vibrational transition.
- The most likely transition will be to the vibrational state with its turning point vertically above the center of the ground vibrational state.
- **Selection Rules** for electronic transitions are based on angular momentum change and molecular symmetry change.
- Transition dipole moments are enhanced by distance of electron travel, long in this case, and diminished by the weak orbital overlap.
- **Electronic excited states** may lose energy by emitting photons of light or by transferring energy to neighboring molecules by collision.
- Energy transferred by collision is stored in the vibrations, rotations and motions through space (translations) of the molecule to which it is transferred.
- **Fluorescence** occurs very soon after an excited electronic and vibrational state is created by the absorption of a photon.
- An excited molecule may lose vibrational energy through collisions with neighboring molecules. This is Radiationless Decay prior to fluorescence.
- Fluorescent transitions are very rapid allowed transitions.
- Fluorescent transitions do not have a change in multiplicity.
- **Phosphorescence** occurs, after an excited Electronic singlet state is created by the absorption of a photon.

## Chapter Summary

This chapter further expands on the fundamentals of Molecular Spectroscopy with a focus on Lasers, Laser Spectroscopy and Photochemistry. Molecular spectroscopy is a primary source of information regarding the structures of molecules.

## Tutorial Features

- Concept map showing inter-connections of concepts.
- Definition slides introduce terms as they are needed.
- Examples given throughout to illustrate how the concepts apply.
- A concise summary is given at the conclusion of the tutorial.

## Key Concepts

- Stimulated Emission
- Solid, Liquid and Gas Lasers
- Exciplex/Eximer Lasers
- Chemical Lasers
- Dye Lasers
- Applications of Lasers in Chemistry
- UV Photoelectron Spectroscopy
- X-Ray Photoelectron Spectroscopy

## Chapter Review

- **LASER** is an acronym for Light Amplification by Stimulated Emission of Radiation.
- **Stimulated Emission** occurs when photons of light interact with a medium having transitions with matching energy.
- Lasers are designed such that photons produced by a transition in the Laser Medium pass through multiple times by reflection between opposing mirrors.
- A **population inversion** exists when a higher energy state has a larger population than a lower energy state.
- Population Inversion is created and maintained by a process called Pumping.
- When a population inversion exists a single spontaneous photon can stimulate a cascade of resonant photons.
- Laser beams are usually highly collimated and have well defined regions of interaction.
- Wavelengths of light which both fit the cavity and are amplified by the laser medium are Resonant Modes.
- Laser pulses of nanosecond duration may be obtained by modulating the resonance characteristics  $Q$  of the cavity.
- Laser pulses of picosecond to femtosecond duration may be obtained by mode locking.
- **Mode Locking** gives a set of picosecond to femtosecond duration laser pulses separated by a round-trip-time for light in the Laser Cavity, of about one nanosecond.
- A combination of atoms which exists only in an excited state, an Exciplex/Eximer, can provide the radiation for Laser Action.
- **Chemical Lasers** are based on chemical reactions which produce products in excited states. A Dye Laser is able to be tuned continuously over a range of wavelengths.
- **In High-Photon-Flux Spectroscopy**, the high concentration of photons from a Laser source makes multi-photon process possible.

- The overall result of a multi-photon process may be a result that is forbidden in single-photon process.
- **Raman Spectroscopy** benefits from using high intensity, monochromatic Lasers as excitation beams.
- High Intensity Laser excitation beams increase the intensity of the scattered Raman Radiation, increasing the sensitivity of measurement.

## Chapter Summary

This chapter is an introduction to Magnetic Resonance Spectroscopy that includes both NMR and EPR. NMR is the acronym for Nuclear Magnetic Resonance. EPR is the acronym for Electron Paramagnetic Resonance.

## Tutorial Features

- Concept map showing inter-connections of concepts.
- Definition slides introduce terms as they are needed.
- Examples given throughout to illustrate how the concepts apply.
- A concise summary is given at the conclusion of the tutorial.

## Key Concepts

- Electron Paramagnetic Resonance, EPR
- Nuclear Magnetic Resonance, NMR
- NMR and EPR Spectrometers
- Chemical Shift in NMR Spectra
- Pulse Techniques in NMR Spectroscopy
- Solid-State NMR
- EPR Hyperfine Structure

## Chapter Review

- Electrons and many Atomic Nuclei have magnetic moments related to Angular Momentum.
- Electrons have Spin Angular Momentum and may have nonzero Orbital Angular Momentum.
- **Many Atomic Nuclei** have nonzero Spin Angular Momentum which is a property of the nucleus.
- **Magnetic resonance** is possible when atoms with unpaired Electrons or Nuclei with Angular Momentum are placed in a magnetic field.
- Different values of the component of angular momentum,  $\mu_z$ , along the z axis lead to different energies.
- Magnetic Resonance is associated with transitions between the different energy states.
- NMR is the acronym for **Nuclear Magnetic Resonance**.
- EPR is the acronym for **Electron Paramagnetic Resonance**.
- A typical NMR Spectrometer has a Superconducting Magnet that produces a powerful, 4 Tesla or greater, uniform magnetic field.
- A typical NMR Spectrometer has a Radio Frequency Transmitter that provides photons to the NMR Probe to stimulate transitions between the Nuclear Magnetic Energy states in Sample Atomic Nuclei.
- The **Radio Frequency Transmitter** also provides photons to a detector as a reference signal.
- A Computer records the absorption of RF Radiation by the sample due to net transitions from a lower to a higher Nuclear Magnetic Energy state.
- An atomic Nucleus experiences a magnetic field in its local environment which is slightly different (a shift) than the applied Magnetic Field  $B_0$ .
- One magnetic field shift is Chemical Shift.
- Chemical Shift is due to electron currents induced in the electronic environment of a nucleus by  $B_0$ .



- The Chemical Shift for a particular atomic nucleus is different for each chemical environment.
- **Magnetic Resonance** lines often split into groups of lines, giving Fine Structure to a NMR Spectrum.
- Splitting of Magnetic Resonance lines is due to interactions with the Magnetic Moments of nearby nuclei.
- When the signal being monitored by a detector coil is the result of a Pulse of Radiofrequency Radiation capable of exciting all of the protons in a sample, the signal is a FID or Free Induction Decay signal.
- An FID signal yields a Time-Domain curve. The more common NMR spectrum is a Frequency-Domain curve.
- A **Fourier transform** of an FID signal is the common Frequency-Domain NMR spectrum.
- The **Nuclear Overhauser Effect**, NOE, is the result of nuclear dipole-dipole interactions through space rather than through bonds.
- NOE may be used to transfer the relatively high Boltzmann-Distribution of one nuclear-spin system,  $^1\text{H}$ , to another  $^{13}\text{C}$ .
- **Two-Dimensional NMR**, 2D NMR, uses a PEMD Pulse Structure to conduct experiments yielding spin-spin couplings and internuclear distances in molecules.
- Nuclear Overhauser Spectroscopy, NOESY, data can map the internuclear distances of all the NOE, dipole-dipole, interactions in a molecule.
- Solid samples give low resolution NMR Spectra due to line broadening.
- **Spin-Lattice Relaxation Times**,  $T_1$ , for solids are very long due to limited molecular rotation and Spin-Spin Relaxation Times,  $T_2$ , are very short.
- Line-Broadening may be reduced by spinning the sample at very high rates, at the Magic Angle,  $54.74^\circ$  ; Magic-Angle Spinning, MAS.
- Molecules having unpaired electrons may be studied using Electron Paramagnetic Resonance, EPR.
- The equations for Magnetic Resonance apply to the Magnetic Moments of unpaired electrons.
- **EPR Spectrometers** are commonly Continuous-Wave Spectrometers, CW-EPR, similar to the original NMR Spectrometers.
- EPR Spectrometers may be Fourier-Transform Spectrometers, FT-EPR, similar to modern FT-NMR's.
- Frequencies of Electron Spin State transitions, EPR, are microwave frequencies, therefore radiation sources and detectors are microwave rather than RF devices as in NMR.
- EPR Spectra are commonly presented as the first-derivative of absorption. This is done because the detection technique is sensitive to the first-derivative of absorption.
- EPR Spectral Lines are subject to Hyperfine Splitting due to interaction of the unpaired electron with the Nuclear Magnetic Moment.
- **Hyperfine Structure** of an EPR Spectrum helps to identify radicals present in a sample.

## Chapter Summary

This tutorial introduces the Kinetic Theory of Gases and the processes such as: Diffusion, Thermal Conduction, and Viscosity that quantify the processes by which matter or other physical properties move through a gas phase.

### Tutorial Features

- Concept map showing inter-connections of concepts.
- Definition slides introduce terms as they are needed.
- Examples given throughout to illustrate how the concepts apply.
- A concise summary is given at the conclusion of the tutorial.

### Key Concepts

- Kinetic Theory of Gases
- Mean speed of gas molecules
- Mean free path of gas molecules
- Collision frequency
- Diffusion of gas molecules
- Thermal conduction of gases
- Viscosity

### Chapter Review

- There are 5 assumptions in the Kinetic Theory of Gases, some are true for all gases, others are true only for ideal gases.
- **Kinetic Theory** assumes that all gases are made of particles (gas molecules) with mass.
- Kinetic Theory assumes that Gas particles are in constant, rapid, random motion.
- Kinetic Theory assumes that gas-particle collisions are perfectly elastic (no kinetic energy is lost to other forms of energy).
- Kinetic Theory assumes that the volume of gas particles is so small compared to the space between the particles, that the volume of a particle itself is insignificant.
- In an **elastic collision**, the translational kinetic energy of a molecule is the same before and after a collision.
- The mass of a gas molecule is a constant and the velocity of a molecule will be the same before and after it collides with a wall, only direction is changed.
- Gas Pressure is caused by the collision of molecules running into the wall of a container, or a surface.
- **Force** is the momentum change per unit time.
- **Pressure** is the force per unit area.
- Gas Molecules have various speeds.
- Mean speed of gas molecules is determined by integration of the Maxwell distribution function.
- The **mean speed** of gas molecules is slightly different from root mean square speed.
- The **Mean Free Path** for gas molecules is equal to mean speed divided by collision frequency.
- At sea level, a molecule can travel about 339 times its molecular diameter with having a collision with another gas molecule.
- In the tropopause, a molecule can travel about 0.4 mm without any collision.
- **Transport Properties** quantify the ability of a substance to transfer material, energy, or other properties from one place to another.
- Transport processes include the transfer of material, energy or other properties.
- **Flux** is the amount of moving matter or other property, divided by area and time.

- If matter collides with a surface instead of passing it, it is called collision flux.
- **Collision flux** is the number of collisions per unit area per second.
- Diffusion is a flux of matter moving down a concentration gradient.
- A flux of matter is equal to the diffusion coefficient multiplied by the concentration gradient.
- **Thermal conduction** of gases results from the collisions of gas molecules.
- Energy is passed between molecules via collisions.
- An Energy Flux migrates down a temperature gradient.
- **Viscosity** in gases results from the friction between surfaces and moving gas molecules.
- Viscosity is a coefficient in the equation for flux of linear momentum in fluids (gases and liquids).

This tutorial is an introduction to Chemical Kinetics. Chemical Kinetics is the study of rate (or speed) of a reactions. The speed of a reaction is the rate at which reactants disappear and products appear.

### Tutorial Features

- Concept map showing inter-connections of concepts.
- Definition slides introduce terms as they are needed.
- Examples given throughout to illustrate how the concepts apply.
- A concise summary is given at the conclusion of the tutorial.

### Key Concepts

- Kinetics studies
- Rate laws, differential and integrated
- Half-lives
- How activation energy, temperature and rate are related
- Elementary reactions
- Reaction mechanisms

### Chapter Review

- **Kinetics** is the study of the rate (or speed) of a reaction. The speed of a reaction is the rate at which reactants disappear and products appear.
- A **Reaction Rate** is the change of concentration of chemical species involved in a reaction divided by the corresponding time of reaction.
- **Rate Laws** are Mathematical Equations describing the rates of chemical reactions.
- Rate laws are determined experimentally.
- Graphing different powers of reaction rate on the y-axis versus concentration of a reactant on the x-axis, the order with respect to that reactant may be determined.
- A plot of the first power of reaction rate versus reactant concentration will be a straight line with zero slope if the order is zero.
- A plot of the first power of reaction rate versus reactant concentration will be a straight line with non-slope if the order is first.
- A plot of the square root of reaction rate versus reactant concentration will be a straight line with zero slope if the order is second order.
- **Integrated rate laws** relate concentration and time.
- One **Half-life** is the time it takes for a reactant concentration to change to half of its initial concentration.
- Reaction rates depend on the temperature of reaction in addition to the initial concentrations of reactants.
- The **Arrhenius Equation** relates a Rate Constant (proportional to rate) to the ratio of the number of molecular collisions with the correct orientation, activation energy and temperature to total number of collisions
- An **Activated Complex** is the highest energy chemical structure formed in the process of a chemical reaction.
- The **Energy of Activation** for a chemical reaction is the difference between the average energy of the reactants and the energy of an activated complex for the reaction.
- Elementary Reactions are the reaction steps that occur during a chemical reaction.
- **Molecularity** is the number of reacting molecules in an elementary reaction.
- Some reactions generate intermediate chemical species before the final products are formed.



## Chapter Summary

This tutorial is an introduction to more advanced topics in Chemical Kinetics: reaction mechanism, chain reactions, photochemical reactions polymerization reactions and the theory of catalysis.

## Tutorial Features

- Concept map showing inter-connections of concepts.
- Definition slides introduce terms as they are needed.
- Examples given throughout to illustrate how the concepts apply.
- A concise summary is given at the conclusion of the tutorial.

## Key Concepts

- Reaction mechanisms
- Chain Reactions
- Explosions
- Photochemical reactions
- Polymerization
- Catalysis

## Chapter Review

- **Elementary steps** are chemical equations that show a single molecular collision processes.
- The reaction mechanism is a series of elementary steps that add up to the overall equation.
- Elementary steps must add up to equal the overall chemical reaction.
- An intermediate is a species that is produced in an elementary step, and then consumed in a later step.
- The **rate determining step** is the slowest step in the mechanism; it literally determines the rate of an overall reaction.
- Many reactions are chain reactions, such as explosions (gas phase) and polymerization (liquid phase).
- In a **chain reaction**, an intermediate produced in one step creates another intermediate in a subsequent step, and so on.
- There are four types of reactions in the reaction mechanisms of chain reactions: initiation step, propagation step, termination step, and inhibition step.
- There are several types of reactions that can initiate chain reactions, including photolysis, thermolysis, and pyrolysis.
- Many reactions can be initiated by the absorption of light, called photochemical reactions.
- Excited state species in the photochemical reactions have several different possible reaction paths: decomposing, attacking other molecules, and deactivated through collisions.
- **Quantum yield** measures the efficiency of photon absorption in terms of the ratio of product molecules produce to photons absorbed.
- The first step of a photochemical reaction, photolysis, is usually the rate determining step.
- The rate of **photolysis** is determined by the intensity of absorbed radiation.
- Reaction of a molecule that does not absorb photons itself can be stimulated by colliding with a photon absorbing molecule.

- Some photochemical reactions can be slowed down by the addition of a species that removes energy from excited species.
- **Chain polymerizations** are commonly addition reactions in which radicals are added to double bonds (or triple bonds) of unsaturated monomers.
- **Step polymerization** commonly proceeds by a condensation reaction, in which a small molecule such as H<sub>2</sub>O is eliminated in each step.
- A **catalyst** is a substance that increases the rate of a chemical reaction, but itself is not consumed by the overall reaction.
- **Catalysts** accelerate reactions by lowering the activation energy.
- There are two types of catalysts: homogeneous (catalyst is in the same phase as the reaction) or heterogeneous (catalyst is not in the same phase as the reaction).
- When a product of a reaction is a catalyst of the reaction, it is called autocatalysis.
- An **Enzyme** is a catalyst in biochemical reactions.
- Enzymes are usually proteins.

### Chapter Summary

This tutorial is an introduction to yet more advanced topics in Chemical Kinetics: collision theory, diffusion-controlled reactions, Cage effect, activated-complex theory, the Eyring equation, thermodynamic aspects of transition states, potential energy surface.

### Tutorial Features

- Concept map showing inter-connections of concepts.
- Definition slides introduce terms as they are needed.
- Examples given throughout to illustrate how the concepts apply.
- A concise summary is given at the conclusion of the tutorial.

### Key Concepts

- Collision theory
- Diffusion-controlled reactions
- Cage effect
- Activated complex theory
- The Eyring equation
- Thermodynamic aspects of transition states
- Potential energy surface

### Chapter Review

- **Collision Theory** is the basic theory behind kinetics.
- In order for a reaction to occur, reactants must collide in the correct orientation (positions) with the minimum amount of energy to transform from the reactants to the products.
- Very few collisions result in a reaction—but so many collisions occur that the reaction does proceed.
- Molecules must come in contact in order to react.
- Since molecules must collide in order for a reaction to occur, reaction rates depend on the frequency with which molecules collide.
- At room temperature and 1 atm pressure, nitrogen molecules have about 8 billion collisions in one second.
- A nitrogen molecule at room temperature can travel 475 meters in one second.
- A **collision** must have sufficient energy in order for a reaction to occur.
- For a collision to result in a chemical reaction, it must occur with the correct orientation.
- Reactions in liquids occur in a very different manner from reactions in a gas.
- Molecules in a liquid are much closer to each other, do not move as freely as in gas phase, and have longer contact time with neighboring molecules.
- Because the reactant molecules in liquids are forced to stay together for more time than in a gas, they may accumulate enough energy via collisions to transform to products; the cage effect.
- The **cage effect** makes evaluation of activation energy more difficult in liquids than in gases.
- **Reactions in solution** are classified into categories: diffusion-controlled, or activation-controlled, depending on the activation energies.
- Reactions with low activation energy are diffusion-controlled.
- Reactions with high activation energy are activation-controlled.

- The **Stokes-Einstein equation** is used to estimate the rate constant for a diffusion-controlled reaction simply from the temperature and the viscosity of the solvent.
- An **Activated Complex** is the cluster of reactant molecules that represents the configuration corresponding to maximum potential energy along the reaction path.
- A plot of potential energy against the reaction coordinate is a Reaction Profile.
- The **unimolecular reaction rate constant** of an activated complex is proportional to a theoretical frequency associated with vibration-like motion along the reaction coordinate.
- **Activated complex theory** combined with statistical mechanics results in the Eyring equation:
 
$$k_2 = \kappa \frac{kT}{h} K$$
- The **Eyring equation** is used to estimate the rate constants of bimolecular reactions in gas phase.
- Transition states correspond to saddle points on hypothetical potential energy surfaces.
- A **saddle point** on a potential energy surface indicates a transition state for the corresponding reaction.



## Chapter Summary

This chapter is an introduction to crystal structures, and the physical and chemical properties of solid surfaces.

## Tutorial Features

- Concept map showing inter-connections of concepts.
- Definition slides introduce terms as they are needed.
- Examples given throughout to illustrate how the concepts apply.
- A concise summary is given at the conclusion of the tutorial.

## Key Concepts

- Lattices and Unit Cells
- Lattice Planes
- X-Ray Diffraction
- Metallic Bonding in Solids
- Ionic Bonding in Solids
- Covalent Network Bonding in Solids
- Molecular Bonding in Solids
- Surface Composition
- Physisorption and Chemisorption
- Catalysis at Solid Surfaces
- Redox at Solid Surfaces

## Chapter Review

- **Solids** are formed from atoms, molecules, or ions as building blocks arranged in repeating patterns called units cells.
- A **Unit Cell** is an array of crystal-lattice points with parallel sides that generates a Crystal Lattice when moved along the x, y, and z axes as if it were a building block.
- A **crystal lattice** is represented by arranging unit cells, like building blocks, in a three-dimensional array of Lattice Points.
- A **Lattice Point** is a point in space that may be occupied by a structural unit of a crystal such as a molecule or atom.
- 14 different unit-cell patterns, Bravais Lattices: including body centered, face centered, side centered are classified into 7 different crystal systems: including cubic, monoclinic, and triclinic.
- There are three cubic Lattices: simple cubic, face centered cubic and body centered cubic.
- **Face centered cubic** has a structural unit at the center of each face of the unit cell.
- **Body centered cubic** has a structural unit at the center of the unit cell.
- There are two **monoclinic Lattices**: simple, and side-centered.
- Side-centered monoclinic has structural units at the centers of two parallel sides.
- There is only one triclinic Lattice.
- **Planes** containing three or more non-collinear lattice points may be drawn through crystal lattices in many ways and the locations/spacing of these planes are important features of a crystalline solid.
- Lattice Planes lead to X-Ray Diffraction Patterns when X-Rays pass through crystals.
- **X-Ray Diffraction Patterns** are caused by wave interference as X-Rays are scattered by structures in Lattice Planes.

- Solids composed only of metal atoms bond by sharing their Delocalized Bonding Electrons over many atoms in a crystal lattice.
- **Bonding electrons** in metals are Delocalized Bonding Electrons since they roam over extended regions of atoms in a metal-crystal lattice.
- Solids composed of Anions and Cations have ionic bonding caused by attraction between oppositely charged ions.
- **Solids** in which atoms are connected by covalent bonds to adjacent atoms in a continuous manner throughout the crystal are held together by Covalent Network Bonding.
- Solids in which atoms are connected by covalent bonds to adjacent atoms in molecular groupings and molecules are connected by van der Waals forces are Molecular Solids.
- Freshly prepared solid surfaces that are exposed to a gaseous environment quickly become covered with absorbed gas molecules/atoms.
- A large variety of spectroscopic techniques are used to study the compositions of solid surfaces including: photoemission spectroscopy, secondary-ion mass spectroscopy, reflection-absorption infrared spectroscopy, surface-enhanced Raman scattering, and electron energy loss spectroscopy.
- Molecules and atoms held to a surface by van der Waals forces are physisorbed.
- Molecules and atoms that attach to a surface by forming chemical bonds are chemisorbed.
- **Catalytic activity** of a solid surface depends on both surface structure and surface composition.
- Catalytic activity of a solid surface is favored when reactants are chemisorbed by bonding at optimal strength.

### Chapter Summary

This chapter is a guide to Physical Chemistry Laboratory and discusses each step in the process from planning to writing the lab report.

### Tutorial Features

- Concept map showing inter-connections of concepts.
- Definition slides introduce terms as they are needed.
- Examples given throughout to illustrate how the concepts apply.
- A concise summary is given at the conclusion of the tutorial.

### Key Concepts

- Studying/Reviewing Experiment and Related Chemistry
- Organizing and Studying Instrumentation/Equipment and Experimental Method
- Obtaining and Reviewing MSDS's for all Chemicals
- Reviewing and Planning for Safety Concerns
- Setting-up and Calibrating Instrumentation/Equipment
- Making Measurements and Recording Data
- Rejecting Bad Data
- Performing Calculations Based on Good Data
- Tabulating and Graphing Results
- Writing Report
  - Introduction
  - Method
  - Results
  - Discussion

### Chapter Review

- **Physical Chemistry Laboratory** spans an extremely broad range of instruments and types of data from vapor pressure measurement using a simple isoteniscope to the study of molecular rotation rates using a Nuclear Magnetic Resonance Spectrometer, NMR.
- Typical instruments include: calorimeters, spectrophotometers, pH meters, cyclic voltametry equipment, conductivity meters, analytical balances, and microscopes.
- Study an experiment in full detail: theory, experimental equipment, experimental procedure and data analysis.
- Make an efficient and effective data collection and recording plan: primary data tables, data graphs, charts.
- Locate/schedule and check all needed facilities supplies and equipment. Record most recent instrument calibration, recalibrate if required and record measurement precision.
- Locate and Review MSDS's, **Material Safety Data Sheets**, for all chemicals in the experiment. Use MSDS information to plan for safe use and disposal of all chemicals.
- Plan how to organization your laboratory records: which observations to record, how best to record required measurements.
- Review common units for all measurements and make provisions for including units with all measurement records.
- Write an **Introduction** in your laboratory notebook that describes the goals of the experiment and a general statement of the methods to be used.

- Bring together and check all equipment and chemicals. Warm up instruments prior to use. Calibrate instruments as required.
- Set-up equipment and organize work space for efficiency of data taking and safety. Sketch and annotate the experimental set-up in your Laboratory Notebook, noting manufacturers and model numbers for commercial equipment.
- Note any issues or concerns in your laboratory notebook and review measurement and data-taking plans.
- Make and record measurements and observations.
- Record measurements and observations directly into your Laboratory Notebook, never elsewhere.
- Clearly mark data Clouded by known problems with the data-taking process.
- Draw a straight line across Clouded results and make a brief note of the problem.
- Do not include data in your calculations Clouded by known problems with the data-taking process.
- Carefully examine all other data and note any which are Outliers.
- Apply the **Q Test** to all Outliers and discard those data points that fail the Q Test.
- In a Q Test, Q values are compared to Critical Q values from a standard table and if Q of the questionable point is larger than the Critical Q value, that point is an Outlier and should be discarded.
- Tabulate and graph results as appropriate using a spread-sheet program such as Microsoft Excel.
- Use a spread sheet program to fit results to an appropriate functional form, linear for Beer's Law, and calculate the Quality of Fit factor  $R^2$ .
- Record measurements and observations directly into your Laboratory Notebook, never elsewhere.
- **Introductory items** for an experiment report include: Title Page, Abstract and a brief Statement of Purpose and Theory.
- A **Title Page** includes: Your Name and Partners Names, Date of Experiment, Date of Report, Title of Report, Course and Section Numbers.
- The body of an experiment report includes: Description of Experimental Method, Data, and a Narrative Discussion of results.
- An **Experiment Abstract** is a brief, concise and to-the-point summary of the Experiment including: important conclusions, experimental method and other significant insights gained. An Experiment Statement of Purpose and Theory describes the goal of the experiment and outlines the theory on which it is based, in your own words and without a great amount of detail.
- A **Description of Experimental Method** is an outline of the Procedure, including a description of the Apparatus with drawings of the apparatus and equations used in analysis of data.
- A person should be able to duplicate the experiment based on the Description of Experimental Method.
- Data are presented in tables well integrated with sample calculations, associated graphs, drawings and a narrative discussion of results.
- A **Narrative Discussion** includes: interpretation of results including error analysis and comparison of results with accepted data and theory, and references.