《Physical Chemistry》

Ⅰ、General Information

Course Name	**Physical Chemistry**
Course	Compulsory
Semester	3,4
Hours	**112**
Credit Points	3．5
Textbook	P.W.Atkins.《Physical Chemistry》Seventh Edition.Oxford University Press Inc., New York,2002
References	[1]. 宋世谟主编,《物理化学》上、下册，第四版..北京：高教出版社.2001 [2]. 付献彩主编,《物理化学》上、下册. 第三版.南京大学.北京：高教出版社.2001 [3]. 胡英主编,《物理化学》上、中、下册. 第一版，北京：高教出版社.2001 [4]. 付玉普主编,《物理化学》上、下册. 第一版，大连：大连理工大学出版社，2000 [5]. 北京化工大学编,《物理化学例题与习题》.. 第一版,北京：化学工业出版社.2001 [6]. R A.Alberty《Physical Chemistry》 Fifth edition .Tohn Wiley & Sons,Inc. 1979 [7].Keith J.Laidler,JohnH.Meiser. 《Physical Chemistry》The Benjamin/Cummings Publishing Company, Inc

Ⅱ、Contents

Part 1 Equilibrum

Part 1 of the text develops the concepts that are needed for the discussion of equilibria in chemistry. Equilibria include physical change, such as fusion and vaporization, and chemical change, including electrochemistry. The discussion is in terms of thermodynamics, and particularly in terms of enthalpy and entropy. We see that we can obtain a unified view of equilibrium and the direction of spontaneous chang in terms of the chemical potential of substances.

1 The properties of gases（5 hours）

I. The Basic Requirements

The states of the perfect gases

The perfect gas lawsMolecular interaction of real gases

The van der Waals equation

The principle of corresponding states

II. Contents

1. The perfect gas

The states of the perfect gases , the perfect gas laws, the partial pressure and the partial volume

2. Real gases

Molecular interaction: the compression factor, condensation, critical constants

The van der Waals equation

The principle of corresponding states

2 The First Law: the concepts（6 hours）

I. The Basic Requirements

The basic concepts: work, heat, energy, and the First Law

Work and heat: expansion work, heat transactions, enthalpy, and adiabatic changes

Thermochemistry: standard enthalpy changes, standard enthalpies of formation, and the temperature dependence of reaction enthalpies

II. Contents

1.The basic concepts

System, surroundings, work, heat, energy, and the First Law

2. Work and heat

Expansion work: the general expression for work, free expansion, expansion against constant pressure, reversible expansion, and isothermal reversible expansion

Heat transactions: heat capacity

Enthalpy: the definition of enthalpy, the measurement of an enthalpy change, the variation of enthalpy with temperature, the relation between heat capacities

Adiabatic changes: the work of adiabatic change, heat capacity ratio and adiabats

3. Thermochemistry

Standard enthalpy changes: enthalpy of physical change, enthalpyies of chemical change, Hess's law

Standard enthalpies of formation: the ralation enthalpy in terms of enthalpies of formation,group contributions, and enthalpies of formation and molecular modelling

The temperature dependence of reaction enthalpies

4. Tutorial class

3 The First Law: the machinery（6 hours）

I. The Basic Requirements

State functions and exact differentials: state and path functions, exact and inexact differentials

Thermodynamic consequences: changes in internal energy, the temperature dependence of the enthalpy, and the relation between $C_{v,m}$ and $C_{p,m}$

II. Contents

1. State functions and exact differentials

State and path functions

Exact and inexact differentials

2. Thermodynamic consequences

Changes in internal energy: general considerations, the Joule experiment, and changes in internal energy at constant pressure

The temperature dependence of the enthalpy: changes in the enthalpy at constant volume, the isothermal compressibility, and the Joule-Thomson effect

The relation between $C_{v,m}$ and $C_{p,m}$

3. Tutorial class

4 The Second Law: the concepts（6 hours）

I. The Basic Requirements

The direction of spontaneous change: the dispersal of energy, entropy, entropy changes accompanying specific processes, and the Third Law of thermodynamics

Concentrating on the system: the Helmholtz and Gibbs energies, standard molar Gibbs energies

II. Contents

1. The direction of spontaneous change

The dispersal of energy

Entropy: the thermodynamic definition of entropy, the entropy as a state function, the thermodynamic temperature, the Clausius inequality

Entropy changes accompanying specific processes: the entropy of phase transition at the transition pemperature, the expansion of a perfect gas, the variation of entropy with temperature, the measurement of entropy

The Third Law of thermodynamics: the Nernst heat theorem, Third-Law entropies

2. Concentrating on the system

The Helmholtz and Gibbs energies: criteria for spontaneity, some remarks on the Helmholtz energy, maximum work, some remarks on the Gibbs energy, maximum non-expansion work

Standard molar Gibbs energies

3. Tutorial class

5 The Second Law: the machinery（6 hours）

I. The Basic Requirements

Combining the First and Second Laws: the fundamental equarion, and properties of the internal energy

Properties of the Gibbs energy: general considerations, the variation of the Gibbs energy with temperature, the variation of the Gibbs energy with pressure

II. Contents

1. Combining the First and Second Laws

The fundamental equarion

Properties of the internal energy: the maxwell relations, the variation of internal energy with volume

2. Properties of the Gibbs energy

General considerations

The variation of the Gibbs energy with temperature

The variation of the Gibbs energy with pressure: liquids and solids, gases

3. Tutorial class

6 Simple mixtures（9 hours）

I. The Basic Requirements

The thermodynamic description of mixtures: partial molar quantities, the thermodynamics of mixing, the chemical potentials of liquids

The properties of solutions: liquids mixtures, colligative properties

Activities: the solvent activity, the solute activity, the activities of regular solutions

II. Contents

1. The thermodynamic description of mixtures

Partial molar quantities: partial molar volume, partial molar Gibbs energies, the wider significance of the chemical potential, the Gibbs-Duhem equation

The thermodynamics of mixing: the Gibbs energy of mixing, other thermodynamic mixing functions

The chemical potentials of liquids: ideal solutions, ideal-dilute solutions

2. The properties of solutions

Liquids mixtures: ideal solutions, excess functions and regular solutions

Colligative properties: the common features of colligative properties, the elevation of boiling point, the depression of freezing point, solubility, osmosis, vapour-phase osmometry

3. Activities

The solvent activity

The solute activity: ideal-dilute solutions, real solutes, activities in terms of molalities

The activities of regular solutions

4. Tutorial class

7 Chemical equilibrium（6 hours）

I. The Basic Requirements

Spontaneous chemical reactions: the Gibbs energy minimum, the description of equilibrium

The respones of equilibria to the conditions: how equilibria respond to pressure, the response of equilibria to temperature

II. Contents

1. Spontaneous chemical reactions

The Gibbs energy minimum: the reaction Gibbs energy, Exergonic and endergonic reactions

The description of equilibrium: perfect gas equilibria, the general case of a reaction, the relation between equilibrium constants

2. The respones of equilibria to the conditions

How equilibria respond to pressure

The response of equilibria to temperature: the van't Hoff equation, the value of K at different temperatures

3. Tutorial class

8 Phase diagrams（10 hours）

I. The Basic Requirements

Phases, components, and degrees of freedom: definitions, the phase rule

Two-component systems: vapour pressure diagrams, temperature-composition diagrams, liquid-liquid phase diagrams, liquid-solid phase diagrams

II. Contents

1. Phases, components, and degrees of freedom
Definitions
The phase rule: one-component systems, experimental procedures
2. Two-component systems
Vapour pressure diagrams: the composition of the vapour, the interpretation of the diagrams, the lever rule
Temperature-composition diagrams: yhe distillation of mixtures, azeotropes, immiscible liquids
Liquid-liquid phase diagrams: phase separation, critical solution temperatures, the distillation of partially miscible liquids
Liquid-solid phase diagrams: Eutectics, reacting systems, incongruent melting3. Tutorial class

Part 2 Statistical thermodynamics

Statistical thermodynamics provides the link between the microscopic properties of matter and its bulk properties. Two key ideas are introduced in this chapter. The first is the Boltzmann distribution, which is used to predict the populations of states in systems at thermal equilibrium. In this chapter we see its derivation in terms of the distribution of particles over available states. The derivation leads naturally to the introduction of the partition function, which is the central mathematical concept of this and the next chapter. We see how to interpret the partition function and how to calculate it in a number of simple case. We then see how to extract thermodynamic information from the partition function. In the final part of the chapter, we generalize the discussion to include systems that are composed of assemblies of interacting particles.Very similar equations are developed to those in the first part of the chapter, but they are much more widely applicable.

9 Statistical thermodynamics: the concepts（10 hours）

I. The Basic Requirements
The distribution of molecular states: configurations and weights, the molecular partition
The internal energy and the entropy: the internal energy, the statistical entropy
The canonical partition function: the canonical ensemble, the thermodynamic information in the partition function, independent molecules
II. Contents
1. The distribution of molecular states
Configurations and weights: instantaneous configurations, the dominating configuration, the Boltzmann distribution
The molecular partition: an interpretation of the partition function, approximations and factorizations
2. The internal energy and the entropyThe internal energy: the relation between U and q, *the value of β
The statistical entropy
3. The canonical partition function
The canonical ensemble: the concept of ensemble, dominating configurations, fluctuations from the most probable distribution
The thermodynamic information in the partition function: the internal energy, the entropy

Independent molecules: distinguishable and indistinguishable molecules, the entropy of a monatomic gas,

10 Statistical thermodynamics: the machinery（6 hours）

I. The Basic Requirements

Fundamental relations: the thermodynamic functions, the molecular partition function

Using statistical thermodynamics: mean energies, heat capacities, equations of state, residual entropies, equilibrium constants

II. Contents

1. Fundamental relations

*The thermodynamic functions: the Helmholtz energy, the pressure, the enthalpy, the Gibbs energy

The molecular partition function: the translational contribution the rotational contribution, the vibrational contribution, the electronic contribution, the overall partition function

2. Using statistical thermodynamics

Mean energies: the mean translational energy, the mean rotational energy, the mean vobrational energy

Heat capacities: the individual contributions, the overall heat capacity

Equations of state

Residual entropies

Equilibrium constants: the relation between K and the partition function, a dissociatio equilibrium, contributions to the equilibrium constant

Part 3 Change

Part 3 considers the processes by which change occurs. We prepare the ground for a discussion of the rates of reactions by considering the motion of molecules in gases and in liquids. Then we establish the precise meaning of reaction rate, and see how the overall rate, and the complex behaviour of some reactions, may be expressed in terms of elementary steps and the atomic events that take place when molecules meet. Characteristic physical and chemical events that take place at surfaces, including catalysis, and we see how to describe them.

11 The rates of chemical reactions（6 hours）

I. The Basic Requirements

Empirical chemical kinetics: Experimental techniques, the rates of reactions, integrated rate laws, reactions approaching equilibrium, the temperature dependence of reaction rates

Accounting for the rate laws: elementary reactions, consecutive elementary reactions, unimolecular reactions.

II. Contents

1. Empirical chemical kinetics

Experimental techniques: monitoring the progress of a reaction, application of the techniques

The rates of reactions: the definition of rate, rate laws and rate constants, reaction order, the determination of the rate law

Integrated rate laws: first-order reactions, half-lives and time constants, second-order reactions

Reactions approaching equilibrium: first-order reactions close to equilibrium, relaxation methods
The temperature dependence of reaction rates: the Arrhenius parameters, the interpretation of theparameters
2. Accounting for the rate laws
Elementary reactions
Consecutive elementary reactions: the variation of concentrations with time, the rate-determining step, the steady-state approximation, pre-equilibria, the kinetic isotope effect
Unimolecular reactions: the Lindemann-Hinshelwood mechanism, the activation energy of a composite reaction
3. Tutorial class

12 The kinetics of complex reactions（6 hours）

I. The Basic Requirements
Chain reactions: the rate lawsof chain reactions, explosions
Polymerization kinetics: stepwise polymerization, chain polymerization
Homogeneous catalysis: features of homogeneous catalysis, enzymes
Oscillating reactions: autocatalysis, autocatalytic mechanisms of oscillating reactions, bistability, chemical chaos
Photochemistry: kinetics of photophysical and photochemical processes, complex photochemical processes
II. Contents
1. Chain reactions
The rate lawsof chain reactions
Explosions
2. Polymerization kinetics
Stepwise polymerization
Chain polymerization
3. Homogeneous catalysis
Features of homogeneous catalysis
*Enzymes
4. Oscillating reactions
Autocatalysis
*Autocatalytic mechanisms of oscillating reactions
Bistability
Chemical chaos
5. Photochemistry
Kinetics of photophysical and photochemical processes: timescales of photophysical processes, the promary quantum yield
Complex photochemical processes: the overall quantum yield of a photochemical reaction, rate laws of complex photochemical reactions, photosensitization

13 The kinetics of complex reactions（4 hours）

I. The Basic Requirements
Reactive encounters: collision theory, diffusion-controlled reactions, the material-balance

equation
Activated complex theory: the Eyring equation, thermodynamic aspects
The dynamics of molecular collisions: reactive collisions, potential energy surfaces, some results from experiments and calculations
II. Contents
1. Reactive encounters
Collision theory: collision rates in gases, the energy requirement, the steric requirement
Diffusion-controlled reactions
The material-balance equation
2. Activated complex theory
*the Eyring equation: the rate of decay of the activated complex, the concentration of the activated complex, the rate constant, the collision of structureless particles
Thermodynamic aspects
3. The dynamics of molecular collisions
Reactive collisions
Potential energy surfaces
*Some results from experiments and calculations

Part 4 Other

14 Equilibrium electrochemistry（10 hours）

I. The Basic Requirements
The thermodynamic properties of ions in solution: thermodynamic functions of formation, ion activeties
Electrochemical cells: half-reactions and electrodes, varieties of cells, standard potentials
Applications of standard potentials: the electrochemical series, the measurement of pH, thermodynamic functions
II. Contents
1. The thermodynamic properties of ions in solution
Thermodynamic functions of formation: standard functions of formation of ions, contributions to the Gibbs energy of formation, standard entropies of ions in solution
Ion activeties: the difinition of activity, mean activity coefficients, the Debye-Huckel limiting law, the extended Debye-Huckel law
2. Electrochemical cells
Half-reactions and electrodes: half-reactions, reactions at electrodes
Varieties of cells: liquid junction potentials, notation, the cell reaction, the cell potential, the relation between E and $\Delta_r G_m$, the Nernst equation, concentration cells, cells at equilibrium
Standard potentials: the cell emf in terms of individual standard potentials, the measurement of standard potentials, the measurenment of activity coefficients
3. Applications of standard potentials
The electrochemical series
The measurement of pH
Thermodynamic functions
4. Tutorial class

15 Dynamics of electron transfer（6 hours）

I. The Basic Requirements

Electron transfer in heterageneous systems: the electrode-solution interface, the rate of charge transfer, voltammetry, electrolysis, working galvanic cells

II. Contents

1. Electron transfer in heterageneous systems

The electrode-solution interface: the structure of the interface, the lectric potential at the interface

*The rate of charge transfer: the rate laws, the activation Gibbs energy, the Butler-Volmer equation, the low overpotential limit, the high overpotential limit

Voltammetry: concentration polarization, experimental techniques

Electrolysis

Working galvanic cells: the cell potential, fuel cells

16 Surface（6 hours）

I. The Basic Requirements

The physical liquid surface: surface tension, curved surfaces, capilary action

Processes at solid surfaces: physisorption and chemisorption, adsorption isotherms, the rates of surface processes

II. Contents

1. The physical liquid surface

Surface tension

Curved surfaces: bubbles, cavities, and droplets,nucleation

Capilary action: capillary rise, the contact angle

2. Processes at solid surfaces

Physisorption and chemisorption

Adsorption isotherms: the Langmuir isotherm, *The BET isotherm, *other isotherms

The rates of surface processes: the rate of adsorption, the rate of desorption

17 Colloids （4 hours）

I. The Basic Requirements

Classification and preparation, structure and stability, the electrical double layer

II. Contents

Classification and preparation

Structure and stability

The electrical double layer

III、作业

每两学时布置 3-4 道计算题(中、英结合)，每周收一次作业。在教学过程中的适当的知识点可布置 1-2 道综合分析题。

通过习题的联系，使学生学会化学实验数据的处理方法，学会分析问题和解决问题的能力，特别作一些科研和生产实际的数据处理，使学生了解一些科研和生产实例。

VI、 核方式及成绩评定

物理化学课程学习成绩分为上册成绩，包括：

1、 平时作业；

2、阶段测验；

3、期末考试。

三部分合计 100 分。

下册成绩，包括：

1、平时作业；

2、阶段测验；

3、读书报告；

4、期末考试。

四部分合计 100 分。

V、必要的说明

1、注“*”的小节根据学时进度安排是否讲授。

2、阶段测验不占学时。

读书报告：要求学生根据物理化学所学原理，结合查阅科研文献、书籍，了解物理化学原理在科研、生产实践中及学科前沿领域的研究中的结合点，写出读书报告。

执笔人：李蕾

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