#### SYLLABUS, LESSON PLAN, MIDTERM AND FINAL SEMESTER EXAMINATIONS, HANDOUTS AND WORKSHEETS OF PHYSICAL CHEMISTRY I

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ht	misti-PHYSICC - STUDY AND
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By:

Drs. Ali Amran, M.Pd, M.A, Ph.D

Sherly Kasuma Warda Ningsih, S.Si, M.Si

#### CHEMISTRY DEPARTMENT FACULTY OF MATHEMATICS AND NATURAL SCIENCES STATE UNIVERSITY OF PADANG

# Jl. Prof. Dr. Hamka, Kampus UNP Air Tawar Padang, 25131, Telp. (0751)7057420 FACULTY OF MATHEMATICS AND SCIENCE STATE UNIVERSITY OF PADANG

Subject Syllabus (Semester Plan)

### **A.** General Information Code Subject

Study Program Department

Number of Credit : Kim 001 : Physical Chemistry 1 2008 ISTE Students

: Chemistry

Docents **Consultation Place** Lecture time Place/Lecture room

> : C04 : 3 hours : Chemistry Department Office

: 1. Drs. Ali Amran, M.Pd, M.A, Ph.D

2. Deski Beri, S.Si

# **B.** Subject Description

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- This course consists of Introduction to physical chemistry, ideal and non ideal gases, kinetic molecular theory of gas, Chemical Thermodynamics, chemical equilibrium, liquids, solutions and Colloids and Surface Chemistry.
- N Lecture Methods
- <u>a</u> Individual and grouped assignments
- ù, Students presentations
- Discussions
- ω **Final Achievement**

and its applications as well. kinetics molecular of gases, solutions, chemical equilibrium, chemical thermodynamics, liquids and colloids and surface chemistry This course is designed to encourage students to understand the theoretical and empirical concepts of an ideal and non ideal gases,

## Refferences

## Compulsary:

- Adamson, A.W., Text Book of Physical Chemistry, John Willey & Sons, New York
- Adamson, A.W., (1985), Physical Chemistry of Surfaces, John Willey & Sons, New York.
- Atkins, P.W., (2006) Physical Chemistry (Eighth Edition), Oxford Univ. Press, London
- Bahl, B.S, Tuli, G.D., Bahl, Arun, (1997), Essentials of Physical Chemistry, S.Chand & Company Ltd., New Delhi
- Barrow, Gordon M.,(1996) Physical Chemistry (sixth Edition), Mc Graw Hill, Boston Maron, H. Samuel, Prutton, Carl F., (1964) Principles Of Physical Chemistry, Macmillan Company, New York

### Suggest

- Castellan, W. Gilbert, (1983), Physical Chemistry (Third Edition), Addison-Wesley Publishing Company, Inc. Massahusetts
- Montimer, Robert G., (2008), Physical Chemistry (Third Edition) Elsevier Publishing, Amsterdam

## Ω **Evaluation System (Grading)**

- Criterion
- ġ, Lecture Attendance 5%
- Assignment and task 35%
- Contributions in class 10%
- Midterm Exam 25%
- Final Exam 25%
- 2 **Evaluation Instruments**
- Essay test
- Test based on observation from out date research
- Problem sheet
- Performance evaluation

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- a an ability to communicate concepts and principles in physical chemistry
- an ability to solve problems and exercises
- an ability to design the laboratory prototypes

4	N	-		No of week	J
Student competence to understand some concepts dealing with kinetics particle in box, Boltzmann-Maxwell- statistics and some application of Maxwell- Boltzmann statistics	Student competence to understand some concepts dealing with ideal and non ideal gases, ideality of gases, ideal gas laws, critical phenomenon, and theoretical background related to gases	Student competence to understand general knowledge of physical chemistry, the important of physical chemistry, and the relation of physical chemistry with chemistry and other sciences.	N	Competencies	Detaile of Svllahue
Students are able to make a derivation of molecular kinetics of gas in container, Maxwell-Boltzmann statistics and classical mechanics, gas diffusion and using Graham's law in real times problems	Students are able to derive ideal gas laws, Van der Waal equations and using the equations in daily life	Students have some knowledge about physical chemistry in general.	ω	Achievements Indicators	
	solve problems and design experiment of physical chemistry. Student competence to perform student's personal skills in presenting his/her assignments in front of classroom.	Student competence to read and understanding the text books of physical chemistry. In addition, he/she also competence to	4	Learning Experiences	
<ul> <li>Kinetics Molecular of gases</li> <li>Classical mechanics of Imaginary particle in a container</li> <li>Kinetics particle in container equations, calculation of a particle velocity</li> <li>Boltzmann distribution, and determination of Boltzmann constant</li> <li>Maxwell-Boltzmann statistic mechanics and derivation</li> <li>Mean free-path</li> <li>Gas diffusion and Graham's law</li> <li>Some applications</li> <li>Problem &amp; Solution</li> </ul>	<ul> <li>Ideal and non ideal gases</li> <li>Characteristic and properties of gases,</li> <li>Ideal gas law (Boyle, Charles, Gay-Lussac)</li> <li>Some equations related to non ideal gases or real gases</li> <li>Critical Phenomenon, Compressibility factors</li> <li>Non ideal gases, liquefaction of gases</li> <li>Semi empirical equation of Van der Waal, theoretical backgrounds and derivation</li> <li>Problem &amp; Solution</li> </ul>	<ul> <li>Introduction to physical chemistry</li> <li>The definitions of Physical chemistry, the position of physical chemistry among other branch of science and chemistries</li> <li>The important role of physical chemistry</li> <li>Some physical chemistry term and unit systems, conversion table and some physical and chemical characteristics</li> </ul>	Ű	Topics/Sub-Topics	
ـــ	2		6	Week	
C1, C3, S1 & S2	C1, C3, C6, S1 & S2	C1, C3, S1 & S2	7	References	

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Student competence to understand some concepts dealing with chemical equilibrium, hetero-and homogeneous		Student competence to understand some concepts regarding thermo chemistry, the heat and enthalpies enthalpies	Ot. Just sometimes to				using enthalpies	processes, works and	thermodynamics	concepts dealing with	understand some	Student competence to
Students are able to use some equations in chemical equilibrium to real times problems		Students are able to use thermo chemistry equations to real times problems, Cv, Cp, heats. Students are able to make a design of experiments based on calorimetric measurements	Otidonto om abla ta		problems	thermodynamics	some concepts	have an ability to solve	energy and students	third law of	use first, second and	Students are able to
Student competence to read and understanding the text books of physical chemistry.		of classroom,		suurerit competence to perform student's personal skills in presenting his/her assignments in front	design experiment of physical chemistry.	solve problems and	In addition, he/she		chemistry.	understanding the text	to read and	Student competence
<ul> <li>Chemical Equilibrium</li> <li>Definitions</li> <li>Thermodynamics of equilibrium</li> <li>K<sub>p</sub> and K<sub>c</sub> properties and calculations</li> <li>Homogeneous reaction equilibrium</li> </ul>	Mid Term Exams	<ul> <li>Inermo cnemistry</li> <li>Changes in state at constant Volume and Temperature</li> <li>The relation between C<sub>p</sub> and C<sub>v</sub></li> <li>Thermodynamics application to chemical reactions, the heat of reaction</li> <li>The formation reaction</li> <li>Conventional values of molar enthalpies</li> <li>The determination of heats of tormation</li> <li>Sequences of reactions: Hess's law</li> <li>Heats of solution and dilution</li> <li>Heat of reaction at constant pressure and volume</li> <li>Bond enthalpies</li> <li>Calorimetric measurements</li> <li>Problem &amp; Solution</li> </ul>	Thoma shamistar	<ul> <li>Second law of themodynamics</li> <li>Spontaneous and non spontaneous reactions, free energy</li> <li>Third law of thermodynamics</li> <li>Problem &amp; Solution</li> </ul>	<ul> <li>Work efficiency and Carnot circles</li> <li>Enthalpy of a system</li> <li>Sconnel low of thermodynamics</li> </ul>	- Isothermal expansion work; reversible and	Eiset laurof thermodynamice	<ul> <li>Thermodynamic process, reversible and</li> </ul>	<ul> <li>Intensive and extensive properties</li> </ul>	variables of thermodynamics	<ul> <li>Thermodynamic terms and basic concepts,</li> </ul>	Chemical Thermodynamics
2			······································									2
C4, C6 , S1 & S2		ເມ ເຊ ອ ອ ອ ອ	C3 C8 2 C1									C1, C3, C6, S1& S2

12	6	
Student is able to describe the terms of solutions, ideal solutions and Raoult's law, miscibility of mixtures and distillation principles	Student competence to understand some concepts dealing with liquids, liquids dynamics and some physical properties of liquids	
Student competence to understand some knowledge in solutions, solubility, and miscibility. Students are having some knowledge in liquids mixture,	Students have some knowledge in liquids, liquids physical properties and having some knowledge in measurements of surface tension, viscosity, refractive index and optical activity	
	Student competence to read and understanding the text books of physical chemistry. In addition, he/she also competence to solve problems and design experiment of physical chemistry. Student competence to perform student's personal skills in presenting his/her assignments in front	in addition, he/she also competence to solve problems and design experiment of physical chemistry. Student competence to perform student's personal skills in presenting his/her assignments in front of classroom.
Solutions <ul> <li>Definition</li> <li>Factors affecting solubility</li> <li>Kinds of Solutions</li> <li>Ideal Solutions and Raoult's Law</li> <li>Miscibility (Complete Binary and Temary Mixtures)</li> </ul>	Liquids - Critical Phenomena in liquids - Critical Phenomena in liquids - P-V-T relations - Van der Waal relations on liquefaction of gases - Kinetic molecular forces in liquids - Kinetic molecular forces in liquids - Vapor pressure - Measurements of vapor pressure - Measurements of surface tension - Viscosity of liquids - Measurements of viscosity - Refractive index - Measurements of refractive index - Measurements of optical activity - Problem & Solution	<ul> <li>Equilibrium in liquid states</li> <li>Temperature dependence</li> <li>Heterogeneous reaction equilibrium</li> <li>The equilibrium constant for heterogeneous reactions</li> <li>Effects of pressure/temperature on heterogeneous equilibrium</li> <li>Distribution law</li> <li>Problem &amp; Solution</li> </ul>
2	2	
C4, C6, S1	C4, C6, S1 & S2	

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17 Final Exams	problems Problem & Solution	Solving in real times - Application of Colloids	contracts years and the second s	mining authoris and Mining Automation	phenomenon able to describe - Association of Colloids	colloids and surface   colloids. Students are   of classroom.   - Properties of Sols	colloids and the relation of properties, association assignments in front - Preparations of Sols	dispersion, association systems, colloids presenting his/her - Sols	concepts about colloids dispersion, colloidat personal skills in - Types of Colloidat Systems	understand some describe the colloids to perform student's - Colloidal dispersions	15,16 Student competence to Students are able to Student competence Colloids and surfaces chemistry	- Problem & Solution	- Osmotic pressure of electrolytes	prysical chemistry. pressure	design experiment or - relation between valor pressure and osmour	and a solution of the second and a second and the second and	constitution resource also compatisms to a source source of malacular uninter from	molecular weight from in addition beight - lecture addition of control pressure	determination of Determination of Determination of osmotic measure	processing describe membrane chemistry . Sami nermashia membrane	background of constants. Stridents are able to backs of abusical - Vant Hoffs equation for comparing ressure	concerns and theoretical complic reasonance independence for a factor of the factor of	inderstand some make calculations of to read and - Diffusion and esmosis	14 Student competence to Students are able to Student competence Osmotic measures	- Problem & Solution	calculations.		explain the curvature of solute	Students are able to - Lowering Vapor pressures by small addition	azeotropic mixtures Colligatives properties	distillations and of distillations	and principles of  - Azeotropic Mixtures Distillations and principle	curvature of miscibility - Miscibility of partial solutions	
Exams	blem & Solution	plication of Colloids		celle properties	sociation of Colloids	operties of Sols	eparations of Sols	5	pes of Colloidal Systems	xiloidal dispersions	ds and surfaces chemistry	oblem & Solution	smotic pressure of electrolytes	ssure	station between vapor pressure and osmouc		stemination of molecules unintt from	starininatori oi contour pressure	atermination of osmotic pressure	ait i foit a equation foi valifuto pressuio	ant Hoffe equation for percents	smosle and osmotic pressure	filision and osmosis	hic nrassuras	ant elevation	iculation of molecular weights from boiling	siling point elevation of solutions	solute	wering Vapor pressures by small addition	olligatives properties	distillations	eotropic Mixtures Distillations and principle	scibility of partial solutions	
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#### **LESSON PLAN OF PHYSICAL CHEMISTRY 1**

#### LESSON PLAN

Department	: Chemistry
Subject Title	: Physical Chemistry 1 (Chem. 002)
Topic	: Introduction to Physical Chemistry
Program	: 2008 ISTE Students
Lecture Time	: 3 X 50 minutes
Schedule	: First week

I. Basic Competency

Student competence to understand general knowledge of physical chemistry, the important of physical chemistry, and the relation of physical chemistry with chemistry and other sciences.

#### II. Indicator

Students have some knowledge about physical chemistry in general.

#### III. Topics/Sub-Topics

Introduction to physical chemistry: a) The definitions of Physical chemistry, the position of physical chemistry among other branch of science and chemistries, b) The important role of physical chemistry Some physical chemistry term and unit systems, conversion table and some physical and chemical characteristics.

#### **IV. Learning Methods**

- 1. Individual and grouped assignments
- 2. Students presentations
- 3. Discussions

#### V. Learning Process

Number	Activities	Time
1	<ul><li>Individual and grouped assignments</li><li>a) Student competence to read and understanding the text books of physical chemistry.</li><li>b) In addition, he/she also competence to solve problems and design experiment of physical chemistry.</li></ul>	
2	Students Presentations Student competence to perform student's personal skills in presenting his/her assignments in front of classroom.	
3	Discussions Lecturer ask the students to answer one or two questions to check their understanding about the concepts	

#### VI. Evaluation

a. an ability to communicate concepts and principles in physical chemistry

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- b. an ability to solve problems and exercises
- c. an ability to design the laboratory prototypes

Department	: Chemistry
Subject Title	: Physical Chemistry I (Chem. 001)
Topic	: Ideal and non ideal gases
Program	: 2008 ISTE Students
Lecture Time	: 3 X 50 minutes
Schedule	: Second and third weeks

I. Basic Competency

Student competence to understand some concepts dealing with ideal and non ideal gases, ideality of gases, ideal gas laws, critical phenomenon, and theoretical background related to gases

#### II. Indicator

Students are able to derive ideal gas laws, Van der Waal equations and using the equations in daily life.

**III.** Topics/Sub-Topics

Ideal and non ideal gases

- 1. Characteristic and properties of gases,
- 2. Ideal gas law (Boyle, Charles, Gay-Lussac)
- 3. Some equations related to non ideal gases or real gases
- 4. Critical Phenomenon, Compressibility factors
- 5. Non ideal gases, liquefaction of gases
- 6. Semi empirical equation of Van der Waal, theoretical backgrounds and derivation
- 7. Problem & Solution

#### **IV.** Learning Methods

- 1. Individual and grouped assignments
- 2. Students presentations
- 3. Discussions

Number	Activities	Time
1	<ul> <li>Individual and grouped assignments</li> <li>a) Student competence to read and understanding the text books of physical chemistry.</li> <li>b) In addition, he/she also competence to solve problems and design experiment of physical chemistry.</li> </ul>	
2	Students Presentations Student competence to perform student's personal skills in presenting his/her assignments in front of classroom.	
3	Discussions Lecturer ask the students to answer one or two questions to check their understanding about the concepts	

#### VI. Evaluation

- a. an ability to communicate concepts and principles in physical chemistry
- b. an ability to solve problems and exercises

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c. an ability to design the laboratory prototypes

Department	: Chemistry
Subject Title	: Physical Chemistry I (Chem. 001)
Topic	: Kinetics Molecular of gases
Program	: 2008 ISTE Students
Lecture Time	: 3 X 50 minutes
Schedule	: Fourth week

#### I. Basic Competency

Student competence to understand some concepts dealing with kinetics particle in box, Boltzmann - Maxwell statistics and some application of Maxwell - Boltzmann statistics.

#### II. Indicator

Students are able to make a derivation of molecular kinetics of gas in container, Maxwell-Boltzmann statistics and classical mechanics, gas diffusion and using Graham's law in real times problems.

#### III. Topics/Sub-Topics

Kinetics Molecular of gases

- 1. Classical mechanics of Imaginary particle in a container
- 2. Kinetics particle in container equations, calculation of a particle velocity
- 3. Boltzmann distribution, and determination of Boltzmann constant
- 4. Maxwell-Boltzmann statistic mechanics and derivation
- 5. Mean free-path
- 6. Gas diffusion and Graham's law
- 7. Some applications
- 8. Barometric equations
- 9. Problem & Solution

#### **IV. Learning Methods**

- 1. Individual and grouped assignments
- 2. Students presentations
- 3. Discussions

Number	Activities	Time
1	<ul><li>Individual and grouped assignments</li><li>a) Student competence to read and understanding the text books of physical chemistry.</li><li>b) In addition, he/she also competence to solve problems and design experiment of physical chemistry.</li></ul>	
2	Students Presentations Student competence to perform student's personal skills in presenting his/her assignments in front of classroom.	
3	Discussions Lecturer ask the students to answer one or two questions to check their understanding about the concepts	

#### VI. Evaluation

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- a. an ability to communicate concepts and principles in physical chemistryb. an ability to solve problems and exercisesc. an ability to design the laboratory prototypes

Department	: Chemistry
Subject Title	: Physical Chemistry I (Chem. 001)
Topic	: Chemical Thermodynamics
Program	: 2008 ISTE Students
Lecture Time	: 3 <sup>·</sup> X 50 minutes
Schedule	: Fifth week

I. Basic Competency

Student competence to understand some concepts dealing with chemical thermodynamics, thermodynamics processes, works and using enthalpies.

#### II. Indicator

Students are able to use first, second and third law of thermodynamics, free energy and students have an ability to solve some concepts regarding thermodynamics problems.

#### III. Topics/Sub-Topics

Chemical Thermodynamics

- 1. Thermodynamic terms and basic concepts, variables of thermodynamics
- 2. Types of systems
- 3. Intensive and extensive properties
- 4. Thermodynamic process, reversible and irreversible processes
- 5. First law of thermodynamics
- 6. Isothermal expansion work; reversible and irreversible
- 7. Work efficiency and Carnot circles
- 8. Enthalpy of a system
- 9. Second law of thermodynamics
- 10. Spontaneous and non spontaneous reactions, free energy
- 11. Third law of thermodynamics
- 12. Problem & Solution

#### **IV.** Learning Methods

- 1. Individual and grouped assignments
- 2. Students presentations
- 3. Discussions

Number	Activities	Time
1	Individual and grouped assignments	
	a) Student competence to read and understanding the text	
	books of physical chemistry.	
	b) In addition, he/she also competence to solve problems	
	and design experiment of physical chemistry.	
2	Students Presentations	
	Student competence to perform student's personal skills	
	in presenting his/her assignments in front of classroom.	
3	Discussions	
	Lecturer ask the students to answer one or two questions	
	to check their understanding about the concepts	

#### VI. Evaluation

- a. an ability to communicate concepts and principles in physical chemistry
- b. an ability to solve problems and exercises
- c. an ability to design the laboratory prototypes

Department	: Chemistry
Subject Title	: Physical Chemistry I (Chem. 001)
Topic	: Thermo Chemistry
Program	: 2008 ISTE Students
Lecture Time	: 3 X 50 minutes
Schedule	: sixth and seventh weeks

#### I. Basic Competency

Student competence to understand some concepts regarding thermo chemistry, the heat and enthalpies.

#### II. Indicator

Students are able to use thermo chemistry equations to real times problems,  $C_v$ ,  $C_p$ , heats. Students are able to make a design of experiments based on calorimetric measurements.

#### III. Topics/Sub-Topics

Thermo chemistry

- 1. Changes in state at constant Volume and Temperature
- 2. The relation between  $C_p$  and  $C_v$
- 3. Thermodynamics application to chemical reactions, the heat of reaction
- 4. The formation reaction
- 5. Conventional values of molar enthalpies
- 6. The determination of heats of formation
- 7. Sequences of reactions: Hess's law
- 8. Heats of solution and dilution
- 9. Heat of reaction at constant pressure and volume
- 10. Bond enthalpies
- 11. Calorimetric measurements

#### IV. Learning Methods

- 1. Individual and grouped assignments
- 2. Students presentations
- 3. Discussions

Number	Activities	Time
1	<ul> <li>Individual and grouped assignments</li> <li>a) Student competence to read and understanding the text books of physical chemistry.</li> <li>b) In addition, he/she also competence to solve problems and design experiment of physical chemistry.</li> </ul>	
2	Students Presentations Student competence to perform student's personal skills in presenting his/her assignments in front of classroom.	
3	Discussions Lecturer ask the students to answer one or two questions to check their understanding about the concepts	

#### VI. Evaluation

- a. an ability to communicate concepts and principles in physical chemistry
- b. an ability to solve problems and exercises
- c. an ability to design the laboratory prototypes

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#### LESSON PLAN

Department Subject Title Topic Program Lecture Time Schedule

- : Chemistry
  : Physical Chemistry I (Chem. 001)
  : Chemical Equilibrium
  : 2008 ISTE Students
  : 3 X 50 minutes
  : Ninth week
- I. Basic Competency

Student competence to understand some concepts dealing with chemical equilibrium, heterogeneous and homogeneous reaction.

#### II. Indicator

Students are able to use some equations in chemical equilibrium to real times problems.

#### III. Topics/Sub-Topics

**Chemical Equilibrium** 

- 1. Definitions
- 2. Thermodynamics of equilibrium
- 3. K<sub>p</sub> and K<sub>c</sub> properties and calculations
- 4. Homogeneous reaction equilibrium
- 5. Equilibrium in gas states
- 6. Equilibrium in liquid states
- 7. Temperature dependence
- 8. Heterogeneous reaction equilibrium
- 9. The equilibrium constant for heterogeneous reactions
- 10. Effects of pressure/temperature on heterogeneous equilibrium
- 11. Distribution law
- 12. Problem & Solution

#### IV. Learning Methods

- 1. Individual and grouped assignments
- 2. Students presentations
- 3. Discussions

Number	Activities	Time
1	<ul><li>Individual and grouped assignments</li><li>a) Student competence to read and understanding the text books of physical chemistry.</li><li>b) In addition, he/she also competence to solve problems and design experiment of physical chemistry.</li></ul>	
2	Students Presentations Student competence to perform student's personal skills in presenting his/her assignments in front of classroom.	
3	Discussions Lecturer ask the students to answer one or two questions to check their understanding about the concepts	

#### VI. Evaluation

- a. an ability to communicate concepts and principles in physical chemistryb. an ability to solve problems and exercisesc. an ability to design the laboratory prototypes

Department	: Chemistry
Subject Title	: Physical Chemistry I (Chem. 001)
Topic	: Liquids
Program	: 2008 ISTE Students
Lecture Time	: 3 X 50 minutes
Schedule	: Tenth week

I. Basic Competency

Student competence to understand some concepts dealing with liquids, liquids dynamics and some physical properties of liquids.

#### II. Indicator

Students have some knowledge in liquids, liquids physical properties and having some knowledge in measurements of surface tension, viscosity, refractive index and optical activity.

#### III. Topics/Sub-Topics

Liquids

- 1. Critical Phenomena in liquids
- 2. P-V-T relations
- 3. Van der Waal relations on liquefaction of gases
- 4. Kinetic molecular description
- 5. Intermolecular forces in liquids
- 6. Vapor pressure
- 7. Measurements of vapor pressure
- 8. Surface tension of liquids
- 9. Measurements of surface tension
- 10. Viscosity of liquids
- 11. Measurements of viscosity
- 12. Refractive index
- 13. Measurements of refractive index
- 14. Optical activity
- 15. Measurements of optical activity
- 16. Problem & Solution
- **IV.** Learning Methods
  - 1. Individual and grouped assignments
  - 2. Students presentations

#### 3. Discussions

#### V. Learning Process

Number	Activities	Time
1	<ul> <li>Individual and grouped assignments</li> <li>a) Student competence to read and understanding the text books of physical chemistry.</li> <li>b) In addition, he/she also competence to solve problems and design experiment of physical chemistry.</li> </ul>	
2	Students Presentations Student competence to perform student's personal skills in presenting his/her assignments in front of classroom.	
3	Discussions Lecturer ask the students to answer one or two questions to check their understanding about the concepts	

#### VI. Evaluation

- a. an ability to communicate concepts and principles in physical chemistry
  b. an ability to solve problems and exercises
  c. an ability to design the laboratory prototypes

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Department	: Chemistry
Subject Title	: Physical Chemistry I (Chem. 001)
Topic	: Solutions
Program	: 2008 ISTE Students
Lecture Time	: 3 X 50 minutes
Schedule	: Twelfth and thirteenth weeks

I. Basic Competency

Student is able to describe the terms of solutions, ideal solutions and Raoult's law, miscibility of mixtures and distillation principles

II. Indicator

Student competence to understand some knowledge in solutions, solubility, and miscibility. Students are having some knowledge in liquids mixture, curvature of miscibility and principles of distillations and azeotropic mixtures. Students are able to explain the curvature and to make calculations.

III. Topics/Sub-Topics

Solutions

- 1. Definition
- 2. Factors affecting solubility
- 3. Kinds of Solutions
- 4. Ideal Solutions and Raoult's Law
- 5. Miscibility (Complete Binary and Ternary Mixtures)
- 6. Miscibility of partial solutions
- 7. Azeotropic Mixtures Distillations and principle of distillations
- 8. Colligatives properties
- 9. Lowering Vapor pressures by small addition of solute
- 10. Boiling point elevation of solutions
- 11. Calculation of molecular weights from boiling point elevation
- **IV. Learning Methods** 
  - 1. Individual and grouped assignments
  - 2. Students presentations
  - 3. Discussions

Number	Activities	Time
1	<ul> <li>Individual and grouped assignments</li> <li>a) Student competence to read and understanding the text books of physical chemistry.</li> <li>b) In addition, he/she also competence to solve problems and design experiment of physical chemistry.</li> </ul>	
2	Students Presentations	
	Student competence to perform student's personal skills	
	in presenting his/her assignments in front of classroom.	
3	Discussions	
	Lecturer ask the students to answer one or two questions	
	to check their understanding about the concepts	

#### VI. Evaluation

- a. an ability to communicate concepts and principles in physical chemistry
- b. an ability to solve problems and exercises
- c. an ability to design the laboratory prototypes

Department	: Chemistry
Subject Title	: Physical Chemistry I (Chem. 001)
Горіс	: diffusion and osmosis
Program	: 2008 ISTE Students
Lecture Time	: 3 X 50 minutes
Schedule	: fourteenth week

#### I. Basic Competency

Student competence to understand some concepts and theoretical background of osmotic pressure.

II. Indicator

Students are able to make calculations of osmotic pressure. Students are able to describe membrane, determination of molecular weight from osmotic pressure.

#### III. Topics/Sub-Topics

Diffusion and osmosis

- 1. Osmosis and osmotic pressure
- 2. Vant Hoff's equation for osmotic pressure
- 3. Semi permeable membrane
- 4. Determination of osmotic pressure
- 5. Isotonic solutions
- 6. Determination of molecular weight from osmotic pressure
- 7. Relation between vapor pressure and osmotic pressure
- 8. Osmotic pressure of electrolytes
- 9. Problem & Solution

#### IV. Learning Methods

- 1. Individual and grouped assignments
- 2. Students presentations
- 3. Discussions

#### V. Learning Process

Number	Activities	Time
1	Individual and grouped assignments	
	a) Student competence to read and understanding the text	
	books of physical chemistry.	
	b) In addition, he/she also competence to solve problems	
	and design experiment of physical chemistry.	

2	Students Presentations
	Student competence to perform student's personal skills
	in presenting his/her assignments in front of classroom.
3	Discussions
	Lecturer ask the students to answer one or two questions
	to check their understanding about the concepts

#### VI. Evaluation

- a. an ability to communicate concepts and principles in physical chemistry
- b. an ability to solve problems and exercises
- c. an ability to design the laboratory prototypes

: Chemistry
: Physical Chemistry I (Chem. 001)
: Colloids and Surfaces Chemistry
: 2008 ISTE Students
: 3 X 50 minutes
: Fifteenth and sixteenth weeks

I. Basic Competency

Student competence to understand some concepts about colloids dispersion, association colloids and the relation of colloids and surface phenomenon.

#### II. Indicator

Students are able to describe the colloids dispersion, colloidal systems, colloids properties, association colloids. Students are able to describe colloidal synthesis and able to design problem solving in real times problems.

- III. Topics/Sub-Topics
  - 1. Colloids and surfaces chemistry
  - 2. Colloidal dispersions
  - 3. Types of Colloidal Systems
  - 4. Sols
  - 5. Preparations of Sols
  - 6. Properties of Sols
  - 7. Association of Colloids
  - 8. Micelle properties
  - 9. Emulsion
  - 10. Application of Colloids
- **IV.** Learning Methods
  - 1. Individual and grouped assignments
  - 2. Students presentations
  - 3. Discussions

Number	Activities	Time
1	<ul> <li>Individual and grouped assignments</li> <li>a) Student competence to read and understanding the text books of physical chemistry.</li> <li>b) In addition, he/she also competence to solve problems and design experiment of physical chemistry.</li> </ul>	
2	Students Presentations Student competence to perform student's personal skills in presenting his/her assignments in front of classroom.	
3	Discussions Lecturer ask the students to answer one or two questions to check their understanding about the concepts	

#### VI. Evaluation

- a. an ability to communicate concepts and principles in physical chemistry
- b. an ability to solve problems and exercises
- c. an ability to design the laboratory prototypes

Lecturers :

- 1. Drs. Ali Amran, M.Pd, M.A, Ph.D
- 2. Sherly Kasuma Warda Ningsih, S.Si, M.Si

#### CHEMISTRY DEPARTMENT FACULTY OF MATHEMATICS AND NATURAL SCIENCES STATE UNIVERSITY OF PADANG

#### **MIDTERM EXAMINATION**

Subject	: Physical Chemistry I
Study program	: ISTE Students
Time	: 2 hours
Lecturer	: Drs. Ali Amran, M.Pd, M.A, Ph.D
	Sherly Kasuma Warda Ningsih, S.Si, M.Si

#### ESSAY

- 1. What is an ideal and non ideal gases ? Give applications of ideal gas law ?
- Calculate the partial volumes of H<sub>2</sub>O, O<sub>2</sub>, and N<sub>2</sub> in air saturated with water vapor at 45°C and at 1 atm total pressure. Assume ideal behavior and one mole of total gas.
- 3. Explain in briefly the distribution of molecular velocities in one-dimensional, twodimensional and three-dimensional!
- 4. Calculate  $Z_1$  and  $Z_{11}$  for oxygen at 28°C and 1.2 atm pressure;  $\sigma$  is 5.45 Å
- 5. Calculate the work done by 8 moles of an ideal gas during expansion from 4 atm at 5 °C to 1.5 atm at 43°C against a constant pressure of 0.5 atm. If for the gas  $C_p = 5.0$  calmole<sup>-1</sup> degree<sup>-1</sup>, find also  $\Delta E$ ,  $\Delta H$ , and q for the process.
- 6. Assuming N<sub>2</sub> to be an ideal gas, calculate the work done by 58 g of N<sub>2</sub> in expanding isothermally and reversibly from a volume of 8 liters to 15 liters at 28°C. What are q,  $\Delta E$ ,  $\Delta H$  of the process ?
- 7. Three g of ice at 0°C is added to 25 g of H<sub>2</sub>O at the boiling point. What will be the final temperature and what is the entropy change accompanying the process ? Assume that the heat of fusion of H<sub>2</sub>O is 92 cal/g and the specific heat 1 cal/g-degree.

#### CHEMISTRY DEPARTMENT FACULTY OF MATHEMATICS AND NATURAL SCIENCES STATE UNIVERSITY OF PADANG

#### FINAL EXAMINATION

Subject	: Physical Chemistry I
Study program	: ISTE Students
Time	: 2 hours
Lecturer	: Drs. Ali Amran, M.Pd, M.A, Ph.D
	Sherly Kasuma Warda Ningsih, S.Si, M.Si

#### ESSAY

- 1. Explain the term of vapour pressure, surface tension, viscosity and refractive index ?
- 2. A capillary tube of internal diameter 0.30 mm is dipped into water when water rises 20 cm. Calculate the surface tension of water and mention the unit of surface tension.
- 3. In the determination of surface tension of a liquid by the drop-number method, it gives 60 drops while water gave 22 drops for the same volume. The densities of the liquid and water are 1.005 and 0.998 g/cm<sup>3</sup> respectively. Find the surface tension of the liquid if that of waters is 45 dynes/cm.
- 4. Give definition of solution and explain in briefly the types of solutions?
- 5. How to get the azeotropic mixtures of type I, II and III?
- 6. What is a colloid and types of the colloidal systems?
- 7. What is the essential difference between lyophilic and lyophobic colloids ?
- 8. Explain in briefly the application of colloid in science and technology?

HANDOUTS AND WORKSHEETS OF PHYSICAL CHEMISTRY I



By:

Drs. Ali Amran, M.Pd, M.A, Ph.D Sherly Kasuma Warda Ningsih, S.Si, M.Si

#### **CHEMISTRY DEPARTMENT**

FACULTY OF MATHEMATICS AND NATURAL SCIENCES STATE UNIVERSITY OF PADANG

#### HANDOUTS OF PHYSICAL CHEMISTRY 1

#### HANDOUTS First Week (3 X 50) minutes

#### PHYSICAL CHEMISTRY

#### I. INTRODUCTION

The observation that physical chemistry (like other branches of science) organizes and explains are summarized by scientific laws. A scientific law is summary of experience. The subject is characterized by three main approaches; the discussion of bulk properties in terms of thermodynamics, the use of spectroscopy to explore the behavior of individual atoms and molecules, and the analysis of the rates and mechanisms of chemical change.

#### A. Brief Description of Subject

The definitions of physical chemistry
 Physical chemistry comprises the quantitative and theoretical study of the

properties of the elements in their various states of combination.

#### 2. The important role of Physical Chemistry

Physical chemistry establishes and develops the principles that are used to explain and interpret the observations made in the other branches of chemistry.

#### 3. Some physical chemistry term and unit systems

1. The amount of substance (moles)

Another preliminary idea we need is that in chemistry we are normally concerned with enormous numbers of atoms. The number of atoms in 1 g of matter is of the order of  $10^{22}$  to  $10^{23}$ , which is larger than the number of stars in the visible universe. To express these large numbers it is conventional in chemistry to refer to the amount of substances n and to express that amount in

the unit called the mole. The formal definition og a mole is that it is the amount of substance that contains as many objects (atoms, molecules, formula units, ions, or other specified entities) as there are atoms in exactly 12 g of carbon-12. This number is found experimentally to be approximately  $6.02 \times 10^{23}$ . Therefore, if a sampel contains N specified entities, then the amount of substance it contains is  $n = N/N_A$ , where  $N_A$  is a quantity with units, not a pure number.

#### 2. Energy

The central concept of all explanations in physical chemistry, as in so many other branches of physical science, is that of energy. A formal definition of energy is capacity to do work. We shall often make use of the universal law of nature that energy that energy is conserved, that is energy can be neither created nor destroyed. Therefore, although energy can be transferred from one part of the universe to another (as when water in a baker is heated by electricity generated in a power station), the total quantity of energy available is a constant.

#### 3. Electromagnetic radiation

The energy of the electromagnetic field will be important to us because we shall often be concerned with the absorption and emission of radiation. Indeed, not only does spectroscopy depend crucially on the electromagnetic field, but some species acquire the energy they need to react from radiation.

#### 4. Energy units

All three types of energy, kinetic, potential, and electromagnetic, have two features in common. The most important feature is that they are freely interconvertible from one form to the other.

#### HANDOUTS

Second and Third Week 2 (3 X 50) minutes

#### **II. IDEAL AND NON IDEAL GASES**

Gas is the simplest state of matter, a form of matter that fills any container it occupies. we shall find it helpful to picture a gas as a collection of molecules (or atoms) in continuous random motion, with average speeds that increase as the temperature is raised. A gas differs from a liquid in that, except during collisions, the molecules of a gas are widely separated from one another and move in paths that are largely unaffected by intermolecular forces.

A. Brief Description of Subject

#### 1. Characteristic and properties of gases

Gas is the simplest state of matter, a form of matter that fills any container it occupies. we shall find it helpful to picture a gas as a collection of molecules (or atoms) in continuous random motion, with average speeds that increase as the temperature is raised. A gas differs from a liquid in that, except during collisions, the molecules of a gas are widely separated from one another and move in paths that are largely unaffected by intermolecular forces.

There are two kinds of gas :

- 1. The Perfect gas ( Ideal gases)
- 2. The Real gas (Non ideal gases)

#### 2. Ideal gas law (Boyle, Charles, Gay-Lussac)

Boyle's Law p V= constant, at constant n, T (Eq. 1) Charles's Law and Gay-Lussac's Law V= constant x T, at constant n, pp = constant x T, at constant n, V (Eq. 2)

This expression is consistent with Boyle's law  $(p \ V = \text{constant})$  when n and T are constant, with both forms of Charles's law  $(p \ ex: T, V \ ex; T)$  when n and either V or p are held constant, and with Avogadro's principle (V = n) when p and T are constant. The constant of proportionality, which is found experimentally to be the same for all gases, is denoted R and called the gas constant. The resulting expression :

pV=nRT (Eq. 3)

A gas that obeys eq.3 exactly under all conditions is called a perfect gas (or *ideal gas*).



Fig. 1 Plot of Eq. 3 showing isothermal, isobaric, and isochoric section

3. Some equations related to non ideal gases/ real gases

**Real gases do not obey the perfect gas equation** exactly. Real gases show deviations from the perfect gas equation because molecules interact with one another. Repulsive forces between molecules assist expansion and attractive forces assist compression.

To differentiate the ideal and non ideal gases, there are two methods :

- 1. Compressibility Factor (Z) : Z < 1 and Z > 1
- 2. Critical points (by using van der Waal equation)

#### Deviations from ideality-critical behavior

The equation of state o an actual gas is given in one form by Eq.4

$$PV = A(T) + b(T)P + c(T)P^{2} + ...$$
 (Eq. 4)

Where b(T), c(T) and so on are not only functions of temperature, but also are characteristic of each particular gas. A form that is more useful for theoretical purposes is the following :

$$PV = A(T) (1 + B(T)/V + C(T)/V^2 + ...)$$

Or

$$PV/RT = 1 + B(T)/V + C(T)/V^2 + ....)$$
 (Eq. 5)

This type of equation is known as a virial equation, and B(T) and C(T) are called the second and third virial coefficients, respectively.

The left-hand term of (Eq. 5) PV/RT is called the compressibility factor (Z)

Z = 1, for a perfect gas

Z>1 and Z<1 for the Non ideal gases



Fig 2. Compression and eventual condensation of a vapor

The gas substance which can exist in both the gas and liquid state at a given temperature is often distinguished from gases generally by being called vapor. Clearly, as a vapor is compressed at constant temperature, condensation will begin to occur when the pressure of the vapor has reached the vapor pressure of the liquid. The experiment must be visualized as involving a piston and cylinder immersed in a thermostat bath; the enclosed space contains a certain amount of the substance, initially as vapor, and the piston is steadily pushed into the cylinder.


Fig 3. Isotherm for the real vapor

# 4. Critical Phenomenon

There is not only a critical temperature, but also a critical point, which is the vestigial point left by the condensation line as it just vanishes; alternatively the critical point is the maximum of the broken line of the figure. This point then defines a critical pressure ( $P_c$ ) and a critical volume ( $V_c$ ) as well as  $T_c$ . The critical temperature can also be considered as the temperature above which we speak of a gas rather than of a vapor. Compression of a gas (a gaseous substance above its critical temperature) results not in condensation, but only in a steady increase in pressure.

If the >TC : Still remain gas (Ideal gas behavior)

If the < TC : the gas will be non ideal gas

$$T_c = 8a/27bR$$

$$V_c = 3b$$

$$P_c = a/27b^2$$

$$b = RT_{c'}8P_c$$

$$a = 27(RT_c)^2/64P_c$$

#### 5. Semi empirical equation of van der Waal

Van der Waals introduce between ideal and non ideal gases of critical points ( $T_c$ ,  $V_c$ ,  $P_c$ ) by compressing a certain gas in thermostat bath.

The volume of non ideal gas > the volume of ideal gas, to make the volume of non ideal gas the same as the volume of ideal gas by decreasing the volume of non ideal by b factor;

 $V_{ideal gas} = V_{non ideal gas} - b$   $P_{ideal gas} > P_{non ideal gas}$   $P_{ideal gas} = P_{non ideal gas} + a/V^{2}$   $(P + a/V^{2}) (V-b) = RT$ (for one

(P + a/V<sup>2</sup>) (V-b) = RT (for one mole)(P + na<sup>2</sup>/V<sup>2</sup>) (V-b) = n R T (for n mole)

For one mole gas :

$$\left(p+\frac{a}{v^2}\right)(v-b) = RT$$

For n mole gas :

$$\left(p + \frac{n^2 a}{V^2}\right)(v - nb) = RT$$



Fig 4. Isotherms calculated from the van der Waals's equation

# **B.** Questions and Problems

- 1. What is ideal and nonideal gases?
- 2. What is application of ideal gas law?
- 3. Studying question and some problem in physical chemistry by Adamson
- C. Read the text (Physical Chemistry by Adamson, A.W) in the page 71-92 to improve your understanding
- D. Solving the problems in the page 97-99 as far as you can

# HANDOUTS

Fourth Week

## 3 X 50 minutes

# **III. KINETIC MOLECULAR THEORY OF GASES**

#### A. Brief Description of Subject

#### 01. Introduction

The treatment of ideal and non ideal gas in chapter 1 is carried out largely from a phenomenological point of view. Behavior is described in terms of the macroscopic variables P, V, T, although some molecular interpretation was included in the discussion of the a and b parameters of the van der waals equation.

In the kinetic molecular theory of gases, a gas is considered to be made up of individual molecules, each having kinetic energy in the form of random motion. The pressure and the temperature of a gas are treated as manifestations of this kinetic energy.

# 02. Boltzmann Distribution law

The Boltzmann principle is central to all of the statistical aspects of physical chemistry. A system that is isolated (no exchange of matter, heat, or work with its surrounding), so that its total energy E is constant and the total number of molecules N is also constant. The general statements of the preceding conditions are then :

 $N = \Sigma Ni = constant$ 

 $E = \Sigma$  Niei = constant

# 03. Barometric Equation

A very simple application of the Boltzmann distribution law is to the case of a column of ideal gas in a uniform gravitational field. The potential energy of a molecule of mass m at an elevation h is just mgh, where g is the acceleration due to gravity.

 $Ni = A e^{-e/kT}$ 

The ratio of the numbers of molecules at elevations  $h_2$  and  $h_1$  is just

$$N_2/N_1 = e^{-mg(h - h_1).kT}$$

If the column is at a uniform temperature, if we take  $h_1 = 0$  (i.e sea level)

$$N_h = N_o e^{-mgh.kT}$$

For an ideal gas at constant temperature, N is proportional to concentration C, and molecular weight M is Avogadro's number times m, or

$$M = N_A m$$

Also noting that  $R = N_A$ . k

$$C_h = C_o e^{-Mgh.RT}$$

Since C is proportional to pressure at constant temperature,

$$P_{h} = P_{o}e^{-Mgh.RT}$$
 (Eq.1)

Eq.1 is known as the barometric equation



Fig 1. Decrease of barometric pressure with altitude for air at 298 K

04. The distribution of molecular velocities

# 1. a one-dimensional gas

that is to a system of molecules having only kinetic energy due to the motion along one direction in a space (the x-axis). We assume ideal gaslike behavior.

$$dN(u)/N_A = (m/2\pi kT)^{\frac{1}{2}} [exp(-mu^2/2kT)]du$$
 (Eq.2)

Eq.2 is known as the Maxwell-Boltzmann equation

# 2. The case of a two-dimensional gas

Allow velocities along the x and y directions, given by u and v. the probability function p(u,v) is now the product of the two separate functions, so that the Maxwell-Boltzmann equation two dimensions is

$$dN(u,v)/N_A = A\{exp[-m(u^2 + v^2)/2kT)]\} du dv$$
  
 $dN(u,v)/N_A = m/2\pi kT\{exp[-m(u^2 + v^2/2kT]\} du$   
 $dv$ 



Fig. 3 Molecular velocity distribution for a gas in two dimensions

# 3. A three-dimensional gas

The extension to three dimensions follows the same series of steps. The basic distribution law is :

$$dN(u,v,w)/N_A = A\{exp[-m(u^2 + v^2 + w_2)/2kT]\} du dv dw$$

 $dN(u,v,w)/N_A = (m/2\pi kT)^{3/2} \{exp[-m(u^2 + v^2 + w^2)/2kT]\}du dv dw$ 

c<sup>2</sup> = u<sup>2</sup> + v<sup>2</sup> + w<sup>2</sup> $4\pi c<sup>2</sup> dc = du dv dw$ 

The distribution law in net velocity c is then



Fig 4. Three dimensional velocity distribution for N2 at 25 °C and 1023 °C

# 05. Average quantities from the distribution laws

To summarize this section, the three characteristic velocities for a gas in three dimensions are :

Most probable

$$c_p = (2kT/m)^{\frac{1}{2}}$$
  
 $c^{-} = (8kT/\pi m)_{\frac{1}{2}} = 1.128 c_p$   
root mean square  $(c^{-})^{\frac{1}{2}} = (3kT/m)^{\frac{1}{2}} = 1.225c_p$ 

Numerous organic reagents have been developed for gravimetric determination of inorganic species. We encounter two types of organic reagents. One forms slightly soluble nonionic products called coordination compounds; the other forms products in which the bonding between the inorganic species and the reagent is largely ionic. Example of organic precipitating agents is 8-hydroquinoline, dimethylglyoxime, and sodium tetraphenylboron.

# 06. Some applications of simple kinetic molecular theory's

- 1. Collision frequency on a plane surface
- 2. Graham's law

An important quantity given by simple kinetic molecular theory is the frequency with the molecules hit a plane surface. This frequency is, for example a central to the kinetic treatment of adsorption-desorption processes or more generally, to those of evaporation and condensation.

 $dZ(u) = n_0 (m/2\pi kT)^{\frac{1}{2}} [exp(-mu^2/2kT)] u du$ 

Z = the total surface collision frequency per unit area

...

$$Z = n (kT/2\pi m)^{5}$$

Since n = P/kT

$$Z = P(1/2\pi mkT)^{4} = PNA (1/2\pi MRT)^{4}$$

$$Z_m = p \left( \frac{kT}{2\pi m} \right)^{\frac{1}{2}}$$

P = density

#### 07. Graham's Law

Graham studied the rate of effusion of gases, that is the rate of escape of gas through a small hole or orifice. He found that for a given temperature and pressure difference, the rate of effusion of a gas is inversely proportional to the square root of its density, for the two different gases, then :

$$n_1/n_2 = (p_2/p_1)^{\frac{1}{2}}$$

$$n_1/n_2 = (M_2/M_1)^{\frac{1}{2}}$$

M = molecular weight

## 08. Bimolecular collision frequency

The frequency of collisions between like molecules (identical molecules) symbolized by  $Z_{11}$ . Imagine a molecule of radius  $r_1$  moving with an average velocity  $c_1$ . As it moves it will contact, that is, collide with, any second molecule lying within cylinder o radius  $2r_1$ .

$$Z_1 = 2^{\frac{1}{2}} \pi \sigma_1^2 c_1 n_1 = 4 \sigma_1^2 (\pi k T/m)^{\frac{1}{2}} n_i$$

 $Z_1$  = collision frequency for a molecule

$$Z_{11} = \pi (\frac{1}{2})^{\frac{1}{2}} \sigma_1^2 c_1 n_i^2 = 2\sigma_1^2 (\pi kT/m)^{\frac{1}{2}} n_i^2$$

 $Z_{11}$  = Bimolecular collision frequency (like molecules)

 $Z_{11}$  gives the collisions per unit volume per second

$$Z_{12} = 2 \sqrt{2} \sigma_{12}^{2} (\pi k T/\mu_{12})^{\frac{1}{2}} n_{1} n_{2}$$

 $Z_{12}$  = Bimolecular collision frequency (unlike molecules)

09. Mean free path ( $\lambda$ )

The mean free path ( $\lambda$ ) of a molecule is the average distance traveled between collisions.  $\lambda$  is just the mean velocity divided by the collision frequency,

 $\lambda = c/Z_1$ 

 $\lambda = 1/\sqrt{2} \pi \sigma^2 n$ 

 $\lambda = \mathbf{k} \mathbf{T} / \sqrt{2\pi \sigma^2 P}$ 

B. Questions and Problem

- 1. What is the kinetic molecular theory of gases?
- 2. What is application of kinetic molecular theory of gases !
- 3.

C. Read the text (Physical Chemistry by Adamson, A.W) in the page 92-97 to improve your understanding

D. Solving the problems in the page 97-99 as far as you can

UIIIV. NEGERI PADANG

## HANDOUTS

#### Fifth and sixth Week

# 2(3X 50) minutes

# IV. CHEMICAL THERMODYNAMICS

## A. Brief Description of Subject

#### 01. Thermodynamic terms

The system is what we focus our attention on. The surroundings is everything else in the universe.

We need to consider only the part interacts with the system.

#### 02. Types of systems

An open system : if matter can be transferred through the boundary between the system and its surrounding (an open system can exchange matter end energy with its surroundings).

A closed system : if matter cannot pass through the boundary (can exchange energy with its surroundings, but it cannot exchange matter). Both open and closed systems can exchange energy with their surroundings.

An isolated system : a closed system that has neither mechanical nor thermal contact with its surrounding.

#### 03. Intensive and extensive properties

**Extensive properties** depend on the size (the extent) of the sample. Examples of extensive properties are mass and volume and internal energy.

**Intensive properties** independent on the extent of the sample. Examples of intensive properties temperature, density and pressure.

#### **Expansion Work**

We begin by discussing expansion work, the work arising from a change in volume. This type of work includes the work done by a gas as it expands and drives back the atmosphere. Many chemical reactions result in the generation or consumption of gases (for instance the thermal decomposition of calcium carbonate or the combustion of octane) and the thermodynamic characteristics o a reaction depend on the work it can do. The term "expansion work" also include work associated with negative changes of volume that is compression.

### **Reversible expansion**

A reversible change in thermodynamics is a change that can be reversed by an infinitesimal modification of a variable. The key word 'infinitesimal' sharpens the everyday meaning of the word 'reversible' as something that can change direction. We say that a system is in equilibrium with its surroundings if an infinitesimal change in the conditions in opposite directions results in opposite changes in its state. One example of reversibility that we have encountered already is the thermal equilibrium of two systems with the same temperature. The transfer of energy as heat between the two is reversible because, if the temperature of either system is lowered infinitesimally, then energy flows into the system with the lower temperature. If the temperature of either system at thermal equilibrium is raised infinitesimally, then energy flows out of the hotter system.

$$dW = -P_{ex}dV = -p \, dV \tag{Eq.3}$$

#### **Irreversible expansion**

If, on the other hand, the external pressure differs measurably from the internal pressure, then changing  $p_{ex}$  infinitesimally will not decrease it below the pressure of the gas, so will not change the direction of the process. Such a system is not in

mechanical equilibrium with its surroundings and the expansion is thermodynamically irreversible.

#### Isothermal reversible expansion

\_\_\_\_

Consider the isothermal, reversible expansion of a perfect gas. The expansion is made isothermal by keeping the system in thermal contact with its surroundings (which may be a constant-temperature bath). Because the equation of state is pV = nRT, we know that at each stage p = nRT/V, with V the volume at that stage of the expansion. The temperature T is constant in an isothermal expansion, so (together with n and R) it may be taken utside the integral. It follows that the work of reversible isothermal expansion of a perfect gas from Vi to Vf at a temperature T is

$$\mathbf{w} = -\mathbf{n}\mathbf{R}\mathbf{T}\int^{\mathbf{V}\mathbf{f}} d\mathbf{V}/\mathbf{V} = -\mathbf{n}\,\mathbf{R}\mathbf{T}\,\mathbf{ln}\,(\mathbf{V}\mathbf{f}/\mathbf{V}\mathbf{i}) \tag{Eq.4}$$

When the final volume is greater than the initial volume, as in an expansion, the logarithm in Eq. 4 is positive and hence w < 0. In this case, the system has done work on the surroundings and the internal energy of the system has decreased as a result. The equations also show that more work is done for a given change of volume when the temperature is increased. The greater pressure of the confined gas then needs a higher opposing pressure to ensure reversibility.

#### Enthalpy of system

The change in internal energy is not equal to the energy transferred as heat when the system is free to change its volume. Under these circumstances some of the energy supplied as heat to the system is returned to the surroundings as expansion work (Fig. 4), so dU is less than *dq*. However, we shall now show that in this case the energy supplied as heat at constant pressure is equal to the change in another thermodynamic property of the system, the enthalpy. The definition of enthalpy

The enthalpy (H) is defined as

$$\mathbf{H} = \mathbf{U} + \mathbf{P}\mathbf{v}$$

Where p is the pressure of the system and V is its volume. Because U, p, and V are all state functions, the enthalpy is a state function too. As is true of any state function, the change in enthalpy,  $\Delta H$ , between any pair of initial and final states is independent of the path between them.

The change in enthalpy is equal to the energy supplied as heat at constant pressure (provided the system does no additional work)

dH = dq (at constant pressure, no additional work)  $\Delta H = \Delta U + \Delta P v$   $\Delta H = q_p$  $\Delta H =$  enthalpy changes

#### 04. Thermodynamic processes

- An exothermic process is a process that releases energy as heat into its surroundings. All combustion reactions are exothermic.
- An endothermic process is a process in which energy is acquired from its surroundings as heat. An example of an endothermic process is the vaporization of water.

#### The Internal Energy

In thermodynamics, the total energy of a system is called its internal energy (U). The internal energy is the total kinetic and potential energy of the molecules in the system. We denote by  $\Delta U$  the change in the internal energy when a system changes from an initial state i with internal energy (Ui) to a final state f of internal energy Uf.

$$\Delta U = U\mathbf{f} - U\mathbf{i} \tag{Eq. 1}$$

The first law of thermodynamics expressed as follows : "The internal energy of an isolated system is constant".

#### 06. The second law of thermodynamics

#### Entropy

Entropy is the basic concept for discussing the direction of natural change, but to use it we have to analyse changes in both the system and its surroundings.

The First Law of thermodynamics led to the introduction of the internal energy, *U*. The internal energy is a state function that lets us assess whether a change is permissible: only those changes may occur for which the internal energy of an isolated system remains constant. The law that is used to identify the signpost of spontaneous change, the Second Law of thermodynamics, may also be expressed in terms of another state function, the entropy, *S*. We shall see that the entropy (which we shall define shortly, but is a measure of the energy dispersed in a process) lets us assess whether one state is accessible from another by a spontaneous change. The First Law uses the internal energy to identify *permissible* changes; the Second Law uses the entropy to identify the *spontaneous changes* among those permissible changes.

The Second Law of thermodynamics can be expressed in terms of the entropy: The entropy of an isolated system increases in the course of a spontaneous change:

$$\Delta S_{tot} > 0$$

where  $S_{tot}$  is the total entropy of the system and its surroundings. Thermodynamically irreversible processes (like cooling to the temperature of the surroundings and the free expansion of gases) are spontaneous processes, and hence must be accompanied by an increase in total entropy.

The thermodynamic definition of entropy is based on the expression

# $dS = dq_{rev}/T$

07. The third law of thermodynamics

It follows from the Nernst theorem that, if we arbitrarily ascribe the value zero to the entropies of elements in their perfect crystalline form at T = 0, then all perfect crystalline compounds also have zero entropy at T=0 (because the change in entropy that accompanies the formation of the compounds, like the entropy of all transformations at that temperature, is zero). This conclusion is summarized by the Third Law of thermodynamics:

#### The entropy of all perfect crystalline substances is zero at T = 0

As far as thermodynamics is concerned, choosing this common value as zero is then a matter of convenience. The molecular interpretation of entropy, however, justifies the value S = 0 at T = 0. Table 1. Standard Third-Law entropies at 298 K

	$S_{m}^{o}(JK^{-1}mol^{-1})$
Solids	
Graphite, C (s)	5.7
Diamond, C (s)	2.4
Sucrose, $C_{12}H_{22}O_{11}$ (s)	360.2
Iodine, I <sub>2</sub> (s)	116.1
Liquids	
Benzene, $C_6H_6$ (1)	173.3
Water, H <sub>2</sub> O (1)	69.9
Mercury, Hg(1)	76.0
Gases	
Methane, CH <sub>4</sub> (g)	186.3
Carbon dioxide, CO <sub>2</sub> (g)	213.7
Hydrogen, H <sub>2</sub> (g)	130.7
Helium, He (g)	126.2
Ammonia, NH <sub>3</sub> (g)	192.4

# 08. Free Gibbs energy

One is the Helmholtz energy, A, which is defined as

A = U - TS

The other is the Gibbs energy, G:

G=H-TS

When the state of the system changes at constant temperature, the two properties change as follows:

dA=dU-TdS

dG = dH - TdS

 $\Delta A = \Delta U - T \Delta S$ 

 $\Delta G = \Delta H - T \Delta S$ 

Where :

 $\Delta G = -$  (irreversible process/ spontaneous process)  $\Delta G = 0$  (reversible process)  $\Delta G = +$  (non spontaneous process)

- B. Questions and Problems
  - 1. What is the first law of thermodynamics
  - 2. What is the second law of thermodynamics
  - 3. What is the third law of thermodynamics
  - 4. Studying question in the text book
- C. Read the text (Principles of Physical Chemistry by Samuel) in the page 30-97 to improve your understanding
- D. Solving the problems in the page 69, 99 as far as you can.

### HANDOUTS

Seventh Week

3 X 50 minutes

## V. THERMOCHEMISTRY

#### A. Brief Description of Subject

The preceding chapters have dealt with the physical properties and changes of state of pure substances or fixed mixtures of substances. We now consider the application of the first law of thermodynamics to chemical changes a subject called thermochemistry. The subject is of great practical importance since it deals with the organization of the large amount of data concerning energies of chemical reactions. It also provides the foundation for obtaining chemical bond energies and hence for some aspects of theoretical chemistry.

The quantity of heat evolved or absorbed in a chemical reaction or phase change can be determined by measuring the temperature change in adiabatic process. Since very small temperature changes can be measured, this provides a sensitive method for studying the thermodynamic of chemical reaction and phase changes.

## 1. The relation between Cp and Cv

Cp is the heat capacity at constant pressure is defined as the partial derivative of the enthalpy with respect to temperature we the pressure is held constant. Cv is the heat capacity at constant volume is defined as the partial derivative of the internal energy with respect to temperature when the volume is held constant.

Cv = 3/2 R = 12.472 J/molK Cp = 5/3 R = 20.786 J/molK

2. The change in standard enthalpy

The change in standard enthalpy in a chemical reaction is equal to the summation of the standard enthalpies of formation of the reacting species, each multiplied by its stoichiometric number in specified chemical equation. If the standard enthalpy of reaction is known at one temperature, its value at any other temperature can be calculated if the molar heat capacities of the species involved are known throughout the temperature range involved.

3. Calorimetric measurements

Heats of reaction are determined by using adiabatic calorimeters, that is the reaction or solution process occurs in a container, which immersed in a weighed quantity of water and is surrounded by insulation or adiabatic shield that is kept at the same temperature as the calorimeter so that no heat is gained or lost.

A. Questions and Problems

Read the question and problems in Principles of Physical Chemistry by Samuel in the page 69-72

B. Read the text (Principles Of Physical Chemistry by Samuel) in the page 56 –
 67 to improve your understanding.

#### HANDOUTS

Ninth Week

3 X 50 minutes

#### **VI. CHEMICAL EQUILIBRIUM**

This chapter develops the concept of chemical potential and shows how it is used to account for the equilibrium composition of chemical reactions. The equilibrium composition corresponds to a minimum in the Gibbs energy plotted against the extent of reaction, and by locating this minimum we establish the relation between the equilibrium constant and the standard Gibbs energy of reaction.

Thermodynamic arguments can be used to derive an expression for the electric potential of such cells and the potential can be related to their composition. There are two major topics developed in this connection. One is the definition and tabulation of standard potentials; the second is the use of these standard potentials to predict the equilibrium constants and other thermodynamic properties of chemical reactions.

Chemical reactions tend to move towards a dynamic equilibrium in which both reactants and products are present but have no further tendency to undergo net change. In some cases, the concentration of products in the equilibrium mixture is so much greater than that of the unchanged reactants that for all practical purposes the reaction is 'complete'. However, in many important cases the equilibrium mixture has significant concentrations of both reactants and products.

In this chapter we see how to use thermodynamics to predict the equilibrium composition under any reaction conditions. Because many reactions of ions involve the transfer of electrons, they can be studied (and utilized) by allowing them to take place in an electrochemical cell. Measurements like those

described in this chapter provide data that are very useful for discussing the characteristics of electrolyte solutions and of ionic equilibria in solution.

# Spontaneous chemical reactions

We have seen that the direction of spontaneous change at constant temperature and pressure is towards lower values of the Gibbs energy, G. The idea is entirely general, and in this chapter we apply it to the discussion of chemical reactions.

# The Gibbs energy minimum

We locate the equilibrium composition of a reaction mixture by calculating the Gibbs energy of the reaction mixture and identifying the composition that corresponds to minimum G.

1. Definitions of chemical equilibrium

Chemical reactions move towards a dynamic equilibrium in which both reactants and products are present but have no further tendency to undergo net change.

# 2. Thermodynamic equilibrium

The thermodynamic formulation of equilibrium enables us to establish the quantitative effects of changes in the conditions. The principles of thermodynamics established in the preceding chapters can be applied to the description of the thermodynamic properties of reactions that take place in electrochemical cells, in which, as the reaction proceeds, it drives electrons through an external circuit.

3. Kp and Kc properties and calculations

An equilibrium constant K expressed in terms of activities (or fugacities) is called a thermodynamic equilibrium constant.

4. Temperature dependence

Le Chatelier's principle predicts that a system at equilibrium will tend to shift in the endothermic direction if the temperature is raised, for then energy is absorbed as heat and the rise in temperature is opposed. Conversely, an equilibrium can be expected to shift in the exothermic direction if the temperature is lowered, for then energy is released and the reduction in temperature is opposed. These conclusions can be summarized as follows:

Exothermic reactions: increased temperature favours the reactants.

Endothermic reactions: increased temperature favours the products.

We shall now justify these remarks and see how to express the changes quantitatively.



Fig 1. When a reaction at equilibrium is compressed (from a to b), the reaction responds by reducing the number of molecules in the gasphase (in this case by producing the dimers represented by the linked spheres).



Fig 2. The effectof temperature on a chemical equilibrium can be interpreted in terms of the change in the Boltzmann distribution with temperature and the effectof that change in the population of the species. (a) In an endothermic reaction, the population ofB increases the expense ofAas the temperature is raised. (b) In an exothermic reaction, the opposite happens

The typical arrangement of energy levels for an endothermic reaction is shown in Fig. 2a. When the temperature is increased, the Boltzmann distribution adjusts and the populations change as shown. The change corresponds to an increased population of the higher energy states at the expense of the population of the lower energy states. We see that the states that arise from the B molecules become more populated at the expense of the A molecules. Therefore, the total population of B states increases, and B becomes more abundant in the equilibrium mixture.

Conversely, if the reaction is exothermic (Fig. 2b), then an increase in temperature increases the population of the A states (which start at higher energy) at the expense of the B states, so the reactants become more abundant.

#### Equilibrium electrochemistry

We shall now see how the foregoing ideas, with certain changes of technical detail, can be used to describe the equilibrium properties of reactions taking place

in electrochemical cells. The ability to make very precise measurements of currents and potential differences ('voltages') means that electrochemical methods can be used to determine thermodynamic properties of reactions that may be inaccessible by other methods.

An electrochemical cell consists of two electrodes, or metallic conductors, in contact with an electrolyte, an ionic conductor (which may be a solution, a liquid, or a solid). An electrode and its electrolyte comprise an electrode compartment. The two electrodes may share the same compartment.

Any 'inert metal' shown as part of the specification is present to act as a source or sink of electrons, but takes no other part in the reaction other than acting as a catalyst for it. If the electrolytes are different, the two compartments may be joined by a salt bridge, which is a tube containing a concentrated electrolyte solution (almost always potassium chloride in agar jelly) that completes the electrical circuit and enables the cell to function. A galvanic cell is an electrochemical cell that produces electricity as a result of the spontaneous reaction occurring inside it. An electrolytic cell is an electrochemical cell in which a non-spontaneous reaction is driven by an external source of current.



Fig 3. The salt bridge, essentially an inverted U-tube full of concentrated salt solution in a jelly, has two opposing liquid junction potentials that almost cancel

A. Questions and Problems

Solve the problems and questions by using the text (Physical chemistry by Atkins) in page 235-237

- B. Read the text (Physical chemistry by Atkins) in the page 200 -232 to improve your understanding
- C. Solving the problems in the page 262-265 as far as you can.

# HANDOUTS

# Tenth and eleventh Week 2 (3 X 50) minutes

# VII. LIQUIDS

# A. Brief Description of Subject

1. The kinetic molecular description

We have seen that molecules in a gas are in constant random motion. The spaces between them are large and the intermolecular attractions negligible. However, in a liquid the molecules are in contact with each other. The forces of attraction between the molecules are strong enough to hold them together. The molecule in a liquid move in a random fashion. Most of the physical properties of liquids are actually controlled by the strength of intermolecular attractive forces.



Fig. 1 Molecular model of a liquid with holes indicated

2. Intermolecular forces in liquids

The principal kinds of intermolecular attractions are :

1. Dipole-dipole attractions



Fig. 2 Weak attractions between polar HCl Molecules

2. London forces



- Fig. 3 Explanation of London forces
- 3. Hydrogen bonding



Fig 4. Hydrogen bond

# 3. Vapor pressure

When a liquid is placed in a open vessel, it evaporates. The molecules in the liquid are moving with different kinetic energies. The molecules that posses above-average kinetic energies can overcome the intermolecular forces that hold them in the liquid.



Fig. 5 Illustration of vapour pressure

The process by which molecules of a liquid go into the gaseous state (vapors) is called Vapourazation or Evaporation. The reverse process whereby gas molecules become liquid molecules is called condensation. If the temperature of the liquid is increased, the vapor pressure will increase. This is so because at higher temperature more molecules in the liquid will have larger kinetic energy and will break away from the liquid surface.



Fig 6. Vapour pressure increases with temperature for ethanol and water

- 4. Determination of vapour Pressure
  - 1. The Static method



Fig. 7 Determination of vapour Pressure by static method

# 2. The dynamic method



Fig. 8 Determination of vapour Pressure by dynamic method

5. Surface Tension  $(\gamma)$ 

The surface tension is defined as the force in dynes acting along the surface of a liquid at right angle to any line 1 cm in length. Units of surface tension dyne per centimeter (dyne  $cm^{-1}$ ).



Fig. 9 surface tension is caused by the net inward pull on the surface molecules

- 6. Determination of Surface Tension  $(\gamma)$ 
  - 1. Capillary-rise method



Fig. 10 Rise of liquid in a capillary tube

2. Drop formation method

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3. Ring-detachment method



Fig 12. Du Nuoy ring

4. Maximum Bubble pressure Method



Fig. 13 a simple apparatus for maximum bubble pressure method

7. Viscosity  $(\eta)$ 

A liquid may be considered to be consisting of molecular layers arranged one over the other. When a shearing force is applied to a liquid, it flows. However, the forces of friction between the layers offer resistance to this flow. Viscosity of liquid is a measure of its frictional resistance. In CGS system the unit of  $\eta$  is expressed as g cm<sup>-1</sup> s<sup>-1</sup> (poise)

8. Measurement of Viscosity  $(\eta)$ 

The apparatus commonly used for the determination Viscosity  $(\eta)$  is known as Ostwald Viscometer.



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Fig 14. Ostwald Viscometer

9. Refractive index

The refractive index (n) of a substance is defined as the ratio of the velocity of light in vacuum or air.

N = Sin i/Sin r

Where : i = the angle of incident

 $\mathbf{r}$  = the angle of refraction

# 10. Determination of Refractive index

Refractive index of a liquid can be determined with the help of an instrument called Abbe Refractometer.



Fig 15. Abbe Refractometer

11. Optical Activity

When a plane-polarized light is passed through certain organic compounds, the plane of polarized light is rotated. A compound that can rotate the plane of polarized light is called optically active. This property of a compound is called optical activity.

# 12. Measurement of Optical Activity

Optical activity is measured e]with the help of an instrument known as polarimeter. This is basically a system of polarizers with a sample tube placed in between.

- B. Questions and Problems
  - 1. Define surface tension of a liquid
  - 2. Why viscosity of a liquid decreases with increase in temperature
  - 3. How is viscosity of a liquid determined, discuss the effect of temperature on it
- C. Read the text (Essentials of Physical chemistry by *Bahl*) in the page 343 363 to improve your understanding
- D. Solving the problems in the page 363 365
#### HANDOUTS

# Twelfth and Thirteenth Week 2 (3 X 50) minutes

#### VIII. SOLUTIONS

When several nonreacting substances are mixed, three possible types of mixtures may be obtained : a) a coarse mixture, such as that of salt and sugar; b) a colloidal dispersion, such as results when fine clay is shaken with water; or c) a true solution, obtained when a substance like sugar dissolves in water.

A. Brief Description of Subject

#### 1. Definition of solution

A true solution as a physically homogenous mixture of two or more substances. This definition of a solution places no restriction on either the state of aggregation or the relative amounts of the constituents, and consequently a solution may be gaseous, liquid or solid and may vary in composition within in limits.

#### 2. Factors affecting solubility

The extent to which a substance will dissolve in another varies greatly with different substances and depends on the nature of the solute and solvent, the temperature, and the pressure. In general the effect of pressure on solubility is small unless gases are involved. However, the effect of temperature is usually very pronounced. The direction in which the solubility of a substance in a solvent changes with temperature depends on the heat of solution.

#### 3. Types of solutions

- 1. Solution of a gas in a gas
- 2. Solution of a liquid in a gas
- 3. Solution of a solid in a gas

- 4. Solution of a gas in a solid
- 5. Solution of a liquid in a solid
- 6. Solution of a solid in a solid
- 7. Solution of a gas in a liquid
- 8. Solution of a solid in a liquid
- 9. Solution of a liquid in a liquid

# SOLUTIONS OF GASES IN GASES

All gasses are miscible in all proportions, yielding solution whose physical properties are very additive provided the total pressure is not too high.

# SOLUBILITY OF LIQUIDS AND SOLIDS IN GASES

The vaporization of a liquid and sublimation of a solid into a gas phase may be considered as solution of these substances in a gas. These processes involve first the conversion of the liquid or solid to vapor, and the subsequent solution of the vapor in the gas. Because the vaporization and sublimation pressures of a substance are fixed at any given temperature, the amounts of liquid and solid that can be vaporize into a given volume of gas are limited to the amount necessary to establish the equilibrium pressures.

# SOLUBILITY OF GASES AND LIQUIDS IN SOLIDS

Gases and liquids may be dissolve in solid to form apparently true homogenous solutions. Examples are the solubility of hydrogen in palladium and the solubility of liquid benzene in solid iodine. Both solutions formed are solid.

#### Henry's Law

At any given temperature the solubility of gas in a liquid is directly proportional to the pressure of the gas above the liquid at the equilibrium. This principle is known as Henry's law, and may be formulated as :

C = k.P

Where C is the concentration of the gas in the solution, P is the pressure of the gas above the solution at equilibrium and k a proportionality constant known as Henry's law constant.

P (cmHg)	C (g/liter H <sub>2</sub> O)	C/P = ko
17.5	0.0095	0.000543
30.0	0.0160	0.000533
41.4	0.0220	0.000531
61.0	0.0325	0.000533
76.0	0.0405	0.000537

Table 1. Solubility of Oxygen in Water at 25 °C

#### **Ideal solution**

An ideal solution may be defined as solution in which the various pure constituents involved do not experience any modification of properties beyond that of dilution.

# **Raoult's Law**

Raoult's law deals at any given temperature with the partial vapor pressure above a solution of the constituents in solution. The law state the partial vapor pressure of any volatile constituent of a solution is equal the vapor pressure of the pure constituent multiplied by the mole fraction of that constituent in solution. Thus if we have a solution of two volatile and miscible liquids of composition  $N_A$  and  $N_B$ , where NA and  $N_B$  are the mol fractions of the two constituents, then the vapor pressure of the two constituents above the solution are :

 $P_A = P_A^o \cdot N_A$ 

 $P_B = P^o_B \cdot N_B$ 

 $\mathbf{P} = \mathbf{P}_{A} + \mathbf{P}_{B}$ 

$$= P^{o}_{A} \cdot N_{A} + P^{o}_{B} \cdot N_{B}$$

Since, however  $N_A + N_B = 1$ , than  $N_A = 1 - N_B$ 

$$\mathbf{P} = \mathbf{P}^{\mathbf{o}}_{A}(1-\mathbf{NB}) + \mathbf{P}^{\mathbf{o}}_{B}. \mathbf{N}_{B}$$

$$= (\mathbf{P}^{\mathbf{o}}_{B} - \mathbf{P}^{\mathbf{o}}_{A})\mathbf{N}_{B} + \mathbf{P}^{\mathbf{o}}_{A}$$



Fig. 1 Vapor pressure of Miscible Liquids According to Raoult's Law

In line with these requirements, the ordinates in Fig. 1 at  $N_B = 0$  and  $N_B = 1$  give  $P^o_A$  and  $P^o_B$  respectively. Since the pressures of all intermediate concentrations lie on straight line that includes these points, the solid line in the diagram must represent the total vapor pressure of all possible mixtures of A and B. we see, therefore, that for binary solutions obeying Raolut's law the vapor pressures are intermediate between those of the pure components and lie on a straight line between these points.



Fig. 2 Liquid and Vapor composition Curves an Ideal Solution

In Fig 2, the straight line gives the total pressure above the solution as a function of the mol fraction of B in solution,  $N_B$ , while the curve lying below it represents the total vapor pressure as a function of B in the vapor,  $Y_B$ . To obtain the composition of vapor corresponding to, say, a solution for which  $N_B = 0.2$ , we move vertically to point C to obtain the total pressure of the solution. This same pressure is given also on the vapor composition curve by point D, corresponding to a composition  $Y_B = 0.042$ , and hence for the liquids in question when  $N_B = 0.2$ ,  $Y_B = 0.402$ .

# The Deviation of the Raoult's Law

1. Positive deviation



Fig. 3 vapor pressures of the system Methyl- carbon disulfide at 35.2 °C

# 2. Negative deviation



Fig. 4 Vapor pressures of the system Acetone- Chloroform at 55.1°C



Fig. 5 Types of Binary Vapor pressure Diagrams (Temperature Constant)

- Type I : Systems whose total pressure is intermediate between those of the pure compounds. Examples : Carbon tetrachloride-cyclohexane, carbon tetrachloride-benzene, benzene-toluen, water-methyl alcohol.
- Type II : Systems exhibiting a maximum in the total vapor pressure curve. Examples: Carbon disulfide-methylal, carbon disulfide-acetone, benzene-cyclohexane, benzene-ethyl alcohol.

Type III : Systems exhibiting a minimum in the total vapor pressure curve. Examples : Chloroform –acetone, methyl ether-hydrogen chloride, pyridine-acetic acid.



Fig. 6 Types of Distillation Diagrams Corresponding to Various Pressure Diagrams

# **Distillation of Binary Miscible Solutions**



Fig. 7 Distillation Behavior of Solutions of Type I



Fig. 8 Distillation Behavior of Solutions of Type II



Fig. 9 Distillation Behavior of Solutions of Type III

## **Azeotropic Mixtures**

The constant boiling mixtures described above are referred to either as azeotropes or azeotropic mixtures. At one time it believed that such mixtures correspond to the formation of definite compounds between the two constituents. However, a definite compound should have a definite composition over a given temperature and pressure range.

Туре	A	В	Boiling $point (^{\circ}C)$	Weight % of B
Minimum boiling point	Water	Ethyl alchol	78:15	95 : 57
	Water	n-propyl alcohol	87:72	71 : 70
	Ethyl alcohol	benzene	68:24	67 : 63
Maximum Boiling point	Water	Nitric Acid	120:5	68
	Water	Hydroflouric acid	108 : 5	20:24

Table 2. Boiling points and Composition of Azeotropic Mixtures

# **B.** Questions and Problems

- The partial molar volumes of acetone (propanone) and chloroform trichloromethane) in a mixture in which the mole fraction of CH<sub>3</sub>Cl, is 0.4693 are 74.166 cm ' mol"! and 80.235 cm' mol-J, respectively. What is the volume of a solution of mass 1.000 kg?
- 2. How is Raoult's law modified so as to describe the vapour pressure of real solutions?
- C. Read the text (Essentials of Physical Chemistry by Bahl) in the page 139-165 to improve your understanding.

#### HANDOUTS

#### Fourteenth and fifteenth Week

# 2 (3 X 50) minutes

## IX. COLLOIDS AND SURFACE CHEMISTRY

This chapter is concerned with the introduction of the colloids and surface chemistry, some special properties of colloids and its application in science and technology.

Thromas Graham( 1861) studied the ability of dissolved substance so diffuse into water across a permeable membrane. He observed the crystalline substances such as sugar, urea, and sodium chloride passed through the membrane while others like glue, gelatin and gum Arabic did not. The former he called crystalloids and the latter colloids (Geek, kolla = glue ; eidos = like). Graham thought that the difference in the behavior of crystalloids' and'colloids' was due to the particle size. Later it was realised that any substance, regardless of its nature, could be converted into a colloid by subdividing it into particles of colloidal size.

A. Brief Description of Subject

#### 1. What are colloids

The colloidal solutions or colloidal dispersions are intermediate between true solutions and suspensions. In other words, the diameter of the dispersed particles in a colloidal dispersion is more than that of the solute particles in a true solution and smaller than that of a suspension.



Fig. 1 Particle size (indicated by diameter) range of true solution, colloidal dispersion and suspension

When the diameter of the particles of a substance dispersed in a solvent ranges from about 10 Å to 2,000 Å, the system is termed a colloidal solution, colloidal dispersion, or simply a colloid.

# 2. Types of Colloidal Systems

Type name	Dispersed phase	Dispersion medium	Examples	
Foam	Gas	Liquid	Whipped cream, shaving cream, soda-water froth	
Solid foam	Gas	Solid	cork, foam rubber	
Aerosol	Liquid	Gas	Fog, mist, clouds	
Emulsion	Liquid	Liquid	Milk, hair cream	
Solid emulsion (gel)	Liquid	Solid	Butter, cheese	
smoke	Solid	Gas	Dust, soot in air	
Sol	Solid	Liquid	Paint, ink, colloidal gold	
Solid sol	Solid	Solid	Ruby glass, alloys	

# LYOPHILIC AND LYOPHOBIC SOLS OR COLLOIDS

3. Sols

Sols are colloidal systems in which a solid is dispersed in a liquid. These can be subdivided into two classes :

1. Lyophilic sols (solvent-loving)

Are those in which the dispersed phase exhibits a definite affinity for the medium or the solvent. The examples of lyophilic sols are dispersions of starch, gum, and protein in water.

2. Lyophobic sols (solvent-hating)

Lyophobic sols are those in which the dispersed phase has no attraction for the medium or the solvent.

The examples of lyophobic sols are dispersion of gold, iron (III) hydroxide and sulfur in water.

# Comparison of lyophilic and lyophobic sols :

# Lyophilic sols

- 1. Prepared by direct mixing with dispersion medium
- 2. Little or no charge on particles
- 3. Particles generally solvated
- 4. Viscosity higher than dispersion medium
- 5. Precipitated by high concentration of electrolytes
- 6. Reversible
- 7. Do not exhibit Tyndall effect
- 8. Particles migrate to anode or chatode or not at all

#### Lyophobic Sols

- 1. Not prepared by direct mixing with the medium
- 2. Particles carry positive or negative charge
- 3. No salvation of particles
- 4. Viscosity almost the same of medium, do not set to a gel
- 5. Precipitated by low concentration of electrolytes
- 6. Irreversible
- 7. Exhibit Tyndall effect
- 8. Particles migrate to either anode or cathode

## 4. Preparation of sols

There are two methods for preparation of sols :

- 1. Dispersion methods
  - a. Mechanical dispersion using Colloid mill



Fig. 2 Colloid Mill

b. Bredig's Arc Method



Fig. 3 Bredig's Arc Method

c. By peptization



Fig 4. By peptization

- 2. Aggregation methods
  - a. Double decomposition
  - b. Reduction
  - c. Oxidation
  - d. Hydrolysis
  - e. Change of solvent
- 5. Properties of sols
  - 1. Their colour
  - 2. Optical properties of sols
    - a. Sols exhibit Tyndall Effect
    - b. Ultramicroscope shows up the presence of individual particles

- 3. Kinetic properties of sols
  - a. Brownian Movement



Fig. 5 An illustration of Brownian Movement

- 4. Electrical properties of sols
  - a. The sol particles carry an electric charge
  - b. Electrophoresis
  - c. Electro-osmosis
  - d. Coagulation or precipitation



Fig. 6 An illustration of coagulation of sols

- e. Protective action of sols
- 6. Association of colloids

Substances whose molecules aggregates spontaneously in a given solvent to form particles of colloidal dimensions. The colloidal aggregates of soap or detergent molecules formed in the solvent are referred to as micelles.

7. Emulsions

These are liquid-liquid colloidal system, in other words an emulsion may be defined as a dispersion of finely divided liquid droplets in another liquid. There are two types of emulsion :

- 1. Oil-in-water type (O/W type)
- 2. Water-in-oil type (W/O type)

Properties of emulsion :

- 1. Demulsification
- 2. Dilution

# 8. Application of colloids

1. Foods

Many of our foods are colloidal in nature. Milk is an emulsion of butterfat in water protected by a protein, casein. Salad dressing, gelatin deserts, fruit jellies and whipped cream are other examples. Ice cream is a dispersion of ice in cream. Bread is a dispersion of air in baked dough.

2. Medicines

Colloidal medicine being finely divided, are more effective and are easily absorbed in our system. Halibut-liver and cod-liver oil that we take are, in fact, the emulsions of the respective oils in water. Many ointmeats for application to skin consist of physiologically active components dissolved in oil and made into an emulsion with water. 3. Non-drip or thixotropic paints

All paints are colloidal dispersions of solid pigments in a liquid medium. The modern nondrip or thixotropic paints long-chain polymers. At rest, the chains of molecules are coiled and entrap much dispersion medium. Thus the paint is a semi-solid gel structure.

4. Electrical precipitation of smoke

The smoke coming from industrial plants is a colloidal dispersion of solid particles (carbon, arsenic compounds, cement dust) in air. It is a nuisance and pollutes the atmosphere. Therefore, before allowing the smoke to escape into air, it is treated by Contrell Precipitator. The smoke is led past a series of sharp points charged to high potential (20,000 to 70,000 V). the points discharge high velocity electrons that ionize molecules in air.

5. Clarification of municipal water

The municipal water obtained from natural sources often contains colloidal particles. The process of coagulation is used to remove these. The sol particles carry a negative charge.

6. Formation of Delta

The river water contains colloidal particles of sand and clay which carry negative charge. The sea water, on other hand, contains positive ions such as Na+, Mg2+, Ca2+. As the river water meets sea water, these ions discharge the sand or clay particles which are precipitated as delta.

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DCEAN



Fig. 7 Formation of Delta

# 7. Artificial Kidney machine

The human kidneys purity the blood by dialysis through natural membranes. The toxic waste products such as urea and uric acid pass through the membranes, while colloidal-sized particles of blood proteins (haemoglobin) are retained. Kidney failure, therefore leads to death due to accumulation of poisonous waste products in blood.

8. Adsorption indicators

These indicators function by preferential adsorption of ions onto sol particles. Fluorescence  $(Na^+F^-)$  is an example of adsorption indicator which is used for the titration of sodium chloride solution against silver nitrate solution.

- **B.** Questions and Problems
  - 1. What are colloids
  - 2. How are they classified
  - 3. What the effect of addition of electrolytes to lyophobic sols
- C. Read the text (Essentials of Physical chemistry by Bahl) in the page 645 672 to improve your understanding
- D. Solving the problems in the page 672 674 as far as you can.

#### **Refferences :**

Adamson, A.W., Text Book of Physical Chemistry, John Willey & Sons, New York

Atkins, P.W., (2006) Physical Chemistry (Eighth Edition), Oxford Univ. Press, London

Bahl, B.S, Tuli, G.D., Bahl, Arun, (1997), Essentials of Physical Chemistry, S.Chand & Company Ltd., New Delhi

Barrow, Gordon M., (1996) Physical Chemistry (sixth Edition), Mc Graw Hill, Boston

## WORKSHEET

Fill your answer in the availabled space.!

Calculate the molar volume V and the density of ethane gas at STP, assuming ideal behavior.



Calculate V and  $\rho$  for dry air average molecular weight = 29 g mole<sup>-1</sup> at STP. Repeat the calculation for air saturated with water vapor at 25 °C and 1 atm total pressure. Assume ideal behavior.

The amount 2.731 g of N<sub>2</sub>O<sub>4</sub> is introduced into a 2-liter flask at 25 °C. Partial dissociation into NO<sub>2</sub> occurs, and the equilibrium pressure is 0.8623 atm. Calculate the degree of dissociation ( $\alpha$ ) and the value of Kp.



Calculate the partial volumes of  $H_2O$ ,  $O_2$ , and  $N_2$  in air saturated with water vapor at 50 °C and at 1 atm total pressure. Assume ideal behavior and one mole of total gas.

Derive the van der Waals equation for n moles of gas.

Calculate the second and third virial coefficients for  $NH_3$  assuming it to be a van der Waals gas.

A hot air balloon has a volume of  $100 \text{ m}^3$  and is filled with air at 100 °C. Ambient temperature and pressure are 25 °C and 1 atm, respectively. (a) calculate the lift of the balloon in kg. (b) Suppose that the balloon were filled with He at ambient temperature. Calculate the lift in kg (assume ideal gas behavior).

What is the critical temperature of a van der Waals gas for which Pc is 100 atm and b is  $50 \text{ cm}^3 \text{ mole}^{-1}$ .

Fifty moles of NH<sub>3</sub> is introduced into a two liter cylinder at 25 °C, calculate the pressure if (a) the gas is ideal and (b) it obeys the van der Waals equation.

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Calculate p(c) for  $O_2$  at 25 °C and c = 3 x 10<sup>5</sup> cm sec<sup>-1</sup>.



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A weight of 1 kg falls freely to platform from a height of 10 m. What amount of heat in calories will be evolved when the weight strikes the platform.



A gas in expanding against a constant pressure of 1 atm from 10 to 16 liters absorbs 30 cal of heat. What is the change in internal energy of the gas.

Two liters of N<sub>2</sub> at 0° C and 5 atm pressure are expanded isothermally against a constant pressure of 1 atm until the pressure of the gas is also 1 atm. Assuming the gas to be ideal, what are the values of w,  $\Delta E$  and  $\Delta H$  for the process.

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Calculate the minimum work necessary to compress 20 g of  $O_2$  from 10 to 5 liters at 0° C. How much heat is evolved in the process.



A quantity of ideal gas in an isolated system is expanded isothermally and reversibly at 400 K from a volume  $V_1$  to  $V_2$ . During the expansion the gas absorbs 200 cal of heat from the reservoir in contact with it. Find the entropy change of the gas and the entropy change of the reservoir and the entropy change of the whole system.



Calculate the change in the entropy suffered by 3 moles of an ideal gas, for which Cp=5/2 R cal mole<sup>-1</sup> degree<sup>-1</sup>, on being heated at constant pressure from a temperature of 27° to 327° C.

What is the entropy change in the isothermal compression of 200 g of  $N_2$  from a pressure of 1 to 5 atm at 25°C, assume that  $N_2$  is a perfect gas.



CH<sub>3</sub>COOH melts at  $16.6^{\circ}$  C with a heat of fusion of 44.0 cal/g. Calculate the entropy of fusion per mole.

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Calculate the change in the entropy experienced by 2 moles of an ideal gas, on being heated from a pressure of 5 atm at 50° C to a pressure of 10 atm at 100° C. For the gas Cp = 12.0 cal mole<sup>-1</sup> degree<sup>-1</sup>.



Calculate  $\Delta H^{o}_{298}$  and  $\Delta E_{298}$  for the reaction



A sample consisting of 0.200 g of CH<sub>3</sub>COOH(l) is ignited in a bomb calorimeter containing pure oxygen. The heat capacity of the calorimeter is 12,000 J°C<sup>-1</sup>. What temperature increase should occur?



Calculate  $\Delta H^{\circ}_{298}$  and  $\Delta E_{298}$  for the incomplete combustion reaction

 $C_6H_6(g) + 1\frac{1}{2}O_2(g) \leftrightarrow 6C(s) + 3H_2O(l)$ 

Calculate  $\Delta H^{0}_{298}$  per mole for the cis to trans isomerization of CH<sub>3</sub>CH=CHCH<sub>3</sub>

Calculate the maximum temperature achieved by the mixture when 0.100 g of ethane gas is exploded in a constant-volume adiabatic (that is, insulated) calorimeter containing 10 g of air. The initial temperature is 25°C, assume ideal gas behavior.



Calculate  $\Delta H^{0}_{298}$  per mole for formation of butadiene, using bond energies.

Define the surface tension of a liquid.



At 20 °C toluene rises 1.90 cm in a capillary tube of radius 0.320 mm. Calculate the surface tension of toluene. The density of toluene at 20 °C is 0.866 g/cc.

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The density of a liquid at 25 °C is 1.200 g/mL. Its refractive index  $n^{25}$  is 1.552. Calculate its molar refractivity, molecular weight of liquid = 123.



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The density of a liquid at 25 °C is 1.200 g/mL. Its refractive index  $n^{25}$  is 1.552. Calculate its molar refractivity, molecular weight of liquid = 123.



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Define viscosity and coefficient of viscosity.

Describe one method of determining the viscosity of liquids.

At 20 °C pure water required 102.2 sec to flow the capillary of an Ostwald viscometer, while toluene at 20 °C required 68.9 sec. Calculate the relative viscosity of toluene. Densities of water and toluene are 0.998 and 0.866 g/cm<sup>3</sup>.

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How is the viscosity of a liquid determined in laboratory.

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Define (i) Poise, (ii) surface tension.

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What is the influence of temperature on surface tension.

A solution contains 50% of water, 35% of ethyl alcohol and 15% of acetic acid by weight. Calculate the mol fraction of each component in the mixture.



A Na<sub>2</sub>CO<sub>3</sub> solution is made up by dissolving 22.5 g of Na<sub>2</sub>CO<sub>3</sub>.10H<sub>2</sub>O in H<sub>2</sub>O and adding H<sub>2</sub>O until the total volume is 200 cc. The density of the resulting solution is 1.040 g/cc. Calculate the molarity, normality and mol fraction of Na<sub>2</sub>CO<sub>3</sub> in the solution.



A solution containing 10% of NaCl by weight has a density of 1.071 g/cc. Calculate the molality and molarity of NaCl in the solution.

A gaseous solution was analyzed and found to contain 15% of  $H_2O$ , 10% of CO ad 75%  $N_2$  by volume. What is the mol fraction and percentage by weight of each gas in the mixture.



A mixture of  $H_2$  and  $N_2$  is agitated with 100 cc of water until equilibrium is established. At equilibrium it is found that the total pressure of the gas phase is 840 mmHg and that the gas after drying consists of 35.3%  $H_2$  by volume. Assuming that the vapor pressure of water above the solution is the same as that for pure water, namely 95.5 mmHg at 50 °C, calculate the weights of dissolved  $H_2$ and  $N_2$ .



At 140 °C the vapor pressure of C<sub>6</sub>H<sub>5</sub>Cl is 939.4 mmHg and that of C<sub>6</sub>H<sub>5</sub>Br is 495.8 mmHg. Assuming that these two liquids from an ideal solution, what will be the composition of a mixture of the two which boils at 140 °C under 1 atm pressure, what will be the composition of the vapor at this temperature.



What weight of  $HCl-H_2O$  azeotrope prepared at 740 mmHg pressure will have to added to water in order to prepare 2 liters of 0.50 molar HCl solution.

What weight of HCl-H<sub>2</sub>O azeotrope prepared at 580 mmHg pressure will have to added to water in order to prepare 5 liters of 1.50 molar HCl solution.

A totally immiscible liquid system composed of  $H_2O$  and an organic liquid boils at 90  $_{\circ}C$  when the barometer reads 734 mmHg, the distillate contains 73% weight of the organic liquid. What is the molecular weight and vapor pressure at 90  $^{\circ}C$ .

What are colloids,

Explain why a colloidal solution is not precipitated in the presence of gelatin.

Define gold number, the gold number of A, B,C and D are 0.005, 0.05, 0.5 nad 5 respectively. Which of these has the greatest protective action.

What is electrophoresis.

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What is meant by peptization.

What are emulsions and how are they classified.
What are	emulsions	and	gels.
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What distinguishes between elastic and non-elastic gels.

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Explain the stability of colloids.

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Define number average and weight average molecular weights.

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Describe a method for purifying colloidal solutions.

What are applications of colloids in science and technology.

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