

Semester III

CHE-RC/HG-3016: CHEMISTRY 3

CHEMICAL ENERGETICS, EQUILIBRIA & FUNCTIONAL ORGANIC CHEMISTRY-I

(Credits: Theory-04, Lab-02)

Theory: 60 Lectures

Course Objective: This course contains two broad parts- physical and organic chemistry. In physical chemistry part the students will be taught chemical energetics,

chemical equilibrium and ionic equilibrium. In organic chemistry part, the students will be introduced to different classes of organic compounds.

Learning Outcome: After completion of this course the students will be able to understand the chemical system from thermodynamic points of view. They will also learn two very important topics in chemistry- chemical equilibrium and ionic equilibrium. In organic chemistry part, the students are expected to learn various classes of organic molecules-alkyl halides, aryl halides, alcohols, phenols, ethers, aldehydes and ketones.

Section A: Physical Chemistry-1 (30 Lectures)

Chemical Energetics

Review of thermodynamics and the Laws of Thermodynamics.

Important principles and definitions of thermochemistry. Concept of standard state and standard enthalpies of formations, integral and differential enthalpies of solution and dilution. Calculation of bond energy, bond dissociation energy and resonance energy from thermochemical data. Variation of enthalpy of a reaction with temperature – Kirchoff's equation. Statement of Third Law of thermodynamics and calculation of absolute entropies of substances.

(10 Lectures)

Chemical Equilibrium:

Free energy change in a chemical reaction. Thermodynamic derivation of the law of chemical equilibrium. Distinction between ΔG and ΔG° , Le Chatelier's principle. Relationships between K_p , K_c and K_x for reactions involving ideal gases.

(8 Lectures)

Ionic Equilibria:

Strong, moderate and weak electrolytes, degree of ionization, factors affecting degree of ionization, ionization constant and ionic product of water. Ionization of weak acids and bases, pH scale, common ion effect. Salt hydrolysis-calculation of hydrolysis constant, degree of hydrolysis and pH for different salts. Buffer solutions. Solubility and solubility product of sparingly soluble salts – applications of solubility product principle.

(12 Lectures)

Section B: Organic Chemistry-2 (30 Lectures)

Functional group approach for the following reactions (preparations & reactions) to be studied in context to their structure.

Aromatic hydrocarbons

Preparation (Case benzene): from phenol, by decarboxylation, from acetylene, from benzene sulphonamic acid.

Reactions: (Case benzene): Electrophilic substitution: nitration, halogenation and sulphonation. Friedel-Craft's reaction (alkylation and acylation) (upto 4 carbons on benzene). Side chain oxidation of alkyl benzenes (upto 4 carbons on benzene).

(8 Lectures)

Alkyl and Aryl Halides

Alkyl Halides (Upto 5 Carbons) Types of Nucleophilic Substitution (S_N1 , S_N2 and S_Ni) reactions.

Preparation: from alkenes and alcohols.

Reactions: hydrolysis, nitrite & nitro formation, nitrile & isonitrile formation. Williamson's ether synthesis: Elimination vs substitution.

Aryl Halides Preparation: (Chloro, bromo and iodo-benzene case): from phenol, Sandmeyer & Gattermann reactions.

Reactions (Chlorobenzene): Aromatic nucleophilic substitution (replacement by $-OH$ group) and effect of nitro substituent. Benzyne Mechanism: KNH_2/NH_3 (or $NaNH_2/NH_3$). Reactivity and Relative strength of C-Halogen bond in alkyl, allyl, benzyl, vinyl and aryl halides.

(8 Lectures)

Alcohols, Phenols and Ethers (Upto 5 Carbons)

Alcohols: *Preparation:* Preparation of 1 $^\circ$, 2 $^\circ$ and 3 $^\circ$ alcohols: using Grignard reagent, Ester hydrolysis, Reduction of aldehydes, ketones, carboxylic acid and esters.

Reactions: With sodium, HX (Lucas test), esterification, oxidation (with PCC, alk. $KMnO_4$, acidic dichromate, conc. HNO_3). Oppeneauer oxidation *Diols:* (Upto 6 Carbons) oxidation of diols. Pinacol-Pinacolone rearrangement.

Phenols: (Phenol case) *Preparation:* Cumene hydroperoxide method, from diazonium salts. *Reactions:* Electrophilic substitution: Nitration, halogenation and sulphonation. Reimer-Tiemann Reaction, Gattermann-Koch Reaction, Houben-Hoesch Condensation, Schotten – Baumann Reaction.

Ethers (aliphatic and aromatic): Cleavage of ethers with HI.

Aldehydes and ketones (aliphatic and aromatic): (Formaldehyde, acetaldehyde, acetone and benzaldehyde)

Preparation: from acid chlorides and from nitriles.

Reactions – Reaction with HCN, ROH, $NaHSO_3$, NH_2-G derivatives. Iodoform test. Aldol Condensation, Cannizzaro's reaction, Wittig reaction, Benzoin condensation. Clemensen reduction and Wolff Kishner reduction. Meerwein-Ponndorf Verley reduction.

(14 Lectures)

Recommended Books:

1. T. W. Graham Solomons: *Organic Chemistry, John Wiley and Sons.*
2. Peter Sykes: *A Guide Book to Mechanism in Organic Chemistry, Orient Longman.*
3. I.L. Finar: *Organic Chemistry* (Vol. I & II), E. L. B. S.
4. R. T. Morrison & R. N. Boyd: *Organic Chemistry, Prentice Hall.*
5. Arun Bahl and B. S. Bahl: *Advanced Organic Chemistry, S. Chand.*
6. G. M. Barrow: *Physical Chemistry* Tata McGraw-Hill (2007).

7. G. W. Castellan: *Physical Chemistry* 4th Edn. Narosa (2004).
 8. J. C. Kotz, P. M. Treichel & J. R. Townsend: *General Chemistry* Cengage Learning India Pvt. Ltd., New Delhi (2009).
 9. B. H. Mahan: *University Chemistry* 3rd Ed. Narosa (1998).
 10. R. H. Petrucci: *General Chemistry* 5th Ed. Macmillan Publishing Co.: New York (1985).
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LAB: CHEMISTRY3

CHEMICAL ENERGETICS, EQUILIBRIA & FUNCTIONAL ORGANIC CHEMISTRY-I 60 Lectures

Section A: Physical Chemistry

Thermochemistry

1. Determination of heat capacity of calorimeter for different volumes.
2. Determination of enthalpy of neutralization of hydrochloric acid with sodium hydroxide.
3. Determination of enthalpy of ionization of acetic acid.
4. Determination of integral enthalpy of solution of salts (KNO₃, NH₄Cl).
5. Determination of enthalpy of hydration of copper sulphate.
6. Study of the solubility of benzoic acid in water and determination of ΔH .

Ionic equilibria

pH measurements

- a) Measurement of pH of different solutions like aerated drinks, fruit juices, shampoos and soaps (use dilute solutions of soaps and shampoos to prevent damage to the glass electrode) using pH-meter.
- b) Preparation of buffer solutions:
 - (i) Sodium acetate-acetic acid
 - (ii) Ammonium chloride-ammonium hydroxide

Measurement of the pH of buffer solutions and comparison of the values with theoretical values.

Section B: Organic Chemistry

1. Purification of organic compounds by crystallization (from water and alcohol) and distillation.
2. Criteria of Purity: Determination of melting and boiling points.
3. Preparations: Mechanism of various reactions involved to be discussed. Recrystallisation, determination of melting point and calculation of quantitative yields to be done.
 - (a) Bromination of Phenol/Aniline
 - (b) Benzoylation of amines/phenols
 - (c) Oxime and 2,4 dinitrophenylhydrazone of aldehyde/ketone

Recommended Books

1. A.I. Vogel: Textbook of Practical Organic Chemistry, 5th edition, Prentice-Hall.
2. F. G. Mann & B. C. Saunders, Practical Organic Chemistry, Orient Longman (1960).
3. B.D. Khosla, Senior Practical Physical Chemistry, R. Chand & Co.