

VEER NARMAD SOUTH GUJARAT UNIVERSITY M.Sc.-I (CHEMISTRY)

PROPOSED SYLLABUS TO BE EFFECTIVE FROM JUNE 2018

PAPER-III (PHYSICAL CHEMISTRY)

Max. Marks: 100 (External – 70 + Internal – 30)

Total Periods: 45

SEMESTER-I

UNIT-I: CHEMICAL KINETICS

12 Periods

Theories of Unimolecular gas reactions: Lindemann theory, Kinetics of some complex reactions (i) Reversible reactions (only first order opposed by first order) (ii) Consecutive reactions ($A \rightarrow B \rightarrow C$); Steady state treatment or approximation, Enzyme catalysed reactions, Kinetics of general Chain reaction, Kinetics of photochemical reactions (H_2-Cl_2 and H_2-Br_2), Kinetics, Mechanism, determination of activation energy and chain length of some organic decomposition (i) decomposition of ethane (ii) decomposition of acetaldehyde, Effect of Ionic strength on rates of ionic reactions (Primary and secondary salt effect)
Numerical.

UNIT- II: THERMODYNAMICS

11 Periods

Introduction to Laws of thermodynamics, state and path functions and their applications, thermodynamic description of various types of processes, Maxwell's relations, Partial molar quantities, Calculation of partial molar quantities, determination of partial molar volume and partial molar enthalpy, Ideal and non-ideal liquid mixtures, Thermodynamics functions of mixing of non-ideal solutions (i) free energy of mixing (ii) entropy of mixing (iii) volume of mixing and (iv) enthalpy of mixing, Excess functions (μ^E , G^E , S^E , H^E and V^E) for non ideal solutions and expression for excess thermodynamic functions.
Numerical

UNIT –III STATISTICAL THERMODYNAMICS

11 Periods

Basics of Statistical thermodynamics (Assembly, Canonical ensemble, occupation number, statistical weight factor, probability), Thermodynamic probability, Probability and entropy, Maxwell-Boltzmann, Bose-Einstein and Fermi-Dirac statistics. Lagrange's methods of multipliers, Partition function, Thermodynamic properties in term of partition functions (i) Internal energy (ii) Heat Capacity (iii) Third law of thermodynamics (iv) Helmholtz free energy (v) Enthalpy (vi) Gibb's free energy (vii) Chemical potential (viii) Equilibrium constant Molecular partition functions for an ideal gas, Derivation for Translational, Rotational and Vibrational partition functions
Numerical.

UNIT-IV: POLYMER CHEMISTRY

11 Periods

Types of polymers, Stereochemistry of polymers, Kinetics of polymerization (Addition and Condensation), Thermodynamics of polymerization, Phase techniques of polymerization (Bulk, solution, suspension and emulsion), Number & Mass average Molecular mass, Polydispersity Index (P.D.I) Molecular mass determination by Viscometry and Osmometry, Thermal transitions in polymer: glass transition temperature and its significance,
Numerical

Reference Book:

1. **Physical Chemistry, Atkins, P.W., W.H. Freeman (2017) 10th edition**
2. **Thermodynamics for chemist Samuel Glasstone, East-West Press Pvt. Ltd. (2008)**
3. Principles of Physical Chemistry **Puri B.R., Sharma L.R. and Pathania, M.S., Vishal Publishing Co. 41th ed.** (Kinetics of some complex reactions (i) Reversible reactions (only first order opposed by first order), Consecutive reactions page no. 700-704) Kinetics of general Chain reaction page no. 706-708 Kinetics of photochemical reactions (H_2-Br_2) page no. 351-352 **Maxwell's relations page no. 565** Number & Mass average Molecular mass, Polydispersity Index (P.D.I) Molecular mass determination by Viscometry and Osmometry page no. 1036 -1042
Maxwell-Boltzmann, Bose-Einstein and Fermi-Dirac statistics. Lagrange's methods of multipliers, page no. 629-635
Molecular partition function for an ideal gas, Derivation for Translational, Rotational And Vibrational partition functions page no. 636-641
4. **Chemical Kinetics Laidler K.J. TATA Mc GRAW-HILL PUBLISHING COMPANY LTD., (Theories of unimolecular gas reactions: Lindemann theory Page No. 143-147) Steady state treatment or approximation page no. 327-328** Enzyme catalysed reactions page no. 474-477 Kinetics of photochemical reactions (H_2-Cl_2 and H_2-Br_2) page no. 360-364, 327-328, 358-359 Kinetics, Mechanism and determination of activation energy and chain length of some organic decomposition (i) decomposition of ethane (ii) decomposition of acetaldehyde page no. 386-390
5. **Principles of Chemical Kinetics, James E. House, Elsevier Publication**
6. **Kinetics and Mechanism of Chemical Transformations, Rajaraman, J. and Kuriacose, J., McMillan (2008).**
7. **Kinetics of chemical reactions S.K. Jain, Vishal Publications**
Mechanism and determination of activation energy and chain length of some organic decomposition (i) decomposition of ethane (ii) decomposition of acetaldehyde page no. 141-143, 144-145 Effect of Ionic strength on rates of ionic reactions (Primary and Secondary Salt Effect) page no. 160-162 Kinetics of polymerization (Addition and Condensation) page no. 192-195
8. **A Text Book of Physical chemistry K.L. Kapoor Vol-5 Macmillan India Ltd. 2007**
Effect of Ionic strength on rates of ionic reactions (Primary and Secondary Salt Effect) page no. 164-167
9. **An Introduction to Chemical Thermodynamics R P Rastogi and R R Mishra VIKASH PUBLISHING HOUSE PVT LTD. 6th edition** Introduction to Laws of thermodynamics, state and path functions and their applications, thermodynamic description of various types of processes page no. 1-15, 42-47 **Maxwell's relations page no. 254-258** Partial molar quantities (Partial molar volume, Internal energy, enthalpy, entropy, Gibbs free energy and Work function) page no. 318-325 Thermodynamics functions of mixing of non-ideal solutions (i) free energy of mixing (ii) entropy of mixing (iii) volume of mixing and (iv) enthalpy of mixing page no. 396-397 Calculation of partial molar quantities determination of partial molar volume and partial molar enthalpy page no. 402-413

Excess functions(μ^E , G^E , S^E , H^E and V^E) for non ideal solutions and expression for excess thermodynamic function. Page no. 397-398

(Assembly, Canonical ensemble, occupation number, statistical weight factor, probability page no. 269-273 Thermodynamic probability, Probability and entropy page no. 274-278 Partition function page no. 284 Thermodynamic properties in term of partition functions (i) Internal energy (ii) Heat Capacity (iii) Third law of thermodynamics (iv) Helmholtz free energy (v) Enthalpy (vi) Gibb's free energy (vii) Chemical potential (viii) Equilibrium constant page no. 286- 291

10. Advanced Physical Chemistry D.N.Bajpai S.CHAND & COMPANY LTD. 2nd edition

Effect of Ionic strength on rates of ionic reactions (Primary and secondary salt effect) Page no. 508-512 Partition function page no. 275-276 Derivation for Translational, Rotational and Vibrational partition functions page no. 278-282.

11. Polymer science by V.R.Gowarikar. WILEY EASTERN LTD.

Types of polymers (12). Stereochemistry of polymers (46). Kinetics of polymerisation (105). Phase techniques (71). Number and mass average molecular mass, PDI (90). Molecular mass determination by viscometry and osmometry (404, 392). Glass transition temperature (150)

SEMESTER -I

GROUP-C PHYSICAL PRACTICAL (Any Six)

1. Determine the dissociation constants of a given dibasic acid pH-metrically.
2. Determine the amount of ferrous sulphate / ferrous ammonium sulphate in given flask potentiometrically using ceric salt solution.
3. Verification of Onsager's equation and determination of equivalent conductance at infinite dilution of strong electrolytes
4. Determine the CMC of a surfactant by conductivity measurements.
5. Calculate the molar absorptivity of each of the given two solutions (A) and (B) and also find out concentration of supplied unknown solution colorimetrically.
6. Investigation the reaction between $K_2S_2O_8$ and KI at two different temperatures and calculate the energy of activation for the reaction.
7. To study the phase diagram of a three component system Water – acetic acid – chloroform.
8. Determination of CMC and area per molecule of a surfactant by surface tension measurement.
9. Determine the molecular weight of a given polymer from viscosity measurement.

Note : For instrumental analysis, solution should be prepared by the candidate.

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SEMESTER-II

UNIT-I: THEORIES OF ELECTROLYTIC CONDUCTANCE AND OVER VOLTAGE 11 Periods

Debye-Huckel theory of strong electrolytes, relaxation effect and electrophoretic effect, Debye Falkenhagen effect, Weineffect. Ionic strength and its determination, Debye-Huckel limiting law. Activity and activity coefficient, determination of activity coefficient by (i) solubility (solubility product principle) (ii) EMF method (cell without transference), Determination of dissociation constant of monobasic acid by conductance method and approximate EMF method, Electrolytic polarization, Dissolution and Decomposition potential, Concentration polarization, Decomposition potential and its determination, over voltage, determination of over voltage, theories of over voltage: combination of atom as slow process (Tafel theory)

Numerical.

UNIT-II: SURFACE CHEMISTRY

11 Periods

Adsorption Multilayer Adsorption, the BET adsorption isotherms, derivation of BET equation, determination of surface area and area of cross section of molecules by BET equation. Derivation of Langmuir equation from BET equation. Explanation of different adsorption isotherms, Change in enthalpy, entropy and free energy of adsorption, Adsorption at the surface of liquid: Gibbs adsorption isotherms (derivation). Thermodynamic treatment of adsorption, Surface – Active substances, orientations of surfactants on the surface of solution, surface inactive substances, surface pressure, Insoluble surface films on liquid

Numerical

UNIT-III: COLLOIDS:

11 Periods

Types of colloidal systems, preparation of lyophobic colloidal, Properties of Colloidal systems: (i) electrical properties origin of charges on colloidal, electrical double layer, Zeta potential and its determination by electrophoresis, factor affecting zeta potential, explanation on DLVO theory of colloid stability (ii) Electrokinetic properties: Electrophoresis, electroosmosis.

Surface active agents, critical micellar concentration (CMC), factors affecting the CMC of surfactants, thermodynamics of micellization: mass action and phase separation model, solubilisation, emulsion, types of emulsion, methods for determination of types of emulsion, microemulsion, types of microemulsion, theories of microemulsion.

UNIT IV: MOLECULAR SPECTROSCOPY

12 Periods

Molecular spectra, **Microwave spectroscopy** (Rotational spectroscopy): The Rotation of molecules, Linear molecule, Symmetric tops, Spherical tops, Asymmetric tops, Rotational spectra of rigid diatomic molecule, Intensities of spectral lines, Effect of isotopic substitution, Techniques and instrumentation of rotational spectrum,

IR Spectroscopy: Classical frequency of harmonic oscillator, The classical potential energy of harmonic vibration of a diatomic molecule, Quantum expression of potential energy, energy level diagram, Relative population of energy levels, Mechanism of interaction with radiation, selection rule, determination of force constant, Amplitude of vibration, The anharmonic vibration or oscillator, Morse potential, Vibrational energy of diatomic molecule following the Morse potential, energy level diagram, vibrational transitions.

Vibrational –Rotational spectra of diatomic molecule (CO molecule) Application of Vibrational rotational spectra

Numerical

Reference Book:

1. Atkins, P.W., Physical Chemistry, W.H. Freeman (2017) 10th edition
2. Samuel Glasstone, Introduction to Electro chemistry, East-West Press Pvt. Ltd. (2008)
3. Puri, B.R., Sharma, L.R., and Pathania, M.S., Principles of Physical Chemistry, Vishal Publishing Co. (2017-18) 45th ed. Debye-Huckel theory of strong electrolytes, relaxation effect and electrophoretic effect, **Debye Falkenhagen effect, Wein effect.** Ionic strength and its determination, Debye-Huckel limiting law page 866-874 Insoluble surface films on liquid page no. 1025
Types of colloidal systems, preparation of lyophobic colloidal, Properties of Colloidal systems: (i) electrical properties origin of charges on colloidal, electrical double layer, Zeta potential and its determination by electrophoresis, factor affecting zeta potential, explanation on DLVO theory of colloid stability (ii) Electrokinetic properties: Electrophoresis, electroosmosis. Page no. 989-1001
4. **Fundamentals of Molecular Spectroscopy C N Banwell TATA McGRAW-HILL 15th edition**
Molecular spectra page no. -1 Microwave spectroscopy (Rotational spectroscopy): The Rotation of molecules Linear molecule, Symmetric tops, Spherical tops Asymmetric tops, Rotational spectra of rigid diatomic molecule, Intensities of spectral lines, Effect of isotopic substitution page no. 40-53 Techniques and instrumentation of rotational spectrum page no. 66 –67 Quantum expression of potential energy, energy level diagram, Relative population of energy levels, Mechanism of interaction with radiation, selection rule, determination of force constant, The anharmonic vibration or oscillator, Morse potential, Vibrational energy of diatomic molecule following the Morse potential, energy level diagram, vibrational transitions. Vibrational –Rotational spectra of CO molecule Application of Vibrational rotational spectra page no. 72-88
5. **A Text Book of Physical chemistry K. L. Kapoor Vol-4 Macmillan India Ltd. 3rd edition**
Classical frequency of harmonic oscillator, The classical potential energy of harmonic vibration of a diatomic molecule, Quantum expression of potential energy, energy level diagram, Relative population of energy levels, Mechanism of interaction with radiation, selection rule, determination of force constant, Amplitude of vibration, The anharmonic vibration or oscillator, Morse potential, Vibrational energy of diatomic molecule following the Morse potential, energy level diagram, vibrational transitions page no.

460-471 Vibrational –Rotational spectra of diatomic molecule Application of Vibrational rotational spectra page no. 480-484

Raman Spectrum in detail page no. 488-500

6 A Text Book of Physical Chemistry K. L. Kapoor Vol -5 Macillan India Ltd. 3rd edition

Adsorption Multilayer Adsorption, the BET adsorption isotherms, derivation of BET equation, determination of surface area and area of cross section of molecules by BET equation. Derivation of Langmuir equation from BET equation. Explanation of different adsorption isotherms, Change in enthalpy ,entropy and free energy of adsorption, Adsorption at the surface of liquid : Gibbs adsorption isotherms (derivation). Thermodynamic treatment of adsorption, Surface –Active substances, orientations of surfactants on the surface of solution , surface inactive substances, surface pressure page no. 11-22 , 24-26 , 30-32 ,34-38

7 Advanced Physical Chemistry D.N.Bajpai, S.CHAND & COMPANY LTD. 2nd edition

Activity and activity coefficient, determination of activity coefficient by (i) solubility (solubility product principle) (ii) EMF method (cell without transference), page no. 623-626

SEMESTER -II

GROUP – C PHYSICAL PRACTICAL (Any Six)

1. Determine the dissociation constant and strength of borax solution pH-metrically.
2. Determine the velocity constant of the hydrolysis of ethyl acetate with sodium hydroxide at room temperature by conductance measurements.
3. Determine the solubility of silver chloride in water potentiometrically.
4. To determine the concentration of given components in a mixture colorimetrically.
5. Determine the equilibrium constant of the reaction $\bar{I} + I_2 = I_3^-$ by distribution method.
6. Investigation the reaction between H_2O_2 and HI at two different temperatures and calculate the energy of activation for the reaction
7. Determine the formula of a complex between Cu^{+2} and NH_3 by distribution method.
8. Determine CST of Phenol -Water system
9. Determine CST of Phenol –NaCl system

Note : For instrumental analysis, solution should be prepared by the candidate.