

ANDHRA UNIVERSITY
DEPARTMENT OF CHEMISTRY
M.Sc. (PREVIOUS) CHEMISTRY SYLLABUS
SEMESTER-I
PAPER-I: GENERAL CHEMISTRY-I
(Effective from the admitted batch of 2021-2022)

UNIT – I

[12 Hours]

Rotational spectra of diatomic molecules-rigid rotor-selection rules-calculation of bond length- isotopic effect, second order stark effect and its applications, Infrared spectra of diatomic molecules-harmonic and anharmonic oscillators. Selection rules-overtone-combination bands calculation of force constant, anharmonicity constant and zero point energy. Fermi resonance, simultaneous vibration rotation spectra of diatomic molecules.

UNIT-II

[12 Hours]

Raman effect-classical and quantum mechanical explanations-Rotational Raman and vibrational Raman spectra, Electronic spectra of diatomic molecules-Vibrational coarse structure-intensity of spectral lines-Franck Condon principle-applications, Rotational fine structure-band head and band shading, Charge transfer spectra.

UNIT-III

[12 Hours]

Spin Resonance Spectroscopy: Principle and theory of NMR spectroscopy-Nature of spinning particle and its interaction with magnetic field. Chemical shift and its origin. Spin-Spin interaction- experimental methods. Application of NMR to structural elucidation-Structure of ethanol, dimethylformamide, styrene and acetophenone. Principle and theory of ESR-g-factor, hyperfine interactions-applications of ESR studies to the structure of free radicals, metal complexes.

UNIT-IV

[12 Hours]

Basic concepts of Symmetry and Group theory – Symmetry elements, symmetry operations and point groups – Schoenflies symbols – Classification of molecules into point groups – Axioms of Group theory – Group multiplication tables for C_{2v} and C_{3v} point groups –Similarity Transformation and classes – Representations – reducible and irreducible representations, Mulliken symbols, Orthogonality theorem and its implications, character table and its anatomy.

UNIT-V

[12 Hours]

Basic components of Computers, higher and lower level languages, Microsoft Fortran: constants, variables and operators, arithmetic expressions, assignment and replacement statements, Input and Output statements – Format free and Format directed I/O statements – Iw, Fw.d, Ew.d and Gw.d format specifications, conditional and unconditional statements – Logical IF, Block IF and Go To statements, Do statement – syntax and rules.

Application of Chemical Problems:

Flowcharts and Programs for

1. Statistical Analysis calculation of arithmetic mean, mean deviation, variance and standard deviation of replicate measurements.
2. Solution of Quadratic equation – calculation of the roots of a quadratic equation.
3. Calculation of the pH and hydrogen ion concentration of an aqueous solution of a strong acid taking into account the auto ionization of water.
4. Calculation of the root of a polynomial using Gauss-Newton method – Application to Vander-Waal's equation.
5. Calculation of the rate constant of a first order reaction or calculation of molar extinction coefficient using Beer-Lambert's Law by Linear least-squares method.

Text Books:

1. Symmetry and Spectroscopy of Molecules, K Veera Reddy, New Age International Publishers.
2. Physical Chemistry by Peter Atkins and Julio de Paula, Oxford University Press.
3. Chemical Applications of Group Theory, F. A. Cotton Wiley Eastern Limited New Delhi.
4. Group Theory and its Applications to Chemistry, K. V. Raman, Tata McGraw – Hill Publishing Company Ltd., New Delhi.
5. Computer programming in Fortran-IV by V .Rajaraman, Prentice-Hall of India Pvt. Ltd., New Delhi.
6. Molecular Spectroscopy, - Gordon M. barrow
7. Fundamentals of Molecular Spectroscopy – Banwell.

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PAPER-I: INORGANIC CHEMISTRY-I
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UNIT-1

[12 Hours]

Structure & Bonding: Applications of VSEPR, Valence Bond and Molecular orbital theories in explaining the structures of simple molecules- role of p and d orbitals in π - $d\pi$ bonding, Bent's rule, Non-valence cohesive forces.

Application of MO theory to square planar (PtCl_4^{2-}) and octahedral complexes (CoF_6^{3-} , $\text{Co}(\text{NH}_3)_6^{3+}$).

Walsh diagrams for linear (BeH_2) and bent (H_2O) molecules

UNIT-II

[12 Hours]

Inorganic cage and ring compounds – preparation, structure and reactions of boranes, carboranes, metallocarboranes, Boron–Nitrogen ($\text{H}_3\text{B}_3\text{N}_3\text{H}_3$), Phosphorus–Nitrogen ($\text{N}_3\text{P}_3\text{Cl}_6$) and Sulphur–Nitrogen (S_4N_4 , $(\text{SN})_x$) cyclic compounds. Structure and bonding in higher boranes with (special reference to B₁₂ icosahedra). Electron counting rules in boranes – Wades rules (Polyhedral skeletal electron pair theory).

Polyacids: Introduction to polyacids- Types of polyacids- Isopolyacids, Isopoly molybdates, Isopolytungstates, Isopolyvanadates, Structures of Polyacids $[\text{Mo}_7\text{O}_{24}]^{6-}$, $[\text{V}_{10}\text{O}_{28}]^{6-}$ and $[\text{W}_4\text{O}_{16}]^{8-}$, Heteropolyacids- properties of heteropolyacids and salts, structures of heteropolyacids and theories, Mialalicopause and Roscneium theories, Pauling's theory and keggin's theory, applications of polyacids.

UNIT-III

[12 Hours]

Coordination compounds: Crystal field theory - crystal field splitting patterns in octahedral, tetrahedral, tetragonal, square planar, square pyramidal and trigonal bipyramidal geometries. Calculation of crystal field stabilization energies. Factors affecting crystal field splitting energies – Spectrochemical series, Jahn – Teller theorem (static and dynamic Jahn-Teller theorem) and its consequences, nephelauxetic effect, applications and limitations of CFT; ligand field theory

Experimental evidences for covalence in complexes. Molecular Orbital Theory of bonding for Octahedral, tetrahedral and square planar complexes. π -bonding and MOT-Effect of π - donor and π -acceptor ligands on Δ_o . Experimental evidence for π - bonding in complexes.

UNIT- IV

[12 Hours]

Electronic spectra of transition metal complexes:

Term symbol-Free Ion terms and Energy Levels: Configurations, Terms, States and Microstates, calculation of Microstates for P^2 and d^2 Configuration, Russell- Saunders Coupling Schemes, J-J Coupling scheme, derivation of terms for various configurations P^2 and d^2 configuration, spectroscopic Ground state, Hole Formalism, Energy ordering of terms (Hund's Rules), Selection rules: Laporte orbital selection rule, spin selection rules. Splitting of energy levels and spectroscopic states Orgel diagrams of d^1 to d^9 metal complexes. Interpretation of electronic spectra of aquo Complexes of Ti(III), V(III), Cr(III), Mn(II), Fe(II), Fe(III), Co(II), Ni(II) and Cu(II). Calculation of interelectronic and spectral parameters for d^8 metal complexes.

UNIT- V

[12 Hours]

Tanabe- Sugano diagrams for d^1 - d^9 octahedral and tetrahedral transition metal complexes of 3d series. Calculation of Dq , Racah Parameter (B) and nephelauxetic parameter (β), Charge transfer ($L \rightarrow M$ and $M \rightarrow L$) spectra of metal complexes.

Magnetic properties of metal Complexes: Types of magnetic behavior, Temperature independent paramagnetism. Magnetic properties of transition and inner transition metal complexes – spin and orbital moments – quenching of orbital momentum by crystal fields in complexes. Magnetic susceptibility and its determination by Gouy's method, and Faraday's method. orbital contribution to magnetic moment (O_h and T_d Complexes)

Text books:

1. Advanced Inorganic Chemistry by F.A. Cotton and G. Wilkinson, IV Edition, John Wiley and Sons, New York, 1980.
2. Inorganic Chemistry by J.E. Huheey, III Edition, Harper International Edition, 1983.
3. Theoretical Inorganic Chemistry, II Edition by M.C. Day and J. Selbin, Affiliated East-West press Pvt. Ltd., New Delhi.
4. Inorganic Chemistry by Shriver and Atkins, Oxford University Press (1999).

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UNIT - I

Aliphatic Nucleophilic Substitutions: The SN₂, SN₁, SN_i and SET mechanisms. Substitution reactions of ambident nucleophiles, anchimeric assistance, the neighbouring group mechanism: neighbouring group participation by O, N, S, halogens, aryl groups, alkyl and cycloalkyl groups in nucleophilic substitution reactions. Sigma, Pi bond participation in acyclic and bicyclic systems (Non- classic carbocations). Nucleophilic Substitution at allylic, trigonal and Vinylic carbons. Effect of substrate, attacking nucleophile, leaving group and reaction medium.

UNIT-II

Aliphatic Electrophilic Substitutions: SE₁ SE₂ and SE_i mechanisms. Reactivity- effects of substrate, leaving group and solvent. Reactions- hydrogen exchange, migration of doublebonds, halogenation of aldehydes, ketones, carboxylic acids, acyl halides, sulfoxides and sulphones.

UNIT-III

Stereochemistry and conformational analysis : Optical Isomerism: optical activity, molecular dissymmetry and chirality - elements of symmetry. Fisher's projection D,L. and R,S. configurations - relative and absolute configurations optical isomerism due to asymmetric carbon atoms - optical isomerism in biphenyls, allenes and spirans- optical isomerism of nitrogenous compounds, racemisation and resolution. Geometrical isomerism: E, Z -configurations, properties of geometrical isomers. Conformational analysis: Conformations of acyclic molecules – alkanes and substituted alkanes- compounds having intramolecular hydrogen bonding. Conformations of cyclohexane, mono and disubstituted cyclohexanes and decalins, effect of conformations on reactivity.

UNIT-IV

Chemistry of heterocyclic compounds : Structure, reactivity and synthesis of reduced three membered Heterocycles: (a) Oxirane: Sharpless method, Shi epoxidation, Jacobsen epoxidation, etc, (b) Aziridine; four membered Heterocycles: (a) Oxetane (b) Azetine; five membered Heterocycles: (a) Pyrrole: Paal Knorr, Hantzsch Methods, etc, (b) Thiophene: Paal Knorr, Hinsberg method, etc. (c) Furan: Paal Knorr, Fiest-Benary, Industrial Method, etc.; (d) Pyrazole, Imidazole, Oxazole, Thiazole; Six membered Heterocycles: (a) Pyridine, Pyridazine, pyrimidine and Pyrazine; Aromatic heterocyclics: a) Indole: Fischer indole synthesis, Bischler synthesis, Madelung synthesis, Domino and cascade methods of indole synthesis, (b) Quinoline and Isoquinoline, (c) Coumarins and Chromones.

UNIT-V

Chemistry of Natural Products

A) Terpenoids: - Occurrence, Isolation, isoprene rule, structure elucidation and synthesis of α - Terpineol and α - pinene

B) Steroids:- Nomenclature of steroids, structure elucidation and synthesis and stereochemistry of cholesterol and progesterone

C) Lipids:- Classification, chemistry, properties and function-free fatty acids, triglycerides, phospholipids, glycolipids & waxes conjugated lipids-lipoproteins

Reference Books

1. Advanced Organic Chemistry: Reactions Mechanisms and Structure by Jerry March, Mc.Graw Hill and Kogakush.
2. Organic Chemistry Vol. I (Sixth Ed.) and Vol. II (Fifth Ed.) by I L Finar ELBS.
3. Organic Chemistry (fifth Ed.,) by Morrison and Boyd, PHI, India.
4. Organic Chemistry (fifth edition) by Francis A. Carey Tata Mc Graw Hill publishing Company Limited, New Delhi.
5. Stereochemistry of Organic compounds by Ernest L. Eliel, Samuel H. Wilen
6. Chemistry of natural products by S. V. Bhat, B. A. Nagasampangi and M. Siva kumar, Narosa Publishing House, 6th reprint 2010

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PAPER-I: PHYSICAL CHEMISTRY-I
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UNIT-I

[12 Hours]

Basic concepts of second law of Thermodynamics-Entropy- Entropy changes accompanying different processes-Entropy changes in an ideal gas, entropy changes in the mixing of ideal gases, entropy as a function of V and T and entropy as a function of P and T- Entropy change in isolated systems-Clausius inequality-Helmholtz and Gibbs energy -Maxwell relations - Criteria for spontaneity-variation of Gibbs energy with temperature and pressure for solids, liquids and gases-Concept of fugacity-determination of fugacity coefficient of gases- Thermodynamics of phase transitions- Concept of chemical potential-Location of phase boundaries- (Clausius-Clapeyron equation for Liquid- Vapour, Solid -Liquid and Solid- Vapour boundaries)-Ehrenfest classification of phases.

UNIT-II

[12 Hours]

Thermodynamics of mixtures -partial molar quantities - experimental methods of determination of partial molar quantities -Gibbs-Duhem equation and Duhem-Margules equation-Thermodynamics of mixing of liquids (ΔH_{mix} , ΔG_{mix} and ΔS_{mix}) - Thermodynamics of ideal solutions - Raoult's law - Thermodynamics of colligative properties of dilute solutions - concept of activity and activity coefficient- Experimental determination of activity coefficient - Thermodynamic concept of equilibrium, variation of equilibrium with temperature (Van't Hoff equation) and pressure - Nernst heat theorem, Third law of thermodynamics- exceptions to third law of thermodynamics.

UNIT-III

[12 Hours]

Surface tension- Capillary action- Adsorption-Adsorption isotherms-Freundlich adsorption isotherm, Langmuir adsorption isotherm-limitations - BET adsorption isotherm-estimation of Surface area.Surface active agents, classification of surface active agents, micellization, hydrophobic interaction, critical micellar concentration (CMC), factors affecting the CMC of surfactants, counter ion binding to micelles, thermodynamics of micellization-phase separation and mass action models.

UNIT-IV

[12 Hours]

Chemical Kinetics: Theories of reaction rates- Collision theory-Limitations, Transition state theory.Lindeman's theory of unimolecular reactions -Limitations. Diffusion controlled reactions. Effect of ionic strength on rates of reactions- Primary and secondary salt effects.

Effect of dielectric constant on reactions - kinetic isotope effect -Primary and secondary isotopic effects -Effect of substituent -Linear free energy relationships-Hamett equation -limitations- Taft equation. Kinetics of consecutive reactions, parallel reactions, opposing reactions (Uni molecular steps only, no derivation).

UNIT-V

[12 Hours]

Specific and general acid-base catalysis. Skrabal diagrams. Steady state approximation- Enzyme catalysis- Michaelis -Menten mechanism. Derivation of Kinetic equation and Kinetic parameters. Lock and Key hypothesis-pH dependence of enzyme catalyzed reactions.Fast reactions- different methods of studying fast reactions- flow methods, relaxation methods- temperature jump and pressure jump methods.

Text Books:

1. Physical Chemistry by Peter Atkins and Julio de Paula, Oxford University Press.
2. Chemical Kinetics by K. J. Laidler, McGraw Hill Pub.
3. Physical chemistry by K.L. Kapoor

Reference Books:

1. Thermodynamics for Chemists, Samuel Glasstone
2. Physical chemistry by Puri, Sharma and Pathania
3. Micelles, Theoretical and applied aspects, V. Moroi, Plenum publisher

ANDHRA UNIVERSITY
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M.Sc. (PREVIOUS) CHEMISTRY
PAPER: INORGANIC CHEMISTRY LABORATORY-I
(Effective from the admitted batch of 2021-2022)

1. Synthesis of Inorganic Metal Complexes: Synthesis of 3d transition metal complexes of tetrahedral, square planar and octahedral geometries.

- (i) Preparation of Tetraammine Copper(II) sulphate monohydrate
- (ii) Potassium tris-oxalatoferrate (III) trihydrate
- (iii) Tris-thiourea copper(I) sulphate

2. Systematic SemimicroQualitative Analysis of Inorganicsix radical mixtures

In systematic Semi micro qualitative inorganic analysis, inorganic mixture contains three cations and three anions. The analysis involves identification and conformation of cations and anions containing one less familiar cation (Tungsten, Molybdenum, Zirconium, Thorium, Titanium, Uranium, Cerium, Vanadium, Lithium, Berkelium Etc... and one interfering anion

Anions: CO_3^{2-} , S^{2-} , SO_3^{2-} , Cl^- , Br^- , I^- , NO_3^- , SO_4^{2-} , CH_3COO^- , $\text{C}_2\text{O}_4^{2-}$, $\text{C}_4\text{H}_4\text{O}_6^{2-}$, PO_4^{3-} , CrO_4^{2-} , AsO_4^{3-} , F^- , BO_3^{3-}

Cations: Ammonium (NH_4^+), 1st group: Hg, Ag, Pb, Tl, W; 2nd group: Hg, Pb, Bi, Cu, Cd, As, Sb, Sn, Mo; 3rd group: Fe, Al, Cr, Ce, Th, Ti, Zr, V, U, Be

4th group: Zn, Mn, Co, Ni. 5th group: Ca, Ba, Sr. 6th group: Mg, K, Li

Note: A minimum of 4 inorganic mixtures must be analysed in this Semester

REFERENCE BOOKS:

1. Practical Inorganic Chemistry, G. Marr and B. W. Rockett.
2. Practical Inorganic Chemistry by G.Pass H.Sutchiffe, 2nd edn John Wiley & Sons.
3. Experimental Inorganic/Physical Chemistry, M. A. Malati, Horwood Publishing, Chichester, UK (1999)

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SEMESTER-I
PAPER: PHYSICAL CHEMISTRY LABORATORY-I
(EFFECTIVE FROM THE ADMITTED BATCH OF 2021-2022)

1. Conductometry
 - a) Conductometric titration of strong acid (HCl) vs strong base (NaOH)
 - b) Conductometric titration of weak acid (CH₃COOH) vs strong base NaOH)
 - c) Conductometric titration of mixture of acids (HCl + CH₃COOH) vs strong base (NaOH)
2. Determination of Cell constant of conductivity cell
3. Determination of Dissociation constant of weak acid by conductometric Method
4. Determination of Critical solution temperature of phenol-Water system
5. Determination of effect of electrolyte (NaCl) on the miscibility temperature of Phenol- Water system
6. Determination of composition of Cuprammonium cation using partition Coefficient method
7. To verify Langmuir and Freundlich isotherm for absorption of acetic acid onto activated Charcoal

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Synthesis of Organic compounds

Synthesis, purification and characterization of about ten organic compounds involving one or two stages.

List of some suggested compounds

1. β -Naphthyl methyl ether from β -Naphthol
2. m-dinitrobenzene from Nitrobenzene
3. Azo dye from primary amine
4. Aromatic acid from ester
5. Benzanilide from aniline
6. p-nitroaniline from Acetanilide
7. p-Bromo acetanilide from aniline
8. Phthalimide from phthalic acid
9. 1,2,3-Tribromo benzene from aniline
10. Benzanilide from Benzophenone

Text Books:

1. A Textbook of Practical Organic Chemistry by A. I. Vogel, ELBS and Longman group.
2. Practical Organic Chemistry by Mann and Saunders, ELBS and Longman group.

MODEL QUESTION PAPER
ANDHRA UNIVERSITY
DEPARTMENT OF CHEMISTRY
M.Sc. (PREVIOUS) CHEMISTRY
Paper- I: GENERAL CHEMISTRY-I-Semester-I
(Effective from 2021-2022 admitted batch)

Time: 3 hours

Answer ALL questions
(5x16=80 Marks)

Max. Marks: 80

1. (a) (i) What kind of molecules exhibit microwave spectra.
(ii) Discuss isotope effect in microwave spectra.
(or)
(b) (i) Derive an expression for energy of harmonic oscillator and discuss the selection rules.
(ii) Describe the origin of PQR structure of Vibrational-Rotational spectra.
2. (a) (i) Discuss the classical and quantum mechanical theories of Raman spectra.
(ii) Explain rotational fine structure in electronic spectroscopy?
(or)
(b) (i) State and explain Franck Condon principle.
(ii) Write a short note on charge transfer spectra.
3. (a) (i) Explain the terms spin active nuclei, resonance, Larmor precession and chemical shifts in NMR.
(ii) Explain hyperfine interactions in ESR spectroscopy taking examples.
(or)
(b) (i) What are the factors affecting g value in ESR spectroscopy.
(ii) Explain spin-spin interactions in NMR spectroscopy?
4. (a) (i) State and explain the axioms of group theory.
(ii) State the great Orthogonality theorem and discuss its implications.
(or)
(b) (i) Give the point groups for NH₃, XeF₄, eclipsed C₂H₆, Cis C₂H₄, B₃N₃H₆ and allene.
(ii) Describe the anatomy of character table.
5. (a) (i) Write a flowchart and FORTRAN program for calculation of rate constant of a first order reaction.
(ii) Give the syntax and rules of DO statement.
(or)
(b) (i) Write a flowchart and FORTRAN program for calculation of pH and hydrogen ion concentration of an aqueous solution of a strong acid taking into account the auto ionization of water.
(ii) Write a brief note on format directed Input/output statements.

MODEL QUESTION PAPER
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M.Sc. (PREVIOUS) CHEMISTRY
Paper- II: INORGANIC CHEMISTRY-I Semester-I
(Effective from 2021-2022 admitted batch)

Time: 3 hours

Answer ALL questions
(5x16=80 Marks)

Max. Marks: 80

1. (a) (i) Predict the geometries of ClF_3 , XeF_4 and SF_4 molecules using VSEPR theory.
(ii) What is LCAO method? Predict bond order and bond lengths in O_2^+ and O_2^- ions based on MO energy level diagram
OR
- (b) (i) Draw the MO energy level diagram for $[\text{Co}(\text{NH}_3)_6]^{3+}$ and discuss its magnetic properties.
(ii) Draw the Walsh diagram for H_2O molecule and predict its structure.
2. (a) (i) Discuss the preparation of, structure of, and bonding in $\text{N}_3\text{P}_3\text{Cl}_6$.
(ii) Discuss the structure and properties of borazole.
OR
- (b) (i) Explain Mialalicopause and Roscneium theories, Pauling's theory and keggin's theory of polyacids.
(ii) Explain the method of counting skeletal electrons in cluster compounds
3. (a) (i) Draw and explain the crystal field splitting of 'd' orbitals in square planar and trigonal bipyramidal geometries.
(ii) Discuss the factors affecting crystal field splitting energies.
OR
- (b) (i) What are static and dynamic Jahn-Teller theorem and discuss its consequences
(ii) Write a note on nephelauxetic effect
4. (a) (i) How do Tanabe – Sugano diagrams differ from Orgel diagrams? Draw Tanabe – Sugano diagram for $[\text{V}(\text{H}_2\text{O})_6]^{3+}$
(ii) Draw the Orgel diagram for $[\text{TiCl}_4]^-$ ion and explain the electronic transitions.
OR
- (b) (i) Write an account on Russell – Saunders coupling.
(ii) Derive the term symbols for Ni^{2+} and identify the ground state term symbol

5. (a) (i) Discuss different types of paramagnetic behavior of transition metal complexes
(ii) Calculate the spin only magnetic moments of the $[\text{MnCl}_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$

OR

- (b) (i) Describe the Magnetic properties of inner transition metal complexes
(ii) Determination of magnetic susceptibility a determination by Gouy's and Faraday's methods

MODEL QUESTION PAPER
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M.Sc. (PREVIOUS) CHEMISTRY
Paper- III: ORGANIC CHEMISTRY-I-Semester-I
(Effective from 2021-2022 admitted batch)

Time: 3 hours

Answer ALL questions
(5x16=80 Marks)

Max. Marks: 80

1. a. (i) Explain SN2 reaction with stereo chemical evidence.
(ii) What are non-classical carbocations? Explain them.
(or)
b. (i) Describe neighbouring group participation reactions of Oxygen and Halogens with an examples
(ii) Write a note on nucleophilic substitution reactions at allylic and trigonal carbons

2. a. (i) Explain SE1 and SE2 reactions with examples
(ii) Write a note on halogenations of ketones and carboxylic acids with examples.
(or)
b.(i) Write a note on SEⁱ reaction and Migration of double bonds
(ii) Describe halogenations of sulphoxide and sulphones.

3. a. (i) Explain Optical isomerism of biphenyls and spirans.
(ii) Write about racemisation and resolution with examples.
(or)
(b) (i) Describe the properties of geometrical isomers.
(ii) Write the conformational analysis of cyclohexane with an example.

4. a. (i) Write any two synthesis and reactivity of Oxirane.
(ii) Explain any two synthesis and reactivity of Indole.
(or)
- b (i) Describe the synthesis and properties of Pyridine.
(ii) Write a note on coumarins and chromones with examples.
- 5 a. (i) Explain the synthesis of α - pinene
(ii) Write any synthesis of progesterone.
(or)
- b. (i) Explain triglycerides with examples.
(ii) Write the structure elucidation of cholesterol.

MODEL QUESTION PAPER
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Paper- IV: PHYSICAL CHEMISTRY-I-Semester-I
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Time: 3 hours

Answer ALL questions
(5x16=80 Marks)

Max. Marks: 80

1. (a) (i) Derive Maxwell's relations.
(ii) Define fugacity. How do you determine the fugacity of real gases?
(or)
- (b) (i) Derive Clausius- Clapeyron equation.
(ii) Explain the entropy changes accompanying in different processes.
2. (a) (i) Define partial molar quantity? Explain the experimental methods for determining partial molar quantities.
(ii) Explain briefly about thermodynamics of mixing of liquids.
(or)
- (b) (i) State and explain third law of thermodynamics and write its limitations.
(ii) What is effect of temperature on equilibrium constant?
3. (a) (i) Discuss the features and limitations of Langmuir adsorption isotherm.
(ii) Give a classification of surface-active agents along with examples.
(or)
- (b) (i) What are important features of BET isotherm.
(ii) What is CMC? What are the factors affecting CMC.
4. (a) (i) Discuss the Lindeman theory of unimolecular reaction and its limitations.
(ii) Write a note on diffusion-controlled reactions.
(or)
- (b) (i) Derive an expression for effect of ionic strength on rate of reaction.
(ii) Discuss the kinetics of consecutive reactions.
5. (a) (i) Explain the Michaelis-Menten mechanism for enzyme catalysis.
(ii) Explain the mechanism of specific acid-base catalysis.
(or)
- (b) (i) Explain steady-state approximation with examples.
(ii) Explain temperature jump method for fast reactions and derive an expression for relaxation time.

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SEMESTER-II
PAPER-I: GENERAL CHEMISTRY-II
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Unit I **[12 Hours]**

Wave equation – interpretation of wave function – properties of wave function – normalization and orthogonalisation, operators – linear and non-linear commutators of operators, Postulates of quantum mechanics, setting up of operators observables – Hermitian operator – Eigen values of Hermitian operator.

Unit-II **[12 Hours]**

Wave mechanics of simple systems with constant potential energy, particle in one dimensional box – factors influencing colour – transition – dipole integral, symmetry arguments in deriving the selection rules-the concept of tunneling – particle in a three dimensional box, Rigid rotor, wave mechanics of systems with variable potential energy-simple harmonic oscillator-solution of wave equation-selection rules.

UNIT-III **[12 Hours]**

Hydrogen atom-solution of $R(r)$, $\theta(\theta)$ and $\Phi(\phi)$ equations-probability density in orbitals-shapes of orbitals. Perturbation theory- time independent perturbation (only first order perturbation is to be dealt with) – application to ground state energy of hydrogen and helium atom

UNIT -IV **[12 Hours]**

Variation principle-applications to hydrogen and helium atoms-calculation of zero point energy of harmonic oscillator-many electron atom- Comparison between Perturbation and variation theorems. Hartee-Fock self-consistent field method and introductory concepts of Density functional theory(DFT).

UNIT-V **[12 Hours]**

Valence bond approach-directed valence-hybridization-covalent bond-calculation of ionic and covalent bond contributions in hydrogen molecule. Molecular orbital theory – LCAO approximation – hydrogen molecule ion – hydrogen molecule (fundamental concepts only) – The electronic transitions in the hydrogen molecule.

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PAPER-II: INORGANIC CHEMISTRY-II
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UNIT-I **[12 Hours]**

Metal cluster compounds - definition – evidences for existence of M-M bonds - conditions favorable for formation of M-M bonds – preparation, structure and bonding of the following metal cluster compounds.

$\text{Re}_2\text{Cl}_8^{2-}$, $\text{Mo}_2\text{Cl}_8^{4-}$, $\text{Re}_2(\text{RCOO})_4\text{X}_2$, $\text{Mo}_2(\text{RCOO})_4(\text{H}_2\text{O})_2$, $\text{Cr}_2(\text{RCOO})_4(\text{H}_2\text{O})_2$, $\text{Cu}_2(\text{RCOO})_4(\text{H}_2\text{O})_2$, $\text{Cr}_2\text{Cl}_9^{3-}$, $\text{Mo}_2\text{Cl}_9^{3-}$, $\text{W}_2\text{Cl}_9^{3-}$, Re_3Cl_9 , $\text{Re}_3\text{Cl}_{12}^{3-}$, $\text{Mo}_6\text{Cl}_8^{4+}$, $\text{Nb}_6\text{X}_{12}^{2+}$ and $\text{Ta}_6\text{X}_{12}^{2+}$.

Polyatomic clusters – Zintl ions, Chevrel phases.

UNIT-II **[12 Hours]**

Organometallic compounds - 16 and 18 electron rules.

Isoelectronic relationship - Synthesis, structure, bonding and reactions of carbon monoxide, dinitrogen and nitric oxide complexes.

Isolobal relationship – H, Cl, CH_3 , $\text{Mn}(\text{CO})_5$; S, CH_2 , $\text{Fe}(\text{CO})_4$; P, CH, $\text{Co}(\text{CO})_3$

Synthesis, structure, bonding and reactions of metallocenes with special reference to ferrocene

UNIT-III **[12 Hours]**

Metal Ligand equilibria in solution:

Step wise and overall formation constants and their interaction. Trends in stepwise constants ((statistical effect and statistical ratio), factors affecting the stability of metal complexes; Stability correlations - Irving -William's series, Pearson's theory of hard and soft acids and bases (HSAB), Application of HSAB: Biological functions and toxicology of metals, and medicinal applications; chelate effect and its thermodynamic origin

UNIT-IV **[12 Hours]**

Determination of stability constants of complexes by spectrophotometric method ((Job's method) and pH –metric method(Bjerrum's).

Reactivity of metal complexes – inert and labile complexes. Explanation of lability on the basis of valence bond and crystal field theories.

UNIT- V **[12 Hours]**

Reaction Mechanisms of Metal Complexes:

Reactivity of metal complexes, inert and labile complexes, Kinetics and mechanisms of substitution reactions, kinetics of substitutions reactions in octahedral complexes, acid hydrolysis, Factors affecting acid hydrolysis, Base hydrolysis, Conjugate base mechanism, Anation reactions, substitution reactions in square planar complexes, Trans effect, Mechanism of trans effect, Electron transfer reactions— concept of complementary and non-complementary reactions with examples, inner sphere and outer sphere mechanisms, Marcus theory.

Text books:

1. Advanced Inorganic Chemistry by F.A. Cotton and R.G. Wilkinson, IV Edition, John, John Wiley and Sons, New York, 1980.
2. Inorganic Chemistry by J.E. Huheey, III edition, Harper International Edition, 1983.
3. Organometallic Chemistry-A unified approach by A. Singh and R.C. Mehrotra, Wiley Eastern Ltd.
4. Inorganic Chemistry by Shriver and Atkins, Oxford University Press (1999)
5. Theoretical Inorganic Chemistry, II Edition by M.C. Day and J. Selbin, Affiliated East-West press Pvt. Ltd., New Delhi.
6. Mechanisims of Inorganic reactions in solution by D.Benson, MCgraw Hill, London, 1968.
7. Inorganic chemistry by K.F. Purcell and J.C.Kotz, W.B. Saunders company, New York, 1977.

ANDHRA UNIVERSITY
DEPARTMENT OF CHEMISTRY
M.Sc. (PREVIOUS) CHEMISTRY SYLLABUS
SEMESTER-II
PAPER-III: ORGANIC CHEMISTRY-II

(Effective from the admitted batch of 2021-2022)

UNIT-I

A) Aromaticity: Concept of Aromaticity, Aromaticity of five membered, six membered and fused systems -non-benzenoid aromatic compounds:- cyclopropenylcation, cyclobutadienyldication, cyclopentadienyl anion – tropyliumcation and cyclo octatetraenyl di anion – metallocenes, ferrocenes, azulenes, fulvenes, annulenes, fullerenes. Homo aromaticity, Anti aromaticity and Pseudo aromaticity.

B) Aromatic Nucleophilic Substitutions: The S_NAr, S_N1, benzyne and S_{RN}1 mechanisms. Reactivity: Effect of substrate, leaving group and attacking nucleophile. The Von- Richter, Sommet- Hauser and Smiles rearrangements.

UNIT - II

A) Reactive Intermediates: Generation, structure, stability and reactivity of Reactive intermediates: carbanion, carbocation, free radicals, carbenes and nitrenes.

B) Name Reactions: - Wittig reaction, Grignard reaction, Stork enamine reaction, Michael addition, Mannich Reaction, Diel's-Alder reaction and Ene-reaction,

UNIT-III

Molecular Rearrangements:

Types of molecular rearrangements, migratory aptitude;

Rearrangements to electron deficient carbon: Pinacol-pinacolone, Wagner-Meerwein and Benzil-Benzilic acid,

Rearrangements to electron deficient nitrogen: Beckmann, Hofmann, Curtius, Schmidt and Lossen rearrangements;

Rearrangements to electron deficient oxygen: Baeyer-villiger, Dakin rearrangements;

Other rearrangements: Neber rearrangement and Favorskii rearrangements

UNIT - IV

A) **UV Spectroscopy:** Various electronic transitions, selection rules, effect of solvent on electronic transitions, the absorption laws, chromophores, auxochromes, bathochromic and hypso chromic shifts, hyperchromic and hypochromic effects, Woodward-Fieser rules for conjugated dienes and carbonyl compounds.

B) **Infrared Spectroscopy:** Basic principles: types of molecular vibrations, fingerprint region and identification of functional groups.

C) **Nuclear Magnetic Resonance Spectroscopy (¹H-NMR):** nuclear spin, nuclear resonance, saturation, shielding of magnetic nuclei, chemical shifts, factors affecting the chemical shift, and assignment of chemical shifts.

D) **Mass Spectroscopy:** Basic principles, nitrogen rule and fragmentation pattern of carbonyl compounds and alcohols

UNIT - V

A) **ALKALOIDS:** Occurrence, Isolation, classification based on nitrogen heterocyclic ring and synthesis of quinine and nicotine

B) **Peptides and Proteins:** α-Aminoacids, their general properties and synthesis, Synthesis of peptides by Merrifield solid phase synthesis. Primary, secondary and tertiary structures of proteins

C) **Nucleic acids:** Heterocyclic bases; Purines: Adenine and Guanine; Pyrimidines: Cytosine, Uracil and Thymine; nucleosides, nucleotides Basic concepts of the structures of RNA and DNA

Text books:

1. Organic Chemistry Vol. I (Sixth Edn.) and Vol. II (Fifth Ed.,) by I.L. Finar ELBS.
2. Organic Chemistry (fifth Edn.,) by Morrison and Boyd, PHI, India.
3. Organic Chemistry (fifth edition) by Francis A. Carey Tata McGraw Hill publishing Company Limited, New Delhi.
4. Reaction Mechanism in Organic Chemistry by Mukherjee Sirigh, N Terniitarr, Indiar
5. A guide book to mechanism in Organic Chemistry by Peter Sykes, ELBS.

REFERENCE BOOKS:

1. Advanced organic chemistry by Jerry March (4th Edition)Wiley Eastern. .
2. Stereochemistry of carbon compounds by E.Eliel, John Wiley & Sons, Inc.
3. Stereochemistry of Organic compounds by D. Nasipuri.
4. Chemistry of Natural products by R.S. KalsiKalyani Publishers. 1983.

ANDHRA UNIVERSITY
DEPARTMENT OF CHEMISTRY
M.Sc. (PREVIOUS) CHEMISTRY SYLLABUS
SEMESTER-II
PAPER-IV: PHYSICAL CHEMISTRY -II
(Effective from the admitted batch of 2021-2022)

UNIT-I:

[12 Hours]

Crystal structure of solids: Fundamental of lattices, unit cell, Bravais lattices, symmetry elements in crystals, packing efficiency, radius ratios; Miller indices. Structures and types of solids. Structure determination by X-ray diffraction (Bragg's equation). Magnetic properties of solids-classification of magnetic materials, Magnetic susceptibility, Measurement of magnetic susceptibility. Electric properties- Band theory, the band structure of metals, insulators, and semiconductors. The temperature dependence of the conductivity of extrinsic semiconductors. Superconductivity and occurrence. Meisner effect. Types of superconductors. Theories of superconductivity - BCS theory.

UNIT-II:

[12Hours]

Classification of polymers - Free radical, ionic and Zeigler - Natta Polymerization - kinetics of free radical polymerization - Techniques of polymerization - Glass transition temperature - Factors influencing the glass transition temperature - Number average and Weight average, Molecular weights - molecular weights determination - End group analysis - Osmometry - Light scattering and ultra-centrifugation methods.

UNIT-III:

[12 Hours]

Electrochemistry I: Ionic mobilities and conductivities - Debye-Huckel theory of strong electrolytes, Debye-Huckel onsagar equation-limitations- mean activity coefficient-Verification of Debye-Huckel limiting law. Electrochemical cell- Galvanic and electrolytic cell. Nernst equation-Concentration cell with and without transference- effect of complexation on redox potential- ferricyanide/ ferrocyanide couple, Iron (III) phenonhroline/ Iron(II) phenonhroline couple. Fuel Cells- construction-Variou types- Examples.

UNIT-IV:**[12 Hours]**

Electrochemistry II: The electrode-electrolyte interface. The electrical double layer. The Helmholtz-Perrin parallel-plate model, the Gouy-Chapman diffuse-charge model and the Stern model. Electrode reactions: Charge transfer reactions at the electrode-electrolyte interface. Derivation of Butler-Volmer equation. High field approximation, Tafel equation, Low field equilibrium, over voltage. Theories of over voltage- Corrosion - Concentration polarization - Polarography - Half wave potential and Ilkovic equation.

UNIT-V:**[12 Hours]**

Photochemistry: Electronic transitions in molecules, Franck-Condon principle. Electronically excited molecules- singlet and triplet states, spin-orbit interaction. Quantum yield and its determination. Actinometry. Derivation of fluorescence and phosphorescence quantum yields. Quenching effect- Stern Volmer equation. Photochemical equilibrium and delayed fluorescence- E-type and P-type. Photochemical primary processes, types of photochemical reactions-photodissociation, addition and isomerization reactions with examples.

Text Books:

1. Physical Chemistry by Peter Atkins and Julio de Paula, Oxford University Press.
2. Physical Chemistry by G.W. Castellon, Narosha Publishing House
3. Physical chemistry by K.L. Kapoor.
4. Principles of photochemistry, RohitgeeMukhargee.

ANDHRA UNIVERSITY
DEPARTMENT OF CHEMISTRY
M.Sc. (PREVIOUS) CHEMISTRY
SEMESTER-II
PAPER: INORGANIC CHEMISTRY PRACTICALS-II
(Effective from the admitted batch of 2021-2022)

Quantitative analysis:

1. Volumetric methods of Analysis:

- i) Determination of Ferric iron by photochemical reduction
- ii). Determination of Nickel by EDTA
- iii) Determination of Calcium and Magnesium in a mixture by EDTA
- iv) Determination of Ferrocyanide by Ceric sulphate
- v) Determination of Copper (II) in presence of iron(III)

2. Gravimetric methods of Analysis:

- i) Determination of Zinc as Zinc pyrophosphate
- ii). Determination of Nickel from a mixture of Copper and Nickel.

ANDHRA UNIVERSITY
DEPARTMENT OF CHEMISTRY
M.Sc. (PREVIOUS) CHEMISTRY
SEMESTER-II

PAPER: PHYSICAL CHEMISTRY PRACTICALS -II
(Effective from the admitted batch of 2021-2022)

1. Potentiometric titration of Iron (II) using potassium dichromate
2. Potentiometric titration of strong acid with a strong base using quinhydrone electrode
3. Determination of kinetics of Ester hydrolysis
4. Determination of Equilibrium constant of Potassium Iodide-Iodine system
5. Determination of kinetics of inversion of cane sugar by polarimetry method.
6. Determination of partial molar volume of solute -H₂O system by apparent molar volume method.

ANDHRA UNIVERSITY
DEPARTMENT OF CHEMISTRY
M.Sc. (PREVIOUS) CHEMISTRY
SEMESTER-II
PAPER: ORGANIC CHEMISTRY PRACTICALS -II
(Effective from the admitted batch of 2021-2022)

Identification of the unknown organic compounds

Systematic identification of organic compounds – preliminary tests, detection of extra elements, solubility, common functional group tests (determination of functional group/s in a single compound, if present), preparation of two rational derivatives

The given organic compound must be identified by comparing the melting point /Boiling point of the compound and melting points of its derivatives with the literature

List of suggested compounds

Glucose, fructose, benzaldehyde, p-anisaldehyde, p-chloro benzaldehyde, acetophenone, phenol, cresols, naphthols, esters, p-chloro benzoic acid, aniline, p-toluene, p-anisidine, p-chloroaniline, diphenyl amine, N,N-dimethylaniline, benzamide, naphthalene and anthracene.

TEXT BOOKS

1. A Textbook of Practical Organic Chemistry by A. I. Vogel, ELBS and Longman group.
2. Practical Organic Chemistry by Mann and Saunders, ELBS and Longman group.

MODEL QUESTION PAPER
ANDHRA UNIVERSITY
DEPARTMENT OF CHEMISTRY
M.Sc. (PREVIOUS) CHEMISTRY-II-SEMESTER
PAPER I: GENERAL CHEMISTRY-II
(w.e.f. 2021-2022 admitted batch)

Time: 3 Hours

Answer ALL questions
(5X16 =80 marks)

Maximum marks: 80

- (1) (a) i) Derive Schrodinger wave equation?
ii) Explain the postulates of Quantum mechanics
Or
(b) i) Write notes on Hermitian operator and its properties
ii) Explain normalization and orthogonalisation
- (2) (a) i) Solve the Schrodinger wave equation for a particle in a one-dimensional box.
ii) Write the factors influencing color
Or
(b) i) Derive the Schrodinger wave equation for a simple harmonic oscillator
ii) Describe the concept of tunnelling.
- (3) (a) i) Explain the solutions of $R(r)$, $\theta(\theta)$ and $\Phi(\phi)$ equations of hydrogen atom
ii) Explain probability density in orbitals
Or
(b) i) Explain the time independent perturbation theory to evaluate the ground state energy of helium atom.
ii) Application of above to ground state energy of hydrogen and helium atom
- (4) (a) i) What is variation principle. Write its application to calculation of ground state energy of harmonic oscillator.
ii) Compare Perturbation and variation theorems.
Or
(b) i) Explain Hartee-Fock self-consistent field method for multi electron atoms.
ii) Write a note on Density functional theory (DFT)
- (5) (a) i) Explain quantum mechanical approach of molecular orbital theory.
ii) Calculate the ionic and covalent bond contributions in hydrogen molecule
Or
(b) i) Discuss the valence bond approach of H_2 molecule.
ii) Write the electronic transitions in the hydrogen molecule.

MODEL QUESTION PAPER
ANDHRA UNIVERSITY
DEPARTMENT OF CHEMISTRY
M.Sc. (PREVIOUS) CHEMISTRY-II-SEMESTER
Semester-II
Paper- II: Inorganic Chemistry-II
(Effective from 2021-2022 admitted batch)

Time: 3 hours

Answer ALL questions
(5x16=80 Marks)

Max. Marks: 80

1. a) (i) Discuss the structure and magnetic property of $\text{Cu}_2(\text{RCOO})_4(\text{H}_2\text{O})_2$.
(ii) Write a note on Chevrel phases
OR
(b) (i) Discuss the preparation of, structures of and bonding in $\text{Re}_2\text{Cl}_8^{2-}$.
(ii) Describe the structures of hexanuclear metal clusters.
2. a) (i) Explain the synthesis, structure and reactions of metal carbonyls.
(ii) Explain Isolobal relationship with suitable examples.
OR
b) (i) Describe the preparation of, structure of and bonding in ferrocene.
(ii) What is 18 electron rules? Illustrate with suitable examples
3. a) (i) Explain the factors affecting the stability of coordination compounds.
(ii) Distinguish between stepwise and overall stability constants.
OR
(b) (i) Describe the Irving -William's series, Pearson's theory of hard and soft acids and bases (HSAB),
(ii) What is chelate effect and discuss its thermodynamic origin
4. a) (i) Discuss a spectrophotometric method for the determination of binary formation constant of a metal complex.
(ii) What are inert and labile complexes?
OR
(b) (i) Describe the pH – metric method for the determination of stability constants.
(ii) Explain inert and labile complexes by using crystal field stabilization energies?
5. a) (i) What is acid hydrolysis reactions? Discuss Factors affecting acid hydrolysis reactions
(ii) What is trans effect? Distinguish between the trans effect and trans influence.
OR
b) (i) Give an account of base hydrolysis of Cobalt (III) complexes.
(ii) Discuss the various factors affecting the rates of substitution reactions of octahedral complexes.

MODEL QUESTION PAPER
ANDHRA UNIVERSITY
DEPARTMENT OF CHEMISTRY
M.Sc. (PREVIOUS) CHEMISTRY-II-SEMESTER
Semester -II
Paper- III: Organic Chemistry-II
(Effective from 2021-2022 admitted batch)

Time: 3 hours

Answer ALL questions
(5x16=80 Marks)

Max. Marks: 80

1. a. (i) Explain Aromaticity and Anti aromaticity give examples.
(ii) Write a note on Von- Richter rearrangement
(or)
b. (i) Describe Aromatic Nucleophilic Substitution reactions give examples.
(ii) Write a note on Non-benzenoid aromatic compounds and Annulenes.

- 2 a. (i) Write any two preparations and reactivity of carbocation.
(ii) Write a note on Stork enamine reaction.
(or)
b. (i) Explain carbanion and nitrene

(ii) Briefly explain Mannich Reaction with applications.

- 3 a. (i) Explain Pinacol-pinacolone rearrangement give examples.
(ii) Describe mechanism and applications of Beckmann rearrangement.
(or)
b. (i) Discuss about Baeyer-villager rearrangement.
(ii) Write a note on Favorskii rearrangement.

- 4 a. (i) Write the Woodward-Fieser rules for conjugated dienes.
(ii) Explain types of molecular vibrations in Infrared Spectroscopy.
(or)
b(i) Describe factors affecting the chemical shift.
(ii) Give the fragmentation pattern of alcohols.

5 a. (i) Write the synthesis of nicotine

(ii) Explain Merrifield solid phase synthesis.

(or)

b. (i) Write about Primary, secondary and tertiary structures of proteins.

(ii) How do you differentiate RNA and DNA

MODEL QUESTION PAPER
ANDHRA UNIVERSITY
DEPARTMENT OF CHEMISTRY
M.Sc. (PREVIOUS) CHEMISTRY-II-SEMESTER
Semester -II
Paper- IV: PHYSICAL CHEMISTRY-II
(Effective from 2021-2022 admitted batches)

Time: 3 hours

Answer ALL questions
(5x16=80 Marks)

Max. Marks: 80

1. (a) (i) Derive Bragg's equation
(ii) Explain the theories of superconductivity
(or)
(b) (i) Describe the different methods of measurement of magnetic susceptibility.
(ii) Write a brief note on semiconductors.
2. (a) (i) Give the classification of polymers with examples.
(ii) What are the factors influencing glass transition temperature.
(or)
(b) (i) How is molecular weight of polymers determined by osmometry and light scattering methods.
(ii) Write a brief note on kinetics of free radical polymerization.
3. (a) (i) Explain Debye-Huckel theory of strong electrolytes
(ii) Discuss the effect of complexation on redox potential with examples?
(or)
(b) (i) Derive an expression for EMF of concentration cell without transference.
(ii) Discuss the important features of Debye-Huckel limiting law.
- 4 (a) (i) Derive Butler-Volmer equation
(ii) Explain the Stern model for double layer.
(or)
(b) (i) Explain in detail about polarography.
(ii) Discuss important features of Gouy-Chapman diffuse charge model and Helmholtz parallel plate model
5. (a) (i) Derive Stern-Volmer equation
(ii) State and explain Franck-Condon principle
(or)
(b) (i) Define quantum yield and explain its experimental method determination.
(ii) Discuss the mechanism of photo addition and photo isomerization with examples