

JYOTI NIVAS COLLEGE (AUTONOMOUS), BANGALORE- 95

**I Semester M. Sc. Chemistry
JOC 101: Inorganic Chemistry - I**

52 hrs

Course Objectives

This course aims to impart to the student, knowledge of:

- Advanced principles of bonding in inorganic compounds.
- The chemistry of coordination compound with Pi acceptor ligands
- The structure of important silicon containing compounds and the correlation between their structure and applications.
- The chemistry of non-metal containing compounds such as boranes, borazines, sulphur-nitrogen compounds and phosphorus-nitrogen compounds.
- The structure and applications of isopoly and heteropoly anions of vanadium, molybdenum and tungsten and metal carbonyl clusters.
- The various principles and applications of solvent system, hard-soft acid base (HSAB), theories of acids and bases and concept of super acids.

Course Learning Outcomes

On completion of the course, students should be able to:

- Appreciate the different theories of chemical bonding and be able to apply these theories to solve structures
- Apply IR spectroscopy to discuss structures of pi acceptor containing complexes
- Choose an appropriate solvent for carrying out any chemical reaction based on the principles of acids and bases.
- Apprehend the structures of heteropoly, isopoly anions and metal carbonyl clusters and relate the structure to chemical reactivity.
- Interpret the three-dimensional structure of silicates and catalytically important molecules such as aluminosilicates (zeolites) and apply their knowledge towards selectivity based on structure.
- Illustrate the structure of non-metallic compounds and classify boranes based on STYX.

Unit I

1. Chemical Bonding 1

15 hrs

Ionic bond: Lattice energy, Born-Landé equation, Kapustinskii equation, Born-Haber cycle and its applications, Fajan's rules, Slater's rules, radius-ratio rules, structures of crystal lattices (NaCl, CsCl and ZnS).

Hybridisation, VSEPR model, shapes of molecules – XeF₂, ClF₃, XeF₄, ICl₄⁻, XeF₆, TeCl₆²⁻, IF₇, NO₂, NO₂⁺, NO₂⁻, CO₃²⁻, SO₄²⁻

Energetics of hybridization and

Bent's rules and, Electronegativity and partial ionic character, Covalent bonding: M.O. Theory: σ , π and δ molecular orbitals, MOs of diatomic molecules: homo - N_2 and O_2 and heteronuclear – CO, NO, HF, ICl, Walsh diagrams of BeH_2 and H_2O . Co-ordinate and quadruple bonds. Hydrogen bonds-types and detection, Agostic bond.

Unit II

2. Chemical Bonding 2

11 hrs

Synergic bonding: simple metal carbonyls, nitrosyl, and tertiary phosphine complexes. Structure and bonding in hydride, dihydrogen, dinitrogen, isocyanide. Stereochemical non-rigidity: (TBP, CO scrambling), Stereoisomerism-chirality, optical activity. Absolute configurations, CD, ORD, Cotton effect and magnetic circular dichroism

Unit III

3. Compounds of non-metals

07 hrs

Structure and bonding in boranes, carboranes, metallo-carboranes, styx code explanation with examples (B_2H_6 , B_4H_{10} , B_5H_9 , B_6H_{10} , B_5H_{11} and $B_{10}H_{14}$), Wade's rules, preparation, properties, structure and bonding of borazine, phosphazenes – tri and tetra, sulphur-nitrogen compounds – S_2N_2 , S_4N_4 , $(SN)_x$.

4. Silicates

06 hrs

Principles of structure of silicates, Classification and structures of silicates, isomorphous replacement, pyroxenes, amphiboles, layered (double and triple, distinction between structure of talc and muscovite) and vitreous silicates, zeolites – synthesis of sodalite and ZSM-5, application as molecular sieves, ion-exchange and catalyst.

Unit IV

5. Concepts of Solvent systems and Acids-Bases

06 hrs

Solvent systems; Bronsted and Lewis acids and bases, pH and pKa, Hard and Soft acids and bases (HSAB) - concept, application and limitations, levelling effect, super acids, acid-base concept in non-aqueous media, reactions in liquid BrF_3 and liquid N_2O_4 .

6. Isopoly and heteropoly acids of W, Mo and V

04 hrs

Preparation and structure of: Isopolyvanadates – VO_4^{3-} , $V_2O_7^{4-}$, $(VO_3)_n^{n-}$, $[V_{10}O_{28}]^{6-}$; Isopolymolybdates – di, para ($Mo_7O_{24}^{6-}$), tri, tetra (meta), octa ($Mo_8O_{26}^{4-}$); Isopolytungstates – normal, para, meta ($W_{12}O_{42}^{12-}$, $H_2W_{12}O_{40}^{6-}$); Heteropoly acids of Mo and W – 12 molybdoheteropoly acids, 12 tungstoheteropoly acids; General applications of isopoly and heteropoly acids.

7. Metal clusters

03 hrs

M-M bond and metal atom clusters, bonding in $\text{Re}_2\text{Cl}_8^{2-}$; Metal carbonyl clusters – LNCC's and HNCC's. Electron counting in carbonyl clusters: Wades-Mingos and Lauher rules

References

1. Basic Inorganic Chemistry, F.A.Cotton, G. Wilkinson and P.L. Gaus, John Wiley and sons (1995)
2. Advanced Inorganic Chemistry 3rd, 5th and 6th Editions, F. A. Cotton and G. Wilkinson
3. Inorganic Chemistry, 4th Edition, J.E.Huheey, E.A.KeiterandR.L.Keiter, Addison - Wesley (1993)
4. Inorganic Chemistry, 2nd Edition, D.F. Shriver, P.W. Atkins and C.H. Langford, ELBS (Oxford Univ. Press) (1994)
5. Concise Inorganic Chemistry, 5th Edition, J.D.Lee (1996).
6. Chemistry of the Elementals, N.N. Greenwood and A.E. Earnshaw, Butterworth Heinemann (1997)
7. Essential trends in Inorganic Chemistry, D.M.P.Mingos, Oxford Univ. Press (1998)
8. Materials Science, J.C.Anderson, K.D.Lever, J.M.Alexander and R.D. Rawlings, ELBS, (2000).
9. Structural Inorganic Chemistry, A F Wells, Oxford: Clarendon Press, 1984.
10. Inorganic Chemistry, James E. House, Latest ELBS edition.
11. Basics of Inorganic Chemistry by William Jolly, Latest edition

JYOTI NIVAS COLLEGE (AUTONOMOUS), BANGALORE- 95

M.Sc., I Semester, JOC 101: Inorganic Chemistry - I

End Semester Question Paper Format for Theory

Maximum Marks: 70

Time: 3 Hrs

The question paper shall consist of two parts **A** and **B**. Part **A** shall consist of **12** questions of **2** marks each of which the student answers only **10** questions. Part **B** shall consist of **7** questions of **10** marks each of which the student answers only **5** questions. To give due weightage to all chapters, the question paper shall consist of questions drawn from the respective chapters such that the marks allotted to these chapters are in proportion to the number of teaching hours prescribed. Paper setter is requested to avoid 2 marks questions in Part – B.

Unit	Chapter Title	Hours of Teaching	Marks allotted		
			Part A	Part B	Total
I	1. Chemical bonding 1	15	06	20	26
II	2. Chemical bonding 2	11	06	15	21
III	3. Compounds of non metals	07	04	10	14
	4. Silicates	06	02	08	10
IV	5. Concepts of Solvent systems and Acids-Bases	06	02	08	10
	6. Isopoly and heteropoly acids of W, Mo and V	04	02	06	08
	7. Metal clusters	03	02	03	05
	Total	52	24	70	Part-A:12Qx2M=24 Part-B:7Qx10M=70
	Maximum Marks for students = 70[(Part-A:10Qx2M=20)+(Part-B:5Qx10M=50)]				

JYOTI NIVAS COLLEGE (AUTONOMOUS), BANGALORE- 95

I Semester M. Sc. Chemistry

JOC 102: Organic Chemistry - I

52 hrs

Unit I

1. Nature of Bonding in Organic Molecules **06 hrs**

Delocalized chemical bonding: Conjugation, cross conjugation, Hyperconjugation. Tautomerism
Aromaticity. Huckel's rule of aromaticity. Craig's rule. Aromatic systems with electron numbers
other than six (including azulene, tropone, tropolone and annulenes). Antiaromaticity.
Aromaticity in benzenoids, meso-ionic compounds. Homo-aromaticity. Alternant and non
alternant hydrocarbons, Energy levels in odd and even-alternant hydrocarbons, energy levels for
the benzyl cation, benzyl free-radical and benzyl carbanion.

2. Synthetic Molecular Receptors **04 hrs**

Definition and significance, Structure and function of receptors with molecular clefts, molecular
tweezers, receptors with multiple hydrogen bonding sites, cryptates, cyclodextrins, cyclophanes
and calixarenes

3. Reaction Mechanisms - I **10 hrs**

Generation, structure, stability and reactivity of carbocations, carbanions, carbon free radicals,
carbenes and nitrenes

Classification of reactions and mechanisms: Thermodynamic and kinetic requirements, kinetic
and thermodynamic control, Hammond postulate, Curtin-Hammett principle. Potential energy
diagrams, transition states and intermediates

Methods of determining mechanisms: Based on the structure of products, determination of the
presence of intermediates, isotopic labeling, isotope effects, from stereochemical evidence

Acids and bases: Hard and soft acids and bases. Effect of structure on the strengths of acids and
bases

Effect of structure on reactivity: Resonance and field effects; steric effects. The Hammett
equation and linear free energy relationship, substituent and reaction constants, Taft equation

4. Reaction Mechanisms - II **04 hrs**

Nucleophilic substitution reaction at saturated carbon: S_N1 , S_N2 , S_{Ni} and SET mechanism, Effect
of substrate structure, attacking nucleophile, leaving group, Ambident nucleophiles and
substrates.

Unit II

5. Stereochemistry

10 hrs

Fischer, Newman, Sawhorse and flying wedge projections and their interconversions Optical isomerism: Elements of symmetry and chirality, D-L conventions, CIP rules, R-S and M-P conventions, Chirality in compounds with a stereogenic centre, in allenes, alkylidene, cycloalkanes and spiranes (with a stereogenic axis), Cram's and Prelog's rules

Conformational analysis: Conformational analysis of cycloalkanes: cyclobutane, cyclopentane, cyclohexanes (monosubstituted e.g., methyl, *iso*-propyl, *tert*-butyl and di-substituted cyclohexanes e.g., dialkyl, dihalo, diols) and cycloheptane

Nomenclature and conformations of fused rings and bridged ring systems.

Prochirality: Enantiotopic and diastereotopic atoms, groups and faces.

Unit III

6. Oxidations

12hrs

CrO₃, K₂Cr₂O₇, KMnO₄, OsO₄, SeO₂, Pb(OAc)₄, HIO₄, Ozone, peroxides (H₂O₂, t-BuOOH, and peracids (CF₃COOOH, m-CPBA. Synthesis and application of Jones reagent, Chromyl chloride, Oppenaur oxidation. PDC, PCC, MnO₂.

7. Reductions

06hrs

Complex metal hydrides (LiAlH₄, NaBH₄), dissolving metal reductions (Na/liq.NH₃, Birch, Clemmensen reductions), Baker's Yeast, diimide reduction, catalytic hydrogenation (homogenous and heterogeneous), hydrazine as reducing agents; Wolf-Kishner reduction, Meerwein-Ponndorf-Verley reduction.

REFERENCES

1. Advanced Organic Chemistry – Reactions, Mechanism and Structure, Jerry March, John Wiley (2008).
2. Advanced Organic Chemistry, F A Carey and R J Sundberg Plenum, (1990).
3. A Guide Book to Mechanism in Organic Chemistry, Peter Sykes, Longman, (2000).
4. Structure and mechanism of Organic Chemistry, C K Ingold, Cornell University Press (1999).
5. Organic Chemistry, R T Morrison and R N Boyd, Prentice-Hall, (1998).
6. Principles of Organic Synthesis, R O C Norman and J M Coxon, Blackie Academic and Professional, (1996).
7. Stereochemistry of Organic Compounds, D Nasipuri, New-Age International, (1999).
8. Stereochemistry of Carbon Compounds, E L Eliel, S H Wilen and L N Mander, John Wiley, (1994).
9. Organic Synthesis, Jagadamba Singh and L. D. S. Yadav, Seventh Edition, 2011.

10. Organic Reaction Mechanisms, V. K. Ahluwalia and Rakesh Kumar Parashar, 4th Edition, 2012.
11. Some modern methods of Organic Synthesis, W. Carruthers, Cambridge Uni. Press London, 2ndEdn., 1998.
12. Understanding organic reaction mechanisms, A. Jacob, Cambridge, University Press, 1997.
13. Introduction to organic chemistry, A. Streitweiser, Jr. and C. H. Heathcock, Macmillan, 1985.
14. Organic Chemistry, Volumes I and II, I L Finar, Longman, (1999).

JYOTI NIVAS COLLEGE (AUTONOMOUS), BANGALORE- 95
M.Sc., I Semester, JOC 102: Organic Chemistry - I
End Semester Question Paper Format for Theory

Maximum Marks: 70**Time: 3 Hrs**

The question paper shall consist of two parts **A** and **B**. Part **A** shall consist of **12** questions of **2** marks each of which the student answers only **10** questions. Part **B** shall consist of **7** questions of **10** marks each of which the student answers only **5** questions. To give due weightage to all chapters, the question paper shall consist of questions drawn from the respective chapters such that the marks allotted to these chapters are in proportion to the number of teaching hours prescribed. Paper setter is requested to avoid 2 marks questions in Part – **B**.

Unit	Chapter Title	Hours of Teaching	Marks allotted		
			Part A	Part B	Total
I	1. Nature of bonding in organic molecules	06	04	08	12
	2. Reaction Mechanisms - I	10	04	14	18
	3. Reaction Mechanisms - II	04	02	05	07
II	4. Stereochemistry	10	04	14	18
III	5. Oxidations	09	04	12	16
	6. Reductions	09	04	12	16
IV	7. Synthetic Molecular Receptors	04	02	05	07
	Total	52	24	70	Part A:12Qx2M=24 Part B:7Qx10M=70
Maximum Marks for students = 70 [(Part-A:10Qx2M=20)+(Part-B:5Qx10M=50)]					

JYOTI NIVAS COLLEGE (AUTONOMOUS), BANGALORE- 95

M.Sc., I Semester, JOC 102: Organic Chemistry - I

Model Question Paper 2018

Time: 3 hrs

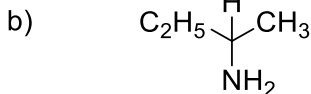
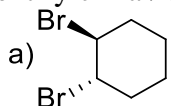
Max Marks: 70

PART - A

1. Answer any **ten** of the following. Each carries **two** marks.

10x2=20

- Write a note on homoaromaticity with an example.
- What are singlet and triplet carbenes.
- Explain cross conjugation with an example.
- Write – Taft equation and explain the terms involved.
- Write the E and Z forms of $C_6H_5C(Br)=CHCOOH$.
- Identify chiral/ achiral molecules.



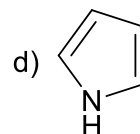
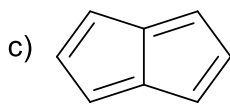
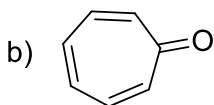
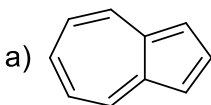
- What are ambident nucleophiles and substrates? Give an example for each.
- Discuss the use of $KMnO_4$ as an oxidizing agent.
- Discuss the use of PCC in organic synthesis
- Explain Wolf-Kishner reduction.
- Write the synthetic utility of Baker's yeast.
- Give an account of structure and function of molecular tweezers.

PART - B

Answer any **five** of the following. Each carries **ten** marks.

5x10= 50

2. a) Which of the following compounds are aromatic, non-aromatic and anti-aromatic? Justify.



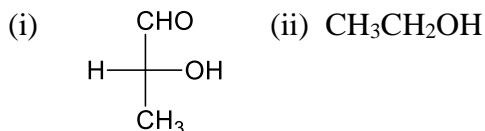
- Explain the utility of $Pb(OAc)_4$ in oxidation of hydroquinones along with mechanism.
- What are alternant and non-alternant hydrocarbons? Explain with suitable examples and predict the energy levels of benzyl radical and benzyl cation. (4+3+3)

3. a) Explain Prelog's rule with an example.

b) Explain Curtin-Hammett principle with an example and free energy diagram.

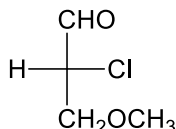
c) Explain HSAB theory with examples. (3+4+3)

4. a) Discuss any two methods used for determining the mechanism.
 b) What is prochirality? Indicate the types of groups/faces present in the following.



- c) Explain Prelog's rule with example. (4+3+3)

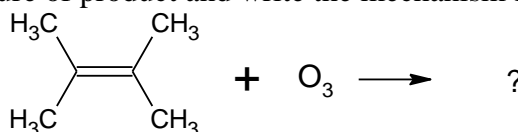
5. a) Give the conformational analysis of cyclopentane and comment on their stability.
 b) What is a CIP rule? Explain how these rules are used to determine R/S conformation of the following.



- c) Discuss Birch reduction taking appropriate examples. (3+4+3)

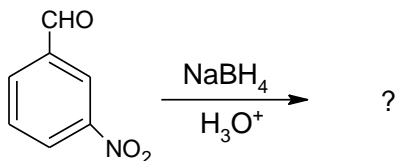
6. a) Outline the mechanism of $\text{S}_{\text{N}}2$ reaction and explain the effects of substrate, leaving groups, attacking nucleophile, solvent on the reaction.
 b) Write a note on molecular clefts. (5+5)

7. a) Give an account of the use of chromium compounds as oxidizing agents.
 b) Predict the structure of product and write the mechanism for the reaction.



- c) Describe the mechanism of Oppenauer oxidation with suitable example. (4+3+3)

8. a) Write a note on catalytic hydrogenation.
 b) Predict the structure of product and write the mechanism of the reaction-



- c) State the importance of diimides as a reducing agent. (4+3+3)

JYOTI NIVAS COLLEGE (AUTONOMOUS), BANGALORE- 95

I Semester M. Sc. Chemistry

JOC 103: Physical Chemistry - I

52 hrs

Unit I: Classical Thermodynamics

1.1 Systems of variable composition **04 hrs**

Partial molar properties – introduction, Partial molar free energy (chemical potential), partial molar volume and their significance. Gibbs-Duhem equation. Variation of chemical potential with temperature and pressure. Simultaneous determination of partial molar volumes of two components of a binary liquid mixture by intercept (reciprocal density) method. Determination of PMV of a solute in a solution by apparent molar volume method. Problems.

1.2 Gases and Solutions **07 hrs**

The concept of fugacity and fugacity coefficient. Determination of fugacity of a gas by graphical and compressibility factor methods. Problems. Raoult's law. Types of deviations of non-ideal solutions from the ideal behaviour. Gibbs-Duhem-Margules equation and its application: Derivation of Raoult's Law, Henry's Law, Phase rule and Nernst Distribution law based on Chemical Potential. Thermodynamic functions of mixing of non-ideal/ideal solutions. Excess thermodynamic functions G^E , S^E , H^E and V^E . Activity and activity coefficient. Determination of mean-ion activity coefficient of an electrolyte (HCl) by EMF method and a sparingly soluble salt by solubility method.

Unit II: Statistical Thermodynamics

2.1 Introductory Aspects and Distribution Laws **05 hrs**

Scope. Concepts of distribution, probability of a distribution (a priori probability and thermodynamic probability) and most probable distribution. The concept of an ensemble. Types of ensembles. Stirling's approximation. Maxwell-Boltzmann, Bose-Einstein and Fermi-Dirac statistics. Derivation of the respective distribution laws using the Lagrange's method of undetermined multipliers. Comparison of M.B., B.E. and F.D. statistics.

2.2 Partition function **04 hrs**

Definition and physical significance. Derivation of expressions for translational, rotational, vibrational and electronic partition functions. Expression of the thermodynamic functions like internal energy, enthalpy, entropy, free energy and heat capacity in terms of partition function. Sackur-Tetrode equation and its significance. Relation between equilibrium constant of a reaction and partition function.

2.3 Applications of statistical thermodynamics

02 hrs

A brief account of the theory of heat capacity of solids: Einstein and Debye Theories. Application of Fermi-Dirac statistics: Evaluation of the electronic contribution to heat capacity of metals.

Unit III

3.0 Non-Equilibrium Thermodynamics

05 hrs

Thermodynamic criteria for non-equilibrium states. Entropy production and entropy flow. Transformations of the generalized fluxes and forces. Phenomenological laws and Onsager's reciprocity relations. Coupled and non-coupled reactions. Electrokinetic phenomena. Principle of detailed balance (microscopic reversibility) as the basis of Onsager's Reciprocity Relations.

Unit IV: Chemical Kinetics

4.1 Introduction to Chemical Kinetics

05 hrs

Macroscopic and Microscopic Kinetics. Review of theories of reaction rate – Arrhenius equation – characteristics, significance of energy of activation, temperature coefficient and its evaluation Collision Theory and Transition State Theory. Comparison of collision theory with transition state theory. Thermodynamic formulation of reaction rates (Wyne-Jones and Eyring treatment). Reaction between ions in solution – influence of ionic strength on reaction rates (primary and secondary salt effects).

4.2 Steady State Kinetics

04 hrs

Chain reactions – general characteristics, chain length and chain inhibition. comparison of photochemical and thermal reactions. Mechanisms of thermal reactions (hydrogen-bromine, hydrogen-chlorine, pyrolysis of acetaldehyde, decomposition of ethane) and photochemical reactions (hydrogen- bromine and hydrogen-chlorine). Comparative study of thermal and photochemical hydrogen-halogen reactions.

4.3 Techniques for Fast reactions

03 hrs

Introduction – need for special techniques. Stopped flow method. Relaxation method (Principle of temperature jump for unimolecular reaction, bimolecular reaction, derivation not required), flash photolysis and shock tube methods.

4.4 Unimolecular Reactions

04 hrs

Introduction - Perrin theory, Lindemann-Christiansen Hypothesis, Hinshelwood treatment, RRK treatment (Qualitative treatment only), RRKM treatment (Qualitative treatment only).

4.5 Kinetics of homogeneous Catalysis

06 hrs

General catalytic mechanisms – Equilibrium treatment: Arrhenius intermediates, Steady state treatment: vant Hoff intermediates, activation energies for catalysed reactions, application to acid base catalysis.

Enzyme catalysis: Comparison of enzymes with chemical catalysts. Mechanism (lock and key) and kinetics of enzyme catalysed reactions – Henri-Michaelis-Menten mechanism, significance of Michaelis-Menten constant, Lineweaver-Burke plot. Effect of enzyme concentration, pH, temperature, activators on enzyme activity. Inhibition of enzymes (Competitive, Non-competitive and uncompetitive, identification based on L.B plots).

Unit V

5.0 Colloids and Surface Chemistry

03 hrs

Stability and properties of colloids. Types of adsorption isotherms. BET adsorption isotherm and its use in the determination of surface area of a solid. Gibbs adsorption isotherm and its significance.

REFERENCES

1. Glasstone S., Thermodynamics for Chemists, Affiliated East-West Press Pvt. Ltd., (1960).
2. Mc. Quarrie D.A., Simon J.D., Molecular Thermodynamics, University Science Books., (1999).
3. Gupta M.C. Statistical Thermodynamics, Wiley Eastern Ltd., (1993).
4. Laidler K.J., Chemical Kinetics 3rd Edition., Pearson Publ., (2013).
5. House J.E., Principles of Chemical Kinetics, Wm C Brown Publisher, Boston (1997).
6. Glasstone S., Text Book of Physical Chemistry, 2nd Edition, Macmillan India Ltd., (1991).
7. Atkins P.W., de Paula J., Physical Chemistry, 7th Edition, Oxford Publ., (2002).
8. Puri B.R, Sharma L.R, Pathannia M.S., Principles of Physical Chemistry, 47th Edition., Shoban Lal Nagin Chand Co., (2017).

JYOTI NIVAS COLLEGE (AUTONOMOUS), BANGALORE- 95
M.Sc., I Semester, JOC 103: Physical Chemistry - I
End Semester Question Paper Format for Theory

Maximum Marks: 70**Time: 3 Hrs**

The question paper shall consist of two parts **A** and **B**. Part **A** shall consist of **12** questions of **2** marks each of which the student answers only **10** questions. Part **B** shall consist of **7** questions of **10** marks each of which the student answers only **5** questions. To give due weightage to all chapters, the question paper shall consist of questions drawn from the respective chapters such that the marks allotted to these chapters are in proportion to the number of teaching hours prescribed. Paper setters are requested to avoid 2 marks questions in Part **B**.

Unit	Chapter Title	Hours of Teaching	Marks Allotted		
			Part A	Part B	Total
I	1.1 Systems of variable composition	04	02	05	07
	1.2 Gases and Solutions	10	04	10	14
	2.1 Introductory Aspects and Distribution Laws	05	02	07	09
	2.2 Partition Functions	04	02	05	07
	2.3 Application of Statistical Thermodynamics	02	-	04	04
III	3.0 Non-equilibrium Thermodynamics	05	02	07	09
IV	4.1 Introduction to Chemical Kinetics	05	02	07	09
	4.2 Steady State Kinetics	04	02	05	07
	4.3 Techniques for Fast reactions	03	-	05	05
	4.4 Unimolecular Reactions	04	02	05	07
	4.5 Kinetics of homogeneous Catalysis	06	04	07	11
V	5.0 Colloids and Surfaces	03	02	03	05
Total		52	24	70	Part-A:12Qx2M=24 Part-B:7Qx10M=70
Maximum Marks for students = 70 [(Part-A:10Qx2M=20)+(Part-B:5Qx10M=50)]					

JYOTI NIVAS COLLEGE (AUTONOMOUS), BANGALORE- 95
M.Sc., I Semester, JOC 103: Physical Chemistry - I
Model Question Paper 2022

Time: 3 hrs

Max Marks: 70

PART - A

1. Answer any **ten** of the following. Each carries **two** marks. **10x2=20**
- Define primary and secondary salt effects.
 - What is meant by 'wall effect'? In which reaction is it observed?
 - Give any two drawbacks of the Hinshelwood Theory.
 - What is meant by General and specific hydrogen ion catalysis?
 - Briefly discuss the lock and key mechanism of enzyme catalysis.
 - Give any two properties of colloids.
 - What are partial molar properties?
 - Define excess thermodynamic function and give the expression for excess chemical potential.
 - Define the term 'activity' and mention the standard state for solvents.
 - Distinguish between microcanonical and grand canonical ensembles.
 - Write the rotational partition function for a homonuclear diatomic molecule.
 - What is the difference between BE and FD statistics?

PART - B

- Answer any **five** of the following. Each carries **ten** marks. **5x10= 50**
- Derive an expression for the rate constant based on the partition function for the activated complex theory.
 - Derive the relation between Arrhenius activation energy and standard enthalpy of activation.
 - Derive the Gibbs adsorption isotherm. (4+3+3)
 - Why are special techniques required to study fast reactions? Discuss the Shock tube method of studying fast reactions.
 - Show that the rate of reaction for the pyrolysis of acetaldehyde has an order of 3/2 by applying the steady state approximation. (5+5)
 - Discuss the Lindeman theory of studying unimolecular reactions.
 - Discuss the various types of enzyme inhibition and how to identify them using the Lineweaver-Burke plots. (5+5)

5. a) Briefly discuss the Michaelis-Menten mechanism.
b) Derive Maxwell-Boltzmann distribution law and express it in its different forms.
c) Derive Sackur-Tetrode equation and explain its significance. (3+4+3)

6. a) Derive Gibbs-Duhem equation. Describe the slope-intercept method for the simultaneous determination of partial molar volumes of two components in a binary liquid mixture.
b) Derive the expression for translational partition function q_t , and using the relation $E_t = NkT^2(d\ln q_t/dt)_v$, evaluate the translational contribution to internal energy E_t . (5+5)

7. a) Obtain expressions for the free energy of mixing of nonideal and an ideal liquid mixture and hence evaluate excess free energy, G^E . Using this obtain expressions for S^E and H^E .
b) How do you determine the activity coefficient of an electrolyte by EMF method? (5+5)

8. a) Give an account of Onsager's reciprocity relations and the principle of detailed balance.
b) Explain the role of statistical thermodynamics in the study of equilibrium properties of matter. Define the terms 'macrostate' and 'microstate'. (6+4)

JYOTI NIVAS COLLEGE (AUTONOMOUS), BANGALORE- 95

I Semester M.Sc. Chemistry

JOC 104: Principles of Chemical Analysis

52 hrs

Unit I

1. Introduction to Data Analysis:

08 hrs

Review: Errors in chemical analysis, accuracy and precision, types of errors- absolute, relative, systematic, random, constant and proportional.

Detection of systematic errors. Nature of random errors, sources, distribution of experimental results. Statistical treatment: samples and population, mean and median. Properties of Gaussian curves – Population mean and sample mean, population standard deviation, area under the curve, sample standard deviation, standard error of the mean. Variance, relative standard deviation (RSD), Coefficient of variation (CV). Confidence intervals. Bivariate data, Correlation coefficients, Regression Analysis: regression lines. Testing of hypothesis: t-test. Determination of Outlier: Q-test.

2. Separation Techniques:

10 hrs

Solvent extraction: Types- Batch, Continuous, efficiency, selectivity, distribution coefficient, Nernst Distribution law, derivation, applications and numerical problems.

Chromatography: Types, Terminology, principles and functioning of Paper, Thin layer, Column, Gas Chromatography, High Performance Liquid Chromatography, Reversed Phase Liquid Chromatography, Super Critical Fluid (SCF) Chromatography, 2D- Thin Layer Chromatography.

Unit II

3. Optical Methods of Chemical Analysis:

06 hrs

Interaction of electromagnetic radiation with matter, deviations from Beer Lambert Law, choice of solvent for UV- Visible spectrophotometry, Sandel sensitivity, Ringbom's plot, Photometric titrations, single and Double beam UV-Visible spectrophotometer, Application of quantitative and qualitative analysis, Principles and Applications of Fluorimetry, Turbidimetry and Nephelometry. Numerical problems on all these techniques.

4. Thermal methods of analysis:

02 hrs

Introduction, general principles and applications of thermogravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC).

Unit III

4. Neutralization Titrations:

05 hrs

Solutions and indicators for acid base titrations- standard solutions, Acid-base indicators, Titration curves: Strong acid vs. strong base, weak acids vs. strong base, and weak base vs. strong acid, pH calculations, polyfunctional acids and bases - phosphoric acid system, composition of polyprotic acid as a function of pH- phosphoric acid, titration curve, titration of amphiprotic species - acid-base behavior of amino acid system.

5. Redox Titrations:

06 hrs

Introduction: Nernst equation, Standard & Formal potentials. Constructing Redox Titration curves - electrode potential during redox titrations, equivalence point potential. Detection of end point: Oxidation reduction indicators: General Redox Indicators, iron (II) complexes of orthophenanthrolines, starch/iodine solutions. Applications: Iron (II) solutions, iodometric titration (involving sodium thiosulfate) Oxidants such as Permanganate, dichromate, Ce (IV), Bromate. Determining water with Karl Fisher reagent.

6. Complexometric Titrations:

05 hrs

Introduction: Formation of complexes, complexation equilibria, suitability of polydentate ligand as titrants, expressions for the different forms of EDTA in solution as a function of pH, conditional formation constants, Effect of pH and titration curve, Selectivity by pH control, masking and demasking reagents, Theory of metal ion indicators, types of EDTA titrations: direct and back titrations.

7. Precipitation titrations:

04 hrs

Introduction: Argentometric titration, shape of titration curves, Solubility product, Theoretical principles of precipitation: Titration curves, Detection of end point, Mohr, Volhard and Fajan's indicators. Applications: Estimation of F^- , K^+ , CO_3^{2-} , $C_2O_4^{2-}$ and mixture of halides.

Unit IV

8. Gravimetric analysis:

06 hrs

Precipitation Gravimetry: properties of precipitates and precipitating agents, factors affecting particle size, mechanism of precipitate formation, experimental control of particle size, conditions for quantitative precipitations, Formation and treatment of precipitates, co-precipitation, precipitation from homogeneous solution, drying and ignition of precipitates, calculation of results from gravimetric data, important precipitating agents such as dimethylglyoxime (DMG) in the estimation of nickel, 8-hydroxyquinoline (oxine) in estimation of aluminium and their significance in inorganic analysis.

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JYOTI NIVAS COLLEGE (AUTONOMOUS), BANGALORE- 95
M.Sc., I Semester, JOC 104: Principles of Chemical Analysis
End Semester Question Paper Format for Theory

Maximum Marks: 70

Time: 3 Hrs

The question paper shall consist of two parts **A** and **B**. Part **A** shall consist of **12** questions of **2** marks each of which the student answers only **10** questions. Part **B** shall consist of **7** questions of **10** marks each of which the student answers only **5** questions. To give due weightage to all chapters, the question paper shall consist of questions drawn from the respective chapters such that the marks allotted to these chapters are in proportion to the number of teaching hours prescribed. Paper setters are requested to avoid two marks questions in Part **B**.

Unit	Chapter Title	Hours of Teaching	Marks allotted		
			Part A	Part B	Total
I	1. Introduction to Data Analysis	08	04	10	14
	2. Separation Techniques	10	04	14	18
II	3. Optical methods of Chemical Analysis	06	02	09	11
	4. Thermal methods of analysis	02	04	-	4
III	5. Neutralization Titrations	05	02	07	9
	6. Redox titrations	06	02	09	11
	7. Complexometric titrations	05	02	07	9
	8. Precipitation titrations	04	02	05	7
IV	9. Gravimetric analysis	06	02	09	11
	Total	52	24	70	Part-A:12Qx2M=24 Part-B:7Qx10M=70
Maximum Marks for students = 70 [(Part-A:10Qx2M=20)+(Part-B:5Qx10M=50)]					

JYOTI NIVAS COLLEGE (AUTONOMOUS), BANGALORE- 95
M.Sc., I Semester, JOC 104: Principles of Chemical Analysis
Model Question Paper 2022

Time: 3 hrs

Max Marks: 70

PART - A

1. Answer any **ten** of the following. Each carries **two** marks. **10x2=20**
- Give an expression for population and sample standard deviation. Explain terms involved.
 - Define and give an expression for standard error of mean.
 - State Nernst distribution law.
 - The distribution ratio for iodine between CS_2 and H_2O is 420. 100 ml of an aqueous solution containing 1.018 mg iodine is equilibrated twice with 50 ml portion of CS_2 . What is the amount of iodine unextracted in H_2O .
 - Discuss about the choice of solvent for UV-Visible spectrophotometry.
 - State the principle of Thermogravimetric analysis.
 - Name the process giving rise to exotherms.
 - Distinguish standard and formal potentials.
 - Define masking and demasking agents with an example.
 - Draw the titration curve of strong acid vs. weak base titration and explain.
 - Explain argentometric titration.
 - How will you estimate nickel using DMG as precipitating agent?

PART - B

- Answer any **five** of the following. Each carries **ten** marks. **5x10= 50**
- Explain three other terms involved in reporting the precision of analytical data.
 - The following results were obtained in the replicate determination of lead content of blood sample: 0.752, 0.756, 0.754, 0.751 and 0.760 ppm Pb. Find the mean, standard deviation, variance, and relative standard deviation in ppt, coefficient of variation and spread. (4+6)
 - What is the amount of Fe^{3+} left unextracted from 100 ml of a solution having 200 mg of Fe(III) and in 6M HCl after 3 extraction with 25 ml of Et_2O ($D=150$)?
 - Explain different types of solvent extraction with examples. (6+4)
 - Illustrate Gas chromatography instrument. Describe the principal components.
 - State and Explain Beer-Lambert Law and give instance of deviation. (5+5)

5. a) What are photometric titrations? Explain any two titration curves where only titrant and both titrant and product absorb.
b) Detect the endpoint of precipitation titration using Volhard method.
c) Write a note on the properties of precipitates and precipitating agent based on gravimetric analysis. (4+3+3)

6. a) Derive the expression of pH for strong acid vs. strong base titration and explain its titration curve.
b) Discuss the acid base behavior of amino acid with titration curve.
c) Write a brief note on the suitability of polydentate ligand as titrant. (4+3+3)

7. a) How will you determine water in various types of solids and organic liquids with Karl Fisher reagent?
b) Discuss the theory of metal in indicator. (5+5)

8. a) Construct redox titration curve and find out electrode potentials during redox titration.
b) Discuss about co-precipitation. (5+5)

JYOTI NIVAS COLLEGE (AUTONOMOUS), BANGALORE- 95

I Semester M. Sc. Chemistry

JOC 105: Mathematics for Chemists (Soft Core)

36 hrs

Unit I

1. Vectors:

04 hrs

Vectors, dot and cross products; scalar and vector triple products and their applications.

2. Matrix Algebra:

08 hrs

Review of different types of matrices (including Hermetian and skew Hermetian); matrix addition and multiplication; determinant of a square matrix, transpose, adjoint and inverse of a square matrix. Solution to system of linear equation (a) by matrix method and (b) by Cramer's Rule. Characteristic equation of a square matrix, eigenvalues and eigen vectors.

Unit II

3. Calculus:

12 hrs

Rule for differentiation; Chain rule (for $f(x)=\sin u, \log u$ etc). Implicit differentiation and parametric differentiation and successive differentiation of order 2 (for explicit functions only). Applications of differentiation: Derivative as a slope of the tangent, derivative as a rate measure-velocity and acceleration. Increasing and decreasing functions-Maxima and minima-second derivative test-point of inflections-problems restricted to polynomial.

Unit III

4. Integrations:

03 hrs

Basic rules-simple substitution-Method of partial fractions-Integration by parts, Define integral and application to areas of plane curves. Functions of several variables: partial derivatives; co-ordinate transformation from cartesian coordinates to spherical and cylindrical coordinates and vice-versa.

5. Elementary differential equation:

03 hrs

Variable separable, exact first order equations, linear and homogeneous equation, Second order homogeneous differential equation with constant coefficients $f(D), y=0$. Solution of differential equation by power series method

6. Fourier series:

03 hrs

Simple problems.

7. Probability:

03 hrs

Review of permutations and combinations. Probability and addition theorem for mutually exclusive events and multiplication theorem for independent events, Curve fitting-Method of least squares

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JYOTI NIVAS COLLEGE AUTONOUOMS, BANGALORE – 95

M.Sc. I Semester, Mathematics for Chemists (Soft Core)

JOC 105

Model Paper

PART A

1. Answer any ten of the following. Each question carries two marks. 10x2=20

1. Find the sine of the angle between the vectors

$$\vec{a} = \hat{j} - 3\hat{k} \quad \text{and} \quad \vec{b} = \hat{i} - \hat{j} + 2\hat{k}$$

2. Find the value of λ if the following vectors are coplanar

$$\hat{i} - \hat{j} + \hat{k}, \quad 2\hat{i} + \hat{j} - \hat{k} \quad \text{and} \quad \lambda\hat{i} - \hat{j} + \lambda\hat{k}$$

3. Find the cofactor matrix of $A = \begin{pmatrix} 2 & 3 \\ 4 & 5 \end{pmatrix}$

4. Find the equation of the tangent to the curve $2(x^3 + y^3) - 9xy = 0$ at (2, 1).

5. If $S = 6t - \frac{1}{2}t^3$, find when the particle comes to rest.

6. Differentiate $y = \log(x + \sqrt{x^2 + a^2})$ w.r.t. x

7. Find the intervals where the function $f(x) = 2x^3 - 96x - 5$ is decreasing or increasing.

8. Evaluate $\int \frac{1}{5 - 4x} dx$

9. Evaluate $\int_0^{\frac{\pi}{2}} e^{\sin x} \cos x dx$

10. Solve $(D^3 - 13D + 12)y = 0$

11. A bag contains 7 white, 6 red and 5 black balls. 2 balls are drawn at random. Find the probability

that they are both white.

12. Find the chance that if a card is drawn at random from a pack of playing cards, it is one of the court cards.

PART B

II Answer any five of the following. Each question carries ten marks. 5x10=50

1. a. Prove the Vector triple product $(\vec{a} \times \vec{b}) \times \vec{c} = (\vec{a} \cdot \vec{c})\vec{b} - (\vec{b} \cdot \vec{c})\vec{a}$

b. Find A and B if $2A - B = \begin{pmatrix} -2 & 1 & -11 \\ -2 & 10 & 2 \\ 5 & -16 & 10 \end{pmatrix}$ and $3A + 4B = \begin{pmatrix} 19 & 40 & 11 \\ -14 & 15 & 36 \\ 13 & -13 & 37 \end{pmatrix}$

2. a. Solve by Cramer's rule : $x + 3z = 10$; $2x + y = 4$; $5y - 4z = -2$

b. Solve the following equations using Matrix method:

$$2x - y + 8z = 13, 3x + 4y + 5z = 18, 5x - 2y + 7z = 20$$

3.a. Find the Eigen values and Eigen vectors of the matrix $\begin{pmatrix} 4 & 1 \\ -1 & 2 \end{pmatrix}$

b. If $y = \frac{(x^2 + 1) \sin x}{1 + x \sec x}$ then find $\frac{dy}{dx}$

4. a. If $x = ae^\theta (\sin \theta - \cos \theta)$, $y = ae^\theta (\sin \theta + \cos \theta)$ then find $\frac{dy}{dx}$ when $\theta = \frac{\pi}{4}$

b. If $x^2 + 2xy + 3y^2 = 1$ then prove that $y_2 = \frac{-2}{(x + 3y)^3}$

5.a. If $u = u = \log(\sqrt{x^2 + y^2 + z^2})$ then find the value of $\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} = \frac{1}{x^2 + y^2 + z^2}$

b. Solve $\frac{dy}{dx} = \frac{x^2 - y^2}{2xy}$

6. a. Solve $\frac{dy}{dx} + 3x^2 y = x^5 e^{x^3}$

b. Find the area enclosed between the parabolas $y^2 = 4x$ and $x^2 = 4y$

7.a. Obtain the Fourier series of $f(x) = x^2$ in $-\pi < x < \pi$

b. Find the line of best fit to the following data.

X	0	5	10	15	20	25
Y	12	15	17	22	24	30
