(Pages : 3) **M – 7140**

Reg. No. : .....

Name : .....

Third Semester M.Sc. Degree Examination, March 2022

Chemistry/Polymer Chemistry/Analytical Chemistry

CH/CL/PC 233 : PHYSICAL CHEMISTRY – III

(2020 Admission)

Time : 3 Hours Max. Marks : 75

SECTION – A

Answer **two** among (a), (b) and (c) from each. Each sub question carries **2** marks.

1. (a) State and explain variation theorem.

   (b) Find the spectroscopic term symbols for Li_2 and O_2.

   (c) Define Fock operator. What is its significance?

2. (a) Estimate C_v of HCl and CO_2 in JK^{-1} mol^{-1} by applying equipartition principle.

   (b) State the physical significance of van der Waals constants and give their units.

   (c) Define mean free path. Calculate the mean free path of oxygen gas in nm at 25°C and 1 atm pressure if the collision diameter is 360 picometer.

3. (a) Draw the NQR energy levels with energies, if the nuclear spin value is 3/2. Explain the impact of quadrupole interactions on NMR lines.

   (b) What are the information that can be gained from photoelectron spectroscopy?

   (c) What is FID? What are the advantages of FTNMR?

P.T.O.

4. (a) Write a note on phenomenological relations in irreversible thermodynamics.

   (b) Write a note on Onsagar reciprocal relations.

   (c) What is mean by thermoelectric phenomena?

5. (a) Compare 6-31G++ and 6-31++ G.

   (b) How is force field different from basis set?

   (c) What is a stationary point? Mention its relevance.

(10 × 2 = 20 Marks)

SECTION – B

Answer either (a) or (b) from each question. Each sub question carries **5** marks.

6. (a) Discuss the quantum mechanics of sp hybridization with an example.

   (b) Apply Huckel's molecular orbital theory to ethylene.

7. (a) Define surface tension and viscosity and methods used to determine them.

   (b) Derive expressions for average velocity and root mean square velocity.

8. (a) Explain Larmor precession and its importance in resonance techniques. A system of protons at 25°C is placed in a 2T magnetic field. Find the ratio of protons in upper to lower state if nuclear g factor value is 5.585 and nuclear magneton is $5 \times 10^{-27} JT^{-1}$.

   (b) Give the applications of ESR spectroscopy in studying reaction rates and mechanism and for analytical purposes.

9. (a) What is mean by thermoelectric phenomena?

   (b) Write a note on Glansdorf- Pregogine equation and its significance.

10. (a) Explain in detail various post HF methods used in computational studies.

    (b) Write a note on any three force fields highlighting their applications

(5 × 5 = 25 Marks)

SECTION – C

Answer any **three** questions. Each question carries **10** marks.

11. Apply valence bond theory to hydrogen molecule.

12. Write an essay on the transport properties and intermolecular forces of gases.

13. Explain the basic principles and applications of Mossbauer spectroscopy. Give the quadrupole and magnetic hyperfine interactions.

14. Sketch and explain the graphical representation of a three-component liquid-liquid system with

    (a) one pair of partially miscible liquids;

    (b) two pairs of partially miscible liquids;

    (c) three pairs of partially miscible liquids.

15. (a) How is semi empirical method different from dft method? Explain in detail.

    (b) Explain in detail the theory, design constrain and applications of MD simulations.

(3 × 10 = 30 Marks)

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(Pages : 3) **M – 7144**

Reg. No. : .....

Name : .....

Third Semester M.Sc. Degree Examination, March 2022

Chemistry/Polymer Chemistry/Analytical Chemistry/Applied Chemistry

CH/CL/CA/PC 233 : PHYSICAL CHEMISTRY – III

(Common for Chemistry (2016 – 2019 Admission) and Polymer Chemistry (2018 – 2019 Admission))

Time : 3 Hours Max. Marks : 75

SECTION – A

Answer any **two** among (a), (b) and (c) from each question. **Each** sub- question carries **2** marks.

1. (a) Write the Hamiltonian for HeH^+ by considering Born-Oppenheimer approximation.

   (b) Show that two molecular orbitals of H_2 are orthogonal.

   (c) How does the bond order of central π-bond in butadiene differ from butadiene cation?

2. (a) Calculate the number of contracted Gaussian functions and Gaussian primitive functions in C_5H_6 if the basis set is $6-31+G^*$.

   (b) Construct a Z-matrix for H_2O_2.

   (c) Explain the Roothans concept of basis function.

P.T.O.

3. (a) What is meant by NQR?

(b) How many lines will the ESR spectrum of the naphthalene negative have?

(c) How does Doppler effect used in Mössbauer spectroscopy?

4. (a) Use the equipartition theorem to estimate the constant-volume molar heat capacity of C_6H_6 in the gas phase at 25°C.

(b) The first electronically excited state of O_2 is $^1\Delta_g$ and lies 7918.1 cm^{-1} above the ground state, which is $^3\sum_g^-$. Calculate the electronic contribution to the molar Gibbs energy of O_2 at 400 K.

(c) Calculate the temperature at which the population of I_2 at v=1 level have half the population as that of the ground state.

5. (a) What is meant by the controlled-potential electrolysis?

(b) A constant current of 0.800 A is used to deposit copper at the cathode and oxygen at the anode of an electrolytic cell. Calculate the number of grams of each product formed in 15.2 min, assuming no other redox reaction occurs.

(c) Calculate the pH of a solution that contains 0.225 M in H_3PO_4 and 0.414 M in NaH_2PO_4.

(10 × 2 = 20 Marks)

SECTION – B

Answer either (a) or (b) of each question. Each sub-question carries **5** marks.

6. (a) Apply HMO method for π bonding in allyl cation. Find the energy of π molecular orbitals. Calculate the delocalization energy and the charge on each carbon atom in allylic anion.

(b) A trial function for a particle in one dimensional box is given by

$\Psi = c_1 x(a-x) + c_2 x^2 (a-x)^2$. Calculate $H_{11}, H_{12}, H_{22}, S_{11}$ and S_{22} if a = 1?

7. (a) What are the force field energy terms and their mathematical expressions involved in molecular mechanics method?

   (b) How does the Hückel theory differ from the extended Hückel theory?

8. (a) Explain the basic principle of ENDOR.

   (b) Explain the mechanism of spin-spin coupling in ^{1}H NMR.

9. (a) Explain how the internal energy and entropy of a system composed of two levels vary with temperature.

   (b) Explain the origin of residual entropy.

10. (a) How do electrogravimetric and coulometric methods differ from potentiometric methods?

    (b) How do you distinguish between a rotating disk electrode and a ring disk electrode?

(5 × 5 = 25 Marks)

SECTION – C

Answer any **three** questions. **Each** question carries **10** marks.

11. Derive expressions for first order correction to energy and wave function for nondegenerate level.

12. Explain the role of exchange correlation functional in density functional theory.

13. Explain the basic principle and its application of Mössbauer spectroscopy.

14. Use concepts of statistical thermodynamics to describe the molecular features that determine the magnitudes of equilibrium constants and their variation with temperature.

15. Explain the principle and application of polarography.

(3 × 10 = 30 Marks)

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(Pages : 3) **N – 5412**

Reg. No. : .....

Name : .....

First Semester M.Sc. Degree Examination, May 2022

Chemistry/Analytical Chemistry/Polymer Chemistry

CH/CL/PC 211 : INORGANIC CHEMISTRY I

(2020 Admission onwards)

Time : 3 Hours Max. Marks : 75

SECTION – A

Answer **any two** among (a), (b) and (c) from each question. Each sub-question carries **2** marks.

1. (a) What is nephelauxetic effect?

   (b) Arrange the following complex ions in the decreasing order of Δ_0 value: $[Cr(CN)_6]^{3-}$, $[CrCl_6]^{3-}$, $[Cr(NH_3)_6]^{3+}$ Justify your answer.

   (c) The ionic radii of M^{2+} ions are expected to decrease smoothly from Ca^{2+} to Zn^{2+}. But the change is not regular. Why?

2. (a) Distinguish between accuracy and precision.

   (b) What are metallochromic indicators? Give an example.

   (c) Calculate the coefficient of variation of the following set of data

   10.28, 10.24, 10.25, 10.25, 10.30

P.T.O.

3. (a) What are solid electrolytes? Give an example.

(b) Give the materials that can be used for making rechargeable batteries

(c) What are inorganic phosphors?

4. (a) Explain why polymerization stops for isopoly anions?

(b) Define zeolite. What are the different type of secondary building units available in the framework of zeolite?

(c) Describe the structure and bonding in XeF_2.

5. (a) List the constituents of photochemical smog.

(b) Give any two properties of water significant to environment.

(c) How can we control soil acidity?

($10 \times 2 = 20$ Marks)

SECTION – B

Answer either (a) or (b) of each question. Each question carries **5** marks.

6. (a) Consider σ-bond formation only, find out the molecular orbitals of a transition metal complex $[ML_6]$ and draw a tentative molecular orbital energy level diagram. Locate the so-called crystal field splitting bands.

(b) How crystal field stabilization energy helps on predicting lattice energies, enthalpies of hydration and ionic radii of the transition metal based coordination compounds?

7. (a) Outline the principles of complexometric titrations. Discuss how EDTA is used for estimation of zinc.

(b) Discuss the various organic reagents used in gravimetric analysis.

8. (a) Give a brief account of SOFCs.

(b) Discuss the structural aspects of metal nitrides.

9. (a) What are silicones? Discuss their synthesis, structures and applications.

(b) Discuss the preparation and structures of isopolyacids of vanadium.

10. (a) Name any two common air pollutants. What are their hazards?

(b) Give a brief account of hydrological cycle.

($5 \times 5 = 25$ Marks)

SECTION – C

Answer **any three** questions, each question carries **10** marks

11. With the help of molecular orbital theory and energy level diagram, explain, how the crystal field splitting energy depends on π-acceptor and π-donor ligands?

12. Explain the applications of TG, DTA and DSC in the study of metal complexes

13. (a) Write a note on fullerides.

(b) Give an account of one dimensional metals.

14. What are zeolites? How they can function as microporous materials and molecular sieves?

15. (a) Give an account of the depletion of ozone layer.

(b) Write briefly on redox status of soil.

($3 \times 10 = 30$ Marks)

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(Pages : 3) **N – 5413**

Reg. No. : .....

Name : .....

First Semester M.Sc. Degree Examination, May 2022

Chemistry/Analytical Chemistry/Polymer Chemistry

CH/CL/PC 212 : ORGANIC CHEMISTRY I

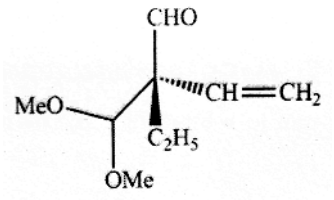
(2020 Admission onwards)

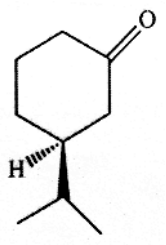
Time : 3 Hours Max. Marks : 75

SECTION – A

Answer two among (a), (b) and c) from each. Each sub question carries **2** marks

1. (a) Assign the configuration (R or S) for

(i) 

(ii) 

(b) Write one example each for chiral, achiral, prochiral and meso form of an organic compound.

(c) Why hydroboration of alkene is stereospecific and regioselective reaction?

2. (a) Sketch the Si / Re faces of acetophenone

(b) Draw the structure of Ibuprofen. Give its uses.

(c) What is Cotton effect? Give its significance.

P.T.O.

3. (a) Arrange the following radicals in the increasing order of their stability

$CH_3\dot{C}H_2, (CH_3)_2\dot{C}H, (CH_3)_3\dot{C}$ and $CH_2 = CH - \dot{C}H_2$.

(b) What is AIBN? Give its structure and applications.

(c) Explain Chichibabin reaction.

4. (a) Give the structure of a classical and non-classical carbonium ion.

(b) Justify the statement with suitable example that "Aryl and vinyl halides show low reactivity towards nucleophilic substitution reaction compared to alkyl halides."

(c) What is Iodolactonisation? Give one example.

5. (a) Explain Saytzeff's rule of elimination reaction.

(b) What is Chugaev reaction?

(c) Illustrate Shapiro reaction with suitable example.

(10 × 2 = 20 Marks)

SECTION – B

Answer either (a) or (b) from each question. Each question carries **5** marks.

6. (a) Give a brief account of the chiral auxiliary and chiral reagents.

(b) Explain octant rule and axial haloketone rule using proper examples.

7. (a) Explain the free radical chlorination of alkenes.

(b) Illustrate (i) Mc-Murry reaction (ii) Pinacol coupling reaction.

8. (a) Discuss the mechanism of S_Ni reaction with examples.

(b) Explain cis and trans hydroxylation of cycloalkenes.

9. (a) Write a note on stereo-aspects of substituents on the rate of addition >C=C< system.

(b) Explain the mechanism of Mannich reaction by using one example.

10. (a) Discuss the stereochemistry of >C=C< bond formation in cyclic systems.

(b) Explain Cis elimination of esters using one example.

(5 × 5 = 25 Marks)

SECTION – C

Answer **any three** questions. Each question carries **10** marks

11. Discuss the conformational analysis of substituted cyclohexane.

12. Describe the structure, formation and stability of nitrenes. Write any two reactions that involving nitrene as intermediates.

13. (a) Discuss the stereochemistry, effect of solvent, structure of leaving group and substrate structure on S_N1 and S_N2 reactions.

(b) Explain the S_NAr reactions.

14. Write a note on normal aldol condensation and crossed aldol condensation.

15. Discuss E1, E2, E1cB mechanisms for the elimination reactions.

(3 × 10 = 30 Marks)

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(Pages : 3) **N – 5414**

Reg. No. : .....

Name : .....

First Semester M.Sc. Degree Examination, May 2022

Chemistry/Polymer Chemistry/Analytical Chemistry

CH/CL/PC 213 : PHYSICAL CHEMISTRY — I

(2020 Admission Onwards)

Time : 3 Hours Max. Marks : 75

SECTION – A

Answer **two** among (a), (b) and (c). Each sub question carries **2** marks.

1. (a) What are the properties of an acceptable wave function?

   (b) Show that $\sin 2x$ is an eigen function of the operator d^2/dx^2. What is the eigen value?

   (c) Mention the properties of Hermitian operators.

2. (a) Distinguish physisorption from chemisorption.

   (b) What are micelles?

   (c) List the steps involved in a surface reactions.

3. (a) What are partial molar properties?

   (b) Define activity and activity coefficients

   (c) What is varit Hoff isotherm?

P.T.O.

4. (a) What are chain reactions?

(b) How are shock waves formed?

(c) Write the Hammett equation.

5. (a) Define class.

(b) What are reducible and irreducible representations?

(c) Give the 3×3 matrix representation of any two symmetry elements.

($10 \times 2 = 20$ Marks)

SECTION – B

Answer either (a) or (b) from each questions. Each sub question carries **5** marks.

6. (a) Normalize the wave function $\psi = A \sin \frac{n\pi}{a} x$ for a particle in 10 box of length 'a'.

(b) Commute $[x, p_x]$.

7. (a) Derive Gibbs adsorption isotherm.

(b) Describe any two methods for the determination of fugacity.

8. (a) Derive Gibbs-Duhem equation.

(b) Get the expressions for internal energy and entropy in terms of partition functions.

9. (a) Discuss the kinetics of the thermal decomposition of N_2O_5.

(b) What is relaxation time? How it is related with rate constants in the reaction A $\rightleftharpoons$ B?

10. (a) State and explain ‘Great orthogonality theorem’ and discuss the important rules related to irreducible representation and their characters.

(b) Using group theory, find the hybridization of BF_3 ,molecule.

(5 × 5 = 25 Marks)

SECTION – C

Answer **any three** questions. Each question carries **10** marks.

11. Explain the five important postulates of quantum mechanics.

12. Describe how will you determine the surface area by BET adsorption theory.

13. Derive the Maxwell’s relation and highlight the significance.

14. Give the basic assumptions of transition state theory of a reaction rate of bimolecular gaseous reaction and derive the Eyring equation.

15. Obtain the raducible representations for NH_3 molecule and from the symmetry types determine the IR and Raman active symmetries.

(3 × 10 = 30 Marks)

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(Pages : 3) **N – 6250**

Reg. No. : .....

Name : .....

Fourth Semester M.Sc. Degree Examination, June 2022

Chemistry/Analytical Chemistry

CH/CL 241 – CHEMISTRY OF ADVANCED MATERIALS

(2020 Admission)

Time : 3 Hours Max. Marks : 75

SECTION – A

Answer any **two** among (a), (b) and (c) from each question. Each sub-question carries **2** marks.

1. (a) What are halochromic materials?

   (b) What is the concept of pseudo elasticity?

   (c) What are self-healing polymers?

2. (a) Name any two polymeric reagents.

   (b) What are liquid crystalline polymers, give examples?

   (c) Explain conducting polymers with examples.

3. (a) Differentiate between SEM and TEM.

   (b) Explain the property photoluminescence.

   (c) Write two applications of XRD.

P.T.O.

4. (a) What are nano biosensors, give two examples?

(b) Define surface plasmon resonance

(c) What are Fullerenes, explain with example.

5. (a) Explain free radical polymerisation.

(b) Write one method for determination of polymer molecular weight.

(c) What is meant by Degree of Crystallinity?

(10 × 2 = 20 Marks)

SECTION – B

Answer either (a) or (b) of each question. Each question carry **5** marks.

6. (a) Explain the principle behind TEM and its application.

(b) Describe the Sol-Gel method for the preparation of nanoparticles.

7. (a) Describe the application of Raman spectroscopy in nano material characterisation.

(b) Explain the basics of EDAX analysis.

8. (a) Distinguish between linear and cyclic polymerization.

(b) Explain number average and mass average molecular weight of polymer.

9. (a) Describe synthesis and application of polyaniline.

(b) Comment on the use of polymers used in drug delivery processes.

10. (a) Describe synthesis and application of ferrofluids.

(b) What are shape memory polymers?

(5 × 5 = 25 Marks)

SECTION – C

Answer any **three** question. Each question carry **10** marks.

11. Describe any two methods for the determination of molecular weights of polymers.

12. Elaborate on various types of carbon nano tube and its application.

13. Illustrate on various types of polymerisation technique with suitable example.

14. Describe on (a) Quinanes (b) Thermochromic (c) Magnetostrictive (d) Spiropyrans materials.

15. Illustrate on AEM and STM techniques for characterisation of nano materials.

(3 × 10 = 30 Marks)

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(Pages : 3) **P – 5286**

Reg. No. : .....

Name : .....

Second Semester M.Sc. Degree Examination, September 2022

Chemistry / Analytical Chemistry/Polymer Chemistry

CH/CL/PC 223 – PHYSICAL CHEMISTRY - II

(2020 Admission Onwards)

Time : 3 Hours Max. Marks : 75

SECTION – A

Answer **two** sub questions among (a) (b) and (c) from each question each sub question carries **2** Marks

1. (a) What are spherical harmonics?

   (b) Distinguish between radial and angular distribution functions

   (c) Discuss Pauli's Anti-symmetric principle.

2. (a) Give any one application of stark effect in rotational spectrum

   (b) For polyatomic molecules like OCS or NH_3 knowledge of one moment of inertia is insufficient to deduce the bond length and bond angles from line spacing in the Rotational spectra, how will you overcome this difficulty?

   (c) What is the condition for a molecule to give rise to rotational Raman scattering?

3. (a) What is the origin of residual entropy?

   (b) Discuss the concept of ensemble.

   (c) State the principle of equi-partition of energy?

P.T.O.

4. (a) Distinguish between Fermions and Bosons

   (b) What is Dulong and Petit's Law?

   (c) Discuss the anomalous heat capacity of hydrogen.

5. (a) What are the significance of Tafel plot?

   (b) What is over voltage? What is its application?

   (c) What are fuel cells? What are its uses?

(10 × 2 = 20 Marks)

SECTION – B

Answer either (a) or (b) from each question, each sub question carries **5** marks.

6. (a) Discuss the spin – orbital coupling.

   (b) Discuss the separation of variables in the wave equation of Hydrogen like systems.

7. (a) Give a brief account on P,Q, and R branches of vibrational rotational spectrum

   (b) Briefly explain Mutual exclusion principle

8. (a) Derive Sachur – Tetrode relation using Partition function

   (b) Derive the relation to show how thermodynamic functions internal energy and entropy related to partition function?

9. (a) Discuss Debye theory of specific heat capacity of solids

   (b) Deduce Fermi – Dirac Distribution Law.

10. (a) Discuss the principle and applications of polarography.

    (b) Briefly explain Debye-Falkenhagen effect.

(5 × 5 = 25 Marks)

SECTION – C

Answer any **three** questions, each question carries **10** Marks

11. Elaborate Vector atom model.

12. (a) Discuss the fundamentals of rotational spectroscopy and how it is used in the elucidation of molecular structure.

    (b) The rotational spectrum of $H^{35}Cl$ has lines equally separated by 6.26×10^{11} Hz. Calculate the bond length of $H^{35}Cl$. **(6+4)**

13. Derive the expression for Maxwell Boltzmann distribution of particles

14. Discuss Einstein theory of heat capacity of solids. What are the limitations of Einstein's theory of heat capacity?

15. Derive Debye- Huckel Onsager equation and discuss.

($3 \times 10 = 30$ Marks)

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(Pages : 3) **P – 5284**

Reg. No. : .....

Name : .....

Second Semester M.Sc. Degree Examination, September 2022

Chemistry / Analytical Chemistry / Polymer Chemistry

CH/CL/PC 221- INORGANIC CHEMISTRY -II

(2020 Admission Onwards)

Time : 3 Hours Max. Marks : 75

SECTION – A

Answer **any two** sub-questions among (a), (b), or (c) from each question.
Each sub-question carries **2** marks

1. (a) What is d-d transition? What is its impact?

   (b) What is difference between Orgel diagram and Tanabe Sugano diagram?

   (c) What is meant by spin state cross over?

2. (a) Discuss the reciprocal lattice concept.

   (b) What are different types of voids formed in close packed structures?

   (c) What is the reason for Schottky defect?

3. (a) Describe the band theory of solids.

   (b) Differentiate between the properties of intrinsic and extrinsic semiconductors.

   (c) What is photovoltaic effect? What are its uses?

4. (a) What is Styx number? What is its significance?

   (b) Discuss the synthesis and applications of phosphorus sesquisulfide.

   (c) What are carboranes? Where do you find applications for carboranes?

P.T.O.

5. (a) Discuss the uses of lanthanide complexes as reagents.

(b) Discuss the splitting of 'f' orbital in cubic ligand field.

(c) What are the main components obtained from the beaches of Kerala? Discuss.

(10 × 2 = 20 Marks)

SECTION – B

Answer either (a) or (b) of each question. Each question carries **5** marks

6. (a) Describe the Gouy's method for the determination of magnetic moment.

(b) Briefly explain the temperature dependence of magnetism of metal complexes.

7. (a) Describe the rotating crystal X-ray diffraction method. Discuss its applications.

(b) Discuss the colour centres in alkali halide crystals.

8. (a) Briefly explain the effect of temperature on conductivity of solids.

(b) What is meant by doping? How is carried out? What are its advantages?

9. (a) What are phosphazines? Discuss the various types of phosphazines.

(b) Discuss the topological approach to boron hydride structure?

10. (a) Discuss the separation techniques used in the extraction of lanthanides

(b) Compare the properties of lanthanides and actinides.

(5 × 5 = 25 Marks)

SECTION – C

Answer **any three** questions. Each question carries **10** marks.

11. Explain the magnetic properties of coordination compounds.

12. Explain the crystal structures of Zinc blend and Wurtizite.

13. What is piezoelectricity? How is it differing from pyroelectricity? Discuss the applications of piezoeolectric and pyroelectrics.

14. Explain the structure, bonding and reactions of diborane.

15. Explain the occurrence, extraction and general properties of actinides.

(3 × 10 = 30 Marks)

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