R–2960	Sub. Code
	536201

M.Sc. DEGREE EXAMINATION, APRIL 2019

Second Semester

Chemistry

STRUCTURAL INORGANIC CHEMISTRY AND PHOTOCHEMISTRY

(CBCS – 2015 onwards)

Time : 3 Hours   Maximum : 75 Marks

Part A   (10 × 2 = 20)

Answer **all** questions.

1.   Define IS – electron rule.

2.   Point out the different metal carbon bond types.

3.   Justify the meaning of transmetallation.

4.   Briefly mention the structure of a fluxional molecule.

5.   Give an example of a metal arene complex.

6.   Differentiate between simple and a cross metathesis reaction.

7.   Define : catenation and heterocatenation.

8.   What is the importance of styx notation?

9.   Indicate the origin of a charge transfer process.

10.   Bring out the importance of photo splitting of water.

Part B (5 × 5 = 25)

Answer **all** questions, choosing either (a) or (b).

11. (a) Mention the various classes of ligands.

Or

(b) Sketch the structure of a introsyl showing terminal bridging.

12. (a) Briefly describe the mechanism of migratory insertion involved in the reaction of an organometallic complex.

Or

(b) Briefly explain the Mansanto process.

13. (a) Indicate the differences in the structural aspects of Fischer and Grubbs type of metal carbene complexes.

Or

(b) Describe the bonding involved in a ferrocene complex.

14. (a) Mention the essential features of cages and clusters.

Or

(b) Point out the characteristic structural aspects of dinuclear and tetranuclear clusters.

15. (a) Indicate the nature of electronic transitions involved in the case of Cr (III) and Co (III) complexes.

Or

(b) How does the photochemical reaction of Pt (II) and Pt (IV) complexes differ?

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R–2960

Part C (3 × 10 = 30)

Answer any **three** questions.

16. (a) Write notes on : Wades rule and isolobal relationship. (5)

    (b) Give a brief account on the features of vibrational spectra of metal carbonyls. (5)

17. (a) Discuss the mechanism of migratory insertion and hydride elimination reactions of organometallic complexes. (5)

    (b) Point out the importance of Wacker process. (5)

18. What are metal carbene complexes? Give a detailed account on the comparison of stability and reactivity of Fischer, Schrock and Grubbs complexes.

19. Describe the structure of silicates and phosphazene polymers.

20. (a) Briefly mention the mechanism of photoaquation and photoanation. (5)

    (b) Indicate the steps involved in solar energy conversion. Point out the drawback encountered. (5)

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R–2960

R–2961

Sub. Code
536202

M.Sc. DEGREE EXAMINATION, APRIL 2019

Second Semester

Chemistry

REACTIVE INTERMEDIATES, PHOTOCHEMICAL AND CONCERTED REACTIONS

(CBCS – 2015 onwards)

Time : 3 Hours   Maximum : 75 Marks

Part A   (10 × 2 = 20)

Answer **all** questions.

1.   Give two examples of 1,4-additions involving organo-Copper reagents.

2.   What is Cram model?

3.   Give two examples of oxymercuration.

4.   What do you mean by memory effect?

5.   How will you generate singlet carbenes?

6.   Give the mechanism of Beckmann rearrangement.

7.   List out the Baldwin's rules for ring closure.

8.   What is Barton deoxygenation?

9.   What are the Woodward-Hoffmann rules?

10. Give two examples of 1,3-dipolar cycloaddition reactions.

Part B (5 × 5 = 25)

Answer the following questions by choosing either (a) or (b) in each questions

11. (a) Give two examples each for aldol and Michael reactions involving boron enolates.

Or

(b) Explain the Felkin-Ahn and Cram chelate models with suitable examples.

12. (a) Write a note on NGP.

Or

(b) Discuss the mechanism of semi-pinacol rearrangement.

13. (a) Give two examples each for addition and insertion reactions using carbenes.

Or

(b) Explain the structure and stability of singlet and triplet nitrenes.

14. (a) Write a note on Gomberg-Bachmann reaction.

Or

(b) Explain Norrish type II reaction.

15. (a) Give the mechanism of Cope and Ene reactions.

Or

(b) Illustrate the β-elimination reactions involving sulfoxides and selenoxides.

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Part C (3 × 10 = 30)

Answer any **three** questions.

16. Explain the mechanism of Julia olefination, acyloin condensation and Darzen reaction.

17. Describe the following reactions:

    (a) Wittig rearrangement

    (b) Peterson olefination.

18. Explain the mechanism of Curtius and Wolff rearrangements.

19. Explain the following:

    (a) Olefin metathesis

    (b) Ullmann reaction.

20. Explain Diels-Alder and Claisen reactions.

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R–2961

R–2962	Sub. Code
	536203

M.Sc. DEGREE EXAMINATION, APRIL 2019

Second Semester

Chemistry

QUANTUM CHEMISTRY, GROUP THEORY KINETICS AND SURFACE CHEMISTRY

(CBCS – 2015 onwards)

Time : 3 Hours   Maximum : 75 Marks

Part A $(10 \times 2 = 20)$

Answer **all** questions.

1. A rigid rotor has no zero point energy whereas a harmonic oscillator has zero point energy. Classify this.

2. Explain orthogonalisation.

3. Identify the point groups for :
    (a) Sphere and
    (b) Equilateral triangle.

4. The CH_3Cl molecule belongs to the point group C_{3V}. List the symmetry elements of the group.

5. Point out the mutual exclusion rule.

6. Mention the selection rule for vibrational IR spectra.

7. Account for the inadequacy of conventional methods to study the kinetics of a fast reaction.

8. Indicate the essential features for an acid-base catalysis process.

9. Define contact angle , θ_C and outline the condition for melting of a liquid on a solid surface.

10. Distinguish between Langmuir-Hinshelwood and Langmuir-Rideal mechanism.

Part B $(5 \times 5 = 25)$

Answer **all** questions, choosing either (a) or (b).

11. (a) Briefly explain the features of perturbation theory.

Or

(b) Describe the following with suitable example. Orthogonalisation and normalisation of wave function.

12. (a) Find out to which irreducible representation the following direct product representation belong to in the C3v point group.

Or

(b) What do you understand by matrix representation?

13. (a) Indicate how the vibrational modes of ammonia molecule are explained using group theory.

Or

(b) Point out the selection rules for $n - \pi^*$ and $\pi - \pi^*$ transitions in formaldehyde.

14. (a) Mention the characteristics of a chain-branching reaction leading to explosion.

Or

(b) How is catalytic efficiency of an enzyme represented?

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15. (a) Distinguish the features of physisorption and chemisoption.

Or

(b) Briefly describe how the catalytic role of a semiconductor arises.

Part C (3 × 10 = 30)

Answer any **three** questions.

16. Calculate the degenaricies of the first five every levels for a particle in three dimensional cubical box, given the energy of particle is

$E_{nx}, n_y, n_z = \left(n_x^2 + n_y^2 + n_z^2\right)/gma^2$ where $n_x, n_y, n_z = 1, 2, 3$.

17. Construct the character table for C_{3V} group.

18. Write an account on : Symmetry adapted linear combination.

19. For a single substrate enzyme catalysed reaction, arrive at Michaelis-Menten equation and describe the role of low [S] and high [S] on rate and accordingly how the kinetic behaviour is change?

20. For a multilayer adsorption phenomenon on a surface, derive BET isotherm.

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R–2962

M.Sc. DEGREE EXAMINATION, APRIL 2019.

Second Semester

Chemistry

**NATURAL PRODUCTS AND INTRODUCTORY
BIOCHEMISTRY**

(CBCS – 2015 onwards)

Time : 3 Hours   Maximum : 75 Marks

Part A   (10 × 2 = 20)

Answer **all** the questions.

1.   How will you prepare cyanidin chloride from quercetin?

2.   Give two reactions of thiazoles and oxazoles.

3.   Give two methods to elucidate the presence of a double bond in cholesterol.

4.   What is circular bireferengence?

5.   What are the classifications of terpenoids? Give example.

6.   Draw the structure of morphine and identify the number of chiral centers.

7.   What are the structural features of griseofulvin?

8.   Write down the structure of vitamin B12.

9.   What are the products of TCA cycle?

10.   What are the classifications of carbohydrates? Give examples.

Part B (5 × 5 = 25)

Answer the following questions by choosing either (a) or (b) in each question.

11. (a) How will you prepare pyrimidines? Give two reactions of pyrimidines.

Or

(b) Write down the structure of purine, adenine, guanine, hypoxanthine and xanthine.

12. (a) Discuss the applications of ORD and CD in configurational assignment with appropriate examples.

Or

(b) How will you elucidate the presence of angular methyl group and the nature of side chain in cholesterol?

13. (a) Explain the structural elucidation of lysergic acid.

Or

(b) How will you synthesize zingiberene?

14. (a) Establish the structure of cephalosporin.

Or

(b) Describe the synthesis of pyridoxine.

15. (a) Describe RNA transcription and translation.

Or

(b) Write a note on mitochondrial electron transport chain.

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R–2963

Part C (3 × 10 = 30)

Answer any **three** questions.

16. Discuss the synthesis and properties of caffeine and indole.

17. (a) Give one method for the synthesis of estrone.

    (b) Explain axial halo-ketone rule.

18. Discuss the structure and stereochemistry of quinine and camphor.

19. (a) Explain the structural features of streptomycin.

    (b) Write a note on the structure and stereochemistry of riboflavin.

20. (a) Explain DNA replication.

    (b) What do you mean by catabolic and anabolic processes?

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3 **R–2963**

R–3322

Sub. Code
536102

M.Sc. DEGREE EXAMINATION, APRIL 2019

First Semester

Chemistry

CONCEPTUAL ORGANIC CHEMISTRY

(CBCS – 2015 onwards)

Time : 3 Hours   Maximum : 75 Marks

Part A $(10 \times 2 = 20)$

Answer **all** the questions.

1.   Is cyclo pentadienyl cation aromatic? Justify your answer.

2.   Draw hyperconjugative structures of toluene.

3.   State Bredt's rule.

4.   Write any one example for allylic substitution reaction.

5.   What is Vilsmier-Haack reaction?

6.   What is Chichibabin reaction?

7.   Define absolute configuration.

8.   Differentiate diastereoisomers and enantiomers.

9.   What is Curtin-Hammett principle?

10.   Sketch the confirmations of ethane. Which of them will be most stable?

Part B $(5 \times 5 = 25)$

Answer **all** the questions, choosing either (a) or (b).

11. (a) Explain the aromaticity of annulenes.

Or

(b) Discuss the factors affecting the strength of acids and bases.

12. (a) What is $E_{1C}B$ reaction? Explain it with an example.

Or

(b) Discuss Saytzeff rule and Hoffmann rule with example.

13. (a) Explain the mechanism of sulphonation of benzene.

Or

(b) Explain ortho, meta and para directing groups with examples.

14. (a) Explain Cahn-Ingold-Prelog rules and indicate how they can be used to assign the R/S configuration of chiral centers.

Or

(b) Discuss the elements of symmetry with suitable examples.

15. (a) Discuss briefly the optical activity of spiranes.

Or

(b) Explain the stereochemistry of biphenyl.

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R–3322

Part C   (3 × 10 = 30)

Answer any **three** the questions.

16. Explain the following with suitable example

    (a)   Kinetic controlled products.

    (b)   Thermodynamic controlled products.

    (c)   Primary kinetic isotopic effect.

    (d)   Secondary kinetic isotopic effect.

17. Describe the effects of substrate structure, nucleophile, solvent polarity and leaving group on nucleophilic substitution reaction.

18. Explain the reaction and mechanism of Gattermann-Koch and Reimer- Tiemann reaction.

19. What is racemisation? Explain the types of racemisation.

20. Elaborate in detail the conformations of mono substituted and disubstituted cyclohexane.

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         R–3322

R–3323

Sub. Code
536103

M.Sc. DEGREE EXAMINATION, APRIL 2019

First Semester

Chemistry

CONCEPTUAL PHYSICAL CHEMISTRY

(CBCS – 2015 onwards)

Time : 3 Hours   Maximum : 75 Marks

Part A $(10 \times 2 = 20)$

Answer **all** the questions.

1.   What are operators?

2.   Define photoelectric effect.

3.   Mention the types of electrode reactions.

4.   Define over potential.

5.   Define rate law and rate constant.

6.   How does primary salt effect differ from secondary effect?

7.   Define entropy.

8.   What are ideal and non-ideal solutions?

9.   Give any to examples of fluorescence.

10. Define photosensitization.

Part B $(5 \times 5 = 25)$

Answer **all** questions, choosing either (a) or (b).

11. (a) Discuss wave - particle duality.

Or

(b) Explain Heisenberg's uncertainty principle.

12. (a) Discuss the Guoy-Chapmann diffuse charge model of the double layer.

Or

(b) Explain Helmholtz-Perrin model and its significance.

13. (a) Derive Bronsted-Bjerrum equation and explain its significance.

Or

(b) Write a note on consecutive reactions.

14. (a) Explain Debye-Huckel limiting law.

Or

(b) Explain phase diagram of a two component system.

15. (a) How will you measure the efficiency of a solar cell? Explain.

Or

(b) Write a note on dye sensitized solar cells.

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Part C $(3 \times 10 = 30)$

Answer any **three** questions.

16. (a) Derive Schrodinger equation. (6)

    (b) Explain black body radiation (4)

17. (a) Derive Butler-Volmer equation. (5)

    (b) Explain Tafel equation. (5)

18. Write briefly on primary salt effect and secondary salt effect.

19. (a) Derive Gibbs-Duhem equation. (5)

    (b) Discuss the applications of Debye-Huckel theory.

20. Write a note on: (a) Photovoltaic cells (b) Perovskites solar cells.

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R–3323

R–3324	Sub. Code
	536303

M.Sc. DEGREE EXAMINATION, APRIL 2019

Third Semester

Chemistry

ADVANCED PHYSICAL CHEMISTRY

(CBCS – 2015 onwards)

Time : 3 Hours   Maximum : 75 Marks

Section A $(10 \times 2 = 20)$

Answer **all** questions.

All questions carry equal marks.

1. The ground configuration of the nitrogen atom $\left(1s^2\,2s^2 2p^3\right)$ splits into the following terms $^2D_{5/2}$, $^2D_{3/2}$, , $^4S_{3/2}$, $^2P_{3/2}$, $^2P_{1/2}$ arrange these in order of increasing energy using Hund's rule.

2. Write the Hamiltonian operator for Helium atom.

3. What type of molecules give rotational spectra? State which of the following molecules give rotational spectra H_2, HCl, CH_4 and CH_3Cl.

4. What are the selection rules for rotation-vibration Raman spectra of diatomic molecules?

5. What is anodic protection?

6. What are the different types of fuel cells?

7. What is the relationship between flux and forces?

8. What is canonical and grand canonical ensembles?

9. What is Schottky defects?

10. What are n-type and p-type semi conductors?

Section B (5 × 5 = 25)

Answer **all** questions choosing either (a) or (b).

All questions carry equal marks.

11. (a) Discuss the self consistent field method for many electron systems.

Or

(b) Determine the radial functions $R_{n,l}(r)$ for

(i) 1s orbital

(ii) 2p orbital.

12. (a) What type of vibrational-rotational spectra is obtained for a diatomic molecule taking it as anharmonic oscillator?

Or

(b) Discuss the electronic transition in a diatomic molecule.

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13. (a) Discuss the electro chemical reactions and performance of Ni-Cd battery.

Or

(b) Discuss the Pourbaix diagram for $Fe - H_2O$ system.

14. (a) Derive the equation for equilibrium constant of a reaction interms of partition function.

Or

(b) Derive the Sakur- Tetrode equation for the entropy of a monoatomic gas.

15. (a) Discuss the super conductors for electrically conducting organic solids.

Or

(b) Explain the self diffusion mechanism for solids.

Section C $(3 \times 10 = 30)$

Answer any **three** questions.

All questions carry equal marks.

16. Obtain an expression for eigen function and eigen value for Hydrogen molecule ion.

17. (a) Derive an expression for the intensities of rotational spectral lines. (5)

(b) The far infrared spectrum of HI consists of series of equally spaced lines with $\Delta \bar{v} = 12.8 cm^{-1}$. What is the inter nuclear distance? (5)

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18. Discuss the electro chemical reactions and performance characteristics of Leclanche cell and $\dfrac{Zn}{MnO_2}$ alkaline battery.

19. Derive the basic equation given by Bose-Einstein statistics.

20. When do the Frenkel defects arise? Derive an expression for the number of Frenkal defects in a crystal.

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