(Pages : 3) **P – 6080**

Reg. No. : .....

Name : .....

Third Semester M.Sc. Degree Examination, January 2023

Chemistry/Polymer Chemistry/Analytical Chemistry

CH/CL/PC 231 : INORGANIC CHEMISTRY – III

(2020 Admission onwards)

Time : 3 Hours Max. Marks : 75

SECTION – A

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

1. (a) Explain with reason : CO is a π-acceptor ligand.

   (b) Give an example each for a tetrahapto and a hexahapto ligand.

   (c) Show that whether $[Fe(CO)_4(pph_3)]$ obeys 18-electron rule or not.

2. (a) Write the overall stability constant "β" in the following reaction.

   $$Ag^+ 2\,NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$$

   (b) What is meant by trans effect?

   (c) Show that SN_2 mechanism involves a 7-coordinated intermediate.

3. (a) What is Gibbs-Donnan equilibrium?

   (b) What is Bohr effect?

   (c) Draw the active site structure of 2Fe-2s proteins.

P.T.O.

4. (a) IR- frequence of $Fe(CO)_5$ is $2002\,cm^{-1}$ and $1979\,cm^{-1}$ predict the geometry and structure of the above carbonyl.

(b) What is Doppler broadening?

(c) Predict the MB spectrum of low-spin $k_3[Fe(CN)_6]$.

5. (a) Define Radioactive constant (λ).

(b) Complete the following nuclear reaction

$$^{27}_{13}Al + ^{4}_{2}He \longrightarrow \underline{\quad ? \quad} + \underline{\quad ? \quad}$$

(c) What is stellar energy? Indicate the elements involved in the stellar energy nuclear reactions.

(10 × 2 = 20 Marks)

SECTION – B

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

6. (a) Represent the structure of Zeise's salt. Emphasis the important features on which metal-alkene bonding is based.

(b) Utilizing IR spectroscopy discuss the structure with two types of modes of binding of CO in the following metal-carbonyls.

(i) $Fe_2(CO)_9$

(ii) $CO_4(CO)_{12}$

7. (a) Describe briefly the Eigen-Wilkins mechanism with suitable example.

(b) Write note on:

(i) Photo-isomerisation

(ii) Photo-aquation reactions

8. (a) Explain the role of calcium in biological systems.

   (b) Account on: Cytochrome $P-450$.

9. (a) Discuss with suitable example the application of ORD spectra in metal complexes.

   (b) Explain the utility of mossbauer spectroscopy in the study on Tin complexes.

10. (a) Give a brief note on Radioactive decay of Transient equilibrium.

    (b) Discuss the important postulates of nuclear shell model.

($5 \times 5 = 25$ Marks)

SECTION – C

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

11. Construct the MO energy level diagram of Ferrocene and explain the structure and bonding using MOT.

12. What is trans effect? Explain the mechanism of trans effect using polarization and π-bonding theories.

13. Discuss in detail the function of PS-I and PS-II in photosynthetic activity.

14. Utilizing ESR spectra, explain the application of inorganic free radicals, such as PH_4, F_2^- and $[BH_3]^-$.

15. Discuss the principles of following counting techniques

    (a) G.M. Counter

    (b) Ionization and Scintillation counters.

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($3 \times 10 = 30$ Marks)

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Third Semester M.Sc. Degree Examination, January 2023

Chemistry / Polymer Chemistry / Analytical Chemistry

CH/CL/PC 232 – ORGANIC CHEMISTRY – III

(2020 Admission Onwards)

Time : 3 Hours Max. Marks : 75

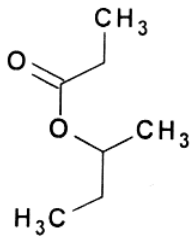
SECTION – A

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

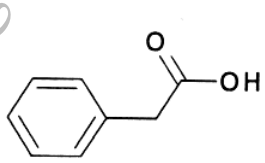
1. (a) What is the effect of solvent's polarity in solution UV spectroscopy?

   (b) How hydrogen bonding affect the IR frequency shifts?

   (c) Pick out the mass spectral fragmentation pattern of the following compounds:



(i)



(ii)

2. (a) What is the theory of NMR spectroscopy?

   (b) What is DEPT? What is its advantage?

   (c) Draw the ^{1}H-NMR spectrum of 4-amino benzaldehyde.

P.T.O.

3. (a) What is lithium exchange reaction? What is its importance?

(b) Write a method for the preparation of Gilman reagent.

(c) What is Tebbe's reagent? What are its uses?

4. (a) What is the mechanism of olefin metathesis?

(b) What is Stepns-Castro coupling?

(c) What are the characteristics of protecting groups?

5. (a) Discuss the mechanism of Clemmensen reduction.

(b) What are the applications of HIO_4?

(c) What are the advantages of ozone oxidation?

(10 × 2 = 20 Marks)

SECTION – B

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

6. (a) Distinguish between soft and hard ionization techniques in mass spectrometry.

(b) Draw the IR spectrum of 2-amino methyl benzoate (methyl anthranilate) and pick out the IR bands.

7. (a) Explain the HSQC and HMQC - NMR techniques.

(b) An organic compound with molecular weight 72 exhibit the following peaks in 1H-NMR : 4.5 (1, s), 2.8 (4, t), 1.1 (3, s). Determine the structure of the compound.

8. (a) How organolithium compounds are prepared? What are their uses?

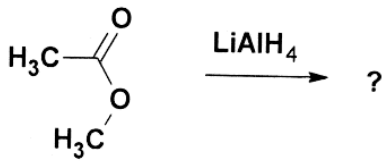
(b) Discuss the preparation and uses of (Benzene) chromium tricarbonyl.

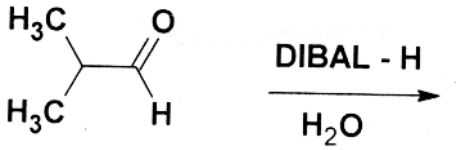
9. (a) Discuss the retrosynthetic analysis of acetanilide.

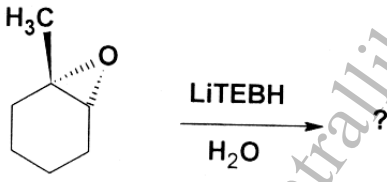
(b) What are the various types of Grubbs catalysts? What are its applications?

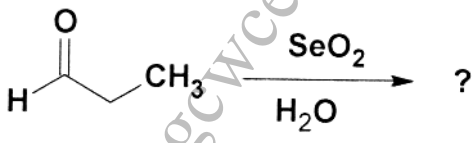
10. (a) Explain the mechanism of McFadyen–Stevens reaction.

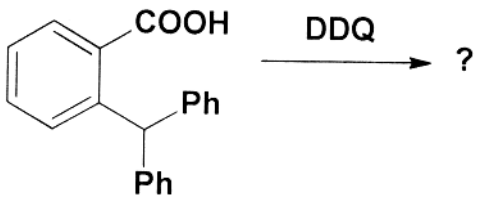
(b) Sketch the products of the following reaction:

(i) 

(ii) 

(iii) 

(iv) 

(v) 

(5 × 5 = 25 Marks)

SECTION – C

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

11. Monitor the Hoffmann degradation reaction of CH_3-O-CH_2CO-NH_2 to CH_3-O-CH_2-NH_2 by infrared and mass spectrometry studies.

12. Follow the Diels – Alder reaction of cis-1,3-butadiene and ethane to form cyclohexene by ^{1}H-NMR spectroscopy.

13. What are Grignard reagents? How are they prepared? Explain its various applications.

14. (a) What is Negishi coupling? Explain its mechanism. What are its advantages?

    (b) Discuss the Umpolung concept. (7 + 3)

15. (a) What is Swar oxidation? Discuss its mechanism.

    (b) What is Wolff-Kishner reduction? Discuss its mechanism.

(3 × 10 = 30 Marks)

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Reg. No. : .....

Name : .....

Third Semester M.Sc. Degree Examination, January 2023

Chemistry/Polymer Chemistry/Analytical Chemistry

CH/CL/PC 233 : PHYSICAL CHEMISTRY – III

(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) Define free valence index. What is its significance?

   (b) State and explain the selection rule for molecular spectra.

   (c) Draw the MO energy level diagram for HF molecule. What is its bond order?

2. (a) Derive an expression for the most probable velocity of gas molecules.

   (b) What is Boyle temperature? Calculate its value for carbon dioxide if van der Waals constant *a* and *b* are respectively 3.59 dm^6 atm mol^{-1} and 0.0427 $dm^3 mol^{-1}$.

   (c) Apply equipartition principle to find the heat capacity of *HCl* (in terms of gas constant) gas molecules.

3. (a) Mention the importance of population of states in NMR spectroscopy.

   (b) Explain the role of quadrupole transitions in Mossbauer spectroscopy.

   (c) Give the origin NQR transitions in some nuclei.

P.T.O.

4. (a) Explain the significance of principle of minimum entropy production.

(b) Sketch and explain the graphical representation of a three-component liquid-liquid system two pairs of partially miscible liquids.

(c) Mention the relevance of Onsager reciprocal relations.

5. (a) Compare RHF, ROHF and UHF.

(b) What are the characteristics of Force Field?

(c) Write a note on Pople type basis set.

(10 × 2 = 20 Marks)

SECTION – B

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

6. (a) Discuss the Hartree - Fock self-consistent field (HFSCF) method in quantum mechanics.

(b) Define hybridization. Explain the quantum mechanics of sp^2 hybridization with an example.

7. (a) Write a short note on various types of intermolecular forces existing in gas molecules.

(b) Discuss the equation of states of real gases other than van der Waals equation.

8. (a) Explain the theory and applications of X-ray photoelectron spectroscopy.

(b) Explain the basic instrumentation of NMR spectroscopy.

9. (a) Apply irreversible thermodynamics in the context of thermal diffusion.

(b) Discuss the non - equilibrium thermodynamic studies of electrokinetic effects.

10. (a) Explain in detail the concept of semi empirical methods.

(b) Explain the relevance of constraints in MD Simulations.

(5 × 5 = 25 Marks)

SECTION – C

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

11. Write the basic principle of Huckel's molecular orbital theory (HMOT). Arrive at the expressions for calculating the pi electron energy and delocalization energy of 1,3 butadiene.

12. Discuss the properties of liquid state by mentioning vapour pressure, surface tension and viscosity.

13. Explain the basic principles and applications of ESR spectroscopy by mentioning the importance of electron *g* factor.

14. Discuss the thermodynamical aspects of various solid-liquid systems.

15. (a) What is z matrix? Write down the necessary steps in generating z matrix of a molecule. Compare the z matrices of eclipsed and staggered ethane.

    (b) Write a note on potential energy surfaces.

(3 × 10 = 30 Marks)

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