R – 6211

Reg. No. : ...........................

Name : ...............................

**First Semester M.Sc. Degree Examination, May 2023**

**Chemistry/Polymer Chemistry/Analytical Chemistry**

**CH 211/CL 211/PC 211 : INORGANIC CHEMISTRY – I**

**(2020 Admission Onwards)**

Time : 3 Hours                                                                 Max. Marks : 75

SECTION – A

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

1.  (a)  Outline the splitting of d orbitals in square pyramidal complex.

    (b)  Describe Nephelauxetic effect.

    (c)  Calculate CFSE for $d^6$ ion in strong octahedral field.

2.  (a)  Define standard deviation.

    (b)  Illustrate the importance of significant figures.

    (c)  List any two indicators used for complexometric titration and explain the chemistry.

3.  (a)  What is molecular magnets.

    (b)  Write a note on chalcogenides.

    (c)  Give at least two examples for materials used as rechargeable batteries.

P.T.O.

4. (a) How silicones are prepared? Account for their water repellent nature?

   (b) Write a note on Zeolites.

   (c) Give two examples for Xenon based coordination complexes.

5. (a) What is photochemical smog and at what condition does this occur.

   (b) What is the unique property of water?

   (c) Give any one method for quantify the soil acidity.

**(10 × 2 = 20 Marks)**

SECTION – B

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

6. (a) Explain Jahn-Teller effect. Discuss its spectral consequences.

   (b) Explain the drawback of crystal field theory.

7. (a) Compare the method of averages and the method of least square for treatment of analytical data.

   (b) Explain the various types of EDTA titrations.

8. (a) What are SOFCs?

   (b) Write a note on inorganic pigments.

9. (a) Briefly discuss the synthesis and structures of different isopolyanions of Mo and W.

   (b) Explain the structure and applications of aluminosilicates.

10. (a) Brief note on catalytic destruction of ozone. What are the major reasons for ozone layer depletion?

    (b) Write a note of hazardous air pollutants and how they affect human health.

**(5 × 5 = 25 Marks)**

## SECTION – C

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

11. Construct MO diagram of octahedral complexes with and without pi bonding and explain the theory behind it.

12. Write a note on classification of errors in treatment of analytical data.

13. What are the peculiarities of solid electrolytes? Explain with example.

14. Give the structure of Xenon fluorides and organo xenon compounds.

15. Explain the hydrologic cycle.

**(3 $\times$ 10 = 30 Marks)**

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**R – 6211**

Reg. No. : ...........................

Name : ...............................

**First Semester M.Sc. Degree Examination, May 2023**

**Chemistry/Polymer Chemistry/Analytical Chemistry**

**CH 212/CL 212/PC 212 : ORGANIC CHEMISTRY – I**
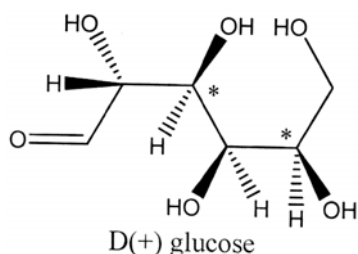
**(2020 Admission Onwards)**

Time : 3 Hours

Max. Marks : 75

SECTION – A

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

1.　(a)　Determine the stereochemistry (R or S) for (*) marked stereogenic centres of the D(+) glucose molecules.



D(+) glucose

　　(b)　Define homotopic ligands.

　　(c)　Write the product of the reduction of (2S,3R)-2,3-dichlorocyclobutanone with $LiAlH_4$ by attack from the Re face side.
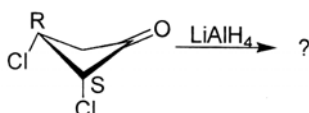
2. (a) Draw the structure of triphenylmethyl radical dimer in benzene.

   (b) Write the reaction of phenylacetylene molecules in presence of copper(II)acetate in pyridine solution.

   (c) Write the Hunsdiecker reaction by taking silver propionate as example.

3. (a) complete the following reaction.
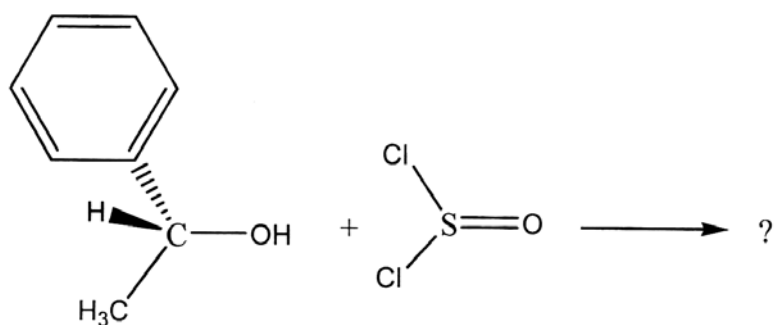


   (b) Write the mechanism of $S_N2'$ reaction.

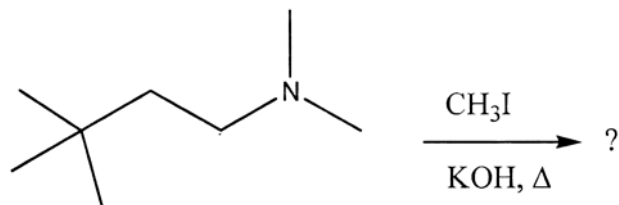   (c) Arrange the following carbocations in decreasing order of their stability.
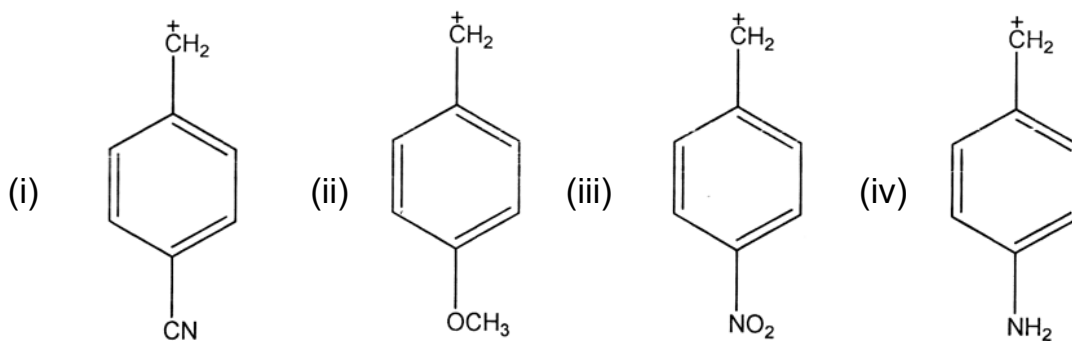


4. (a) Why are *syn*-additions taking place when the addition of hydrogen halide to conjugated alkenes with aromatic unit?

   (b) Write Cannizzaro reaction.
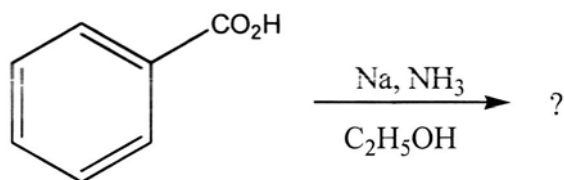
   (c) State the iodo lactonisation with example.

R – 6212

5. (a) Write the mechanism of E1reaction.

(b) Complete the following reaction.



(c) Complete the following reaction.



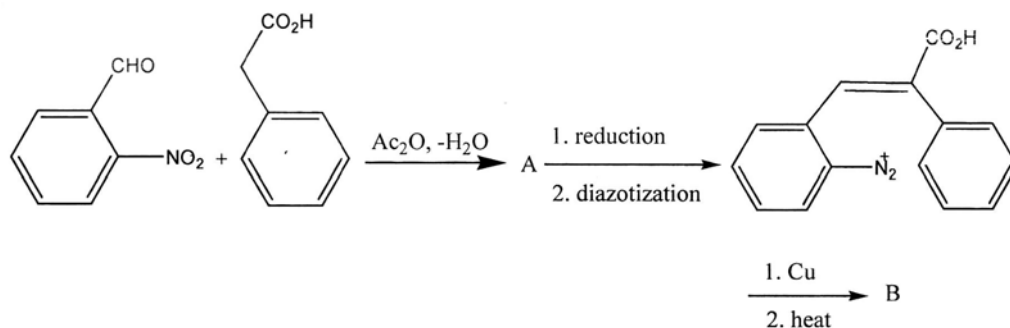**(10 × 2 = 20 Marks)**

SECTION – B

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

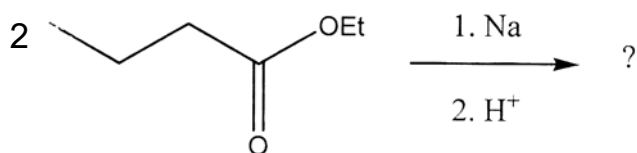6. (a) $\alpha$–phenylpropionaldehyde reacts with methyl magnesium bromide. Predict the more predominant product. Explain your answer based on Cram's rule.

(b) Explain the octant and axial halo ketone rule.

7. (a) Predict the products of the following reactions.

(b) Identify the product of the following reaction and write the mechanism of the reaction.



2

OEt

$\dfrac{\text{1. Na}}{\text{2. H}^+}$ ?

8. (a) Find the product of the following protonation and ionization reaction in super acid medium.

(i)



H

CH$_2$Cl

$SbF_5$-$SO_2$, -60°C



H

Cl

$SbF_5$-$SO_2$, -60°C

? 

(ii)



Cl

$SbF_5$ -$SO_2ClF$, -78°C

?
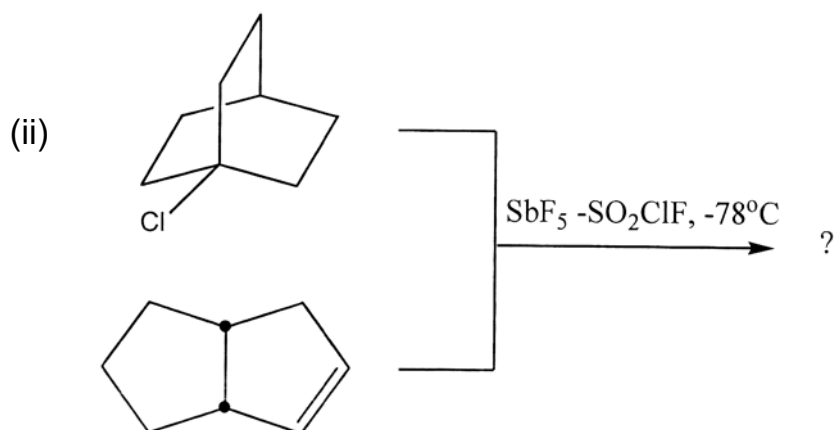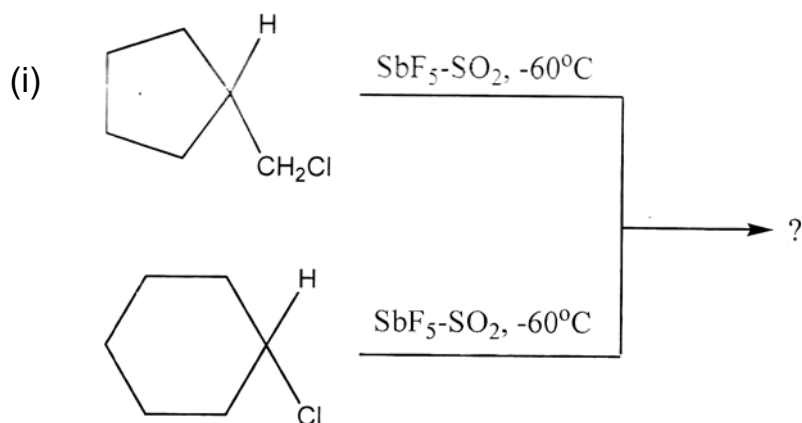
(b) Write the mechanism of the Mitsunobu reaction.

9. (a) (i) Explain the conjugate addition reaction with example.

(ii) Write the product and mechanism of the following reaction.



(b) Complete the following reactions.

(i)



diethyl succinate

ethyl methyl ketone

$\xrightarrow{\text{NaOEt}}$ ?

(ii)



1. pyrrolidine

2. $H_2C$=$CHCH_2Br$

3. $H_2O$

$\longrightarrow$ ?
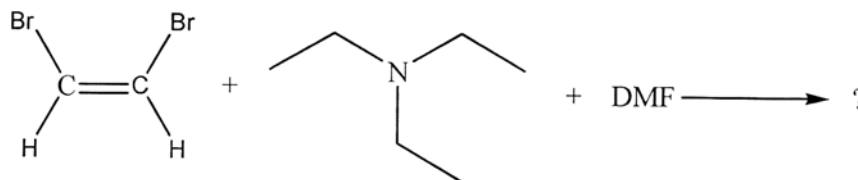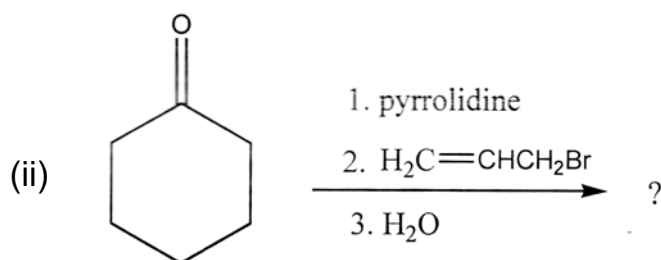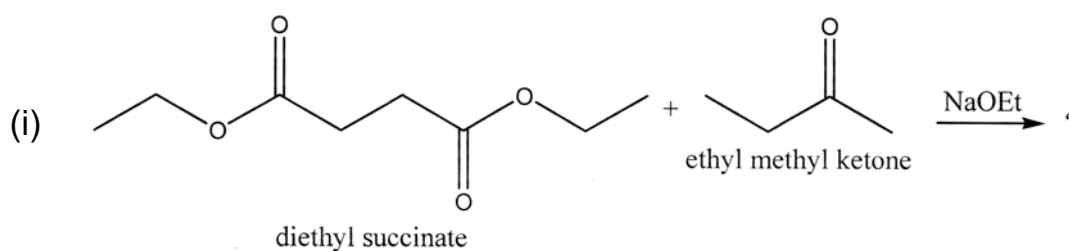
10. (a) Explain the $\beta$–elimination via cyclic transition state of Cope and Xanthate ester pyrolyses.

(b) Write the product of the following reactions.

(i)



1. OH

2. $Ph\diagdown S\diagdown S\diagup Ph$

3. Oxidation

4. 50°C

$\longrightarrow$ ?

5

(ii) 

N≡C— [structure: 4-(1-acetoxyethyl)benzonitrile] $\xrightarrow{600°C}$ ?
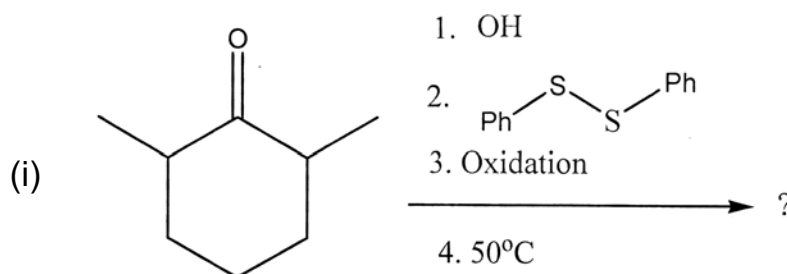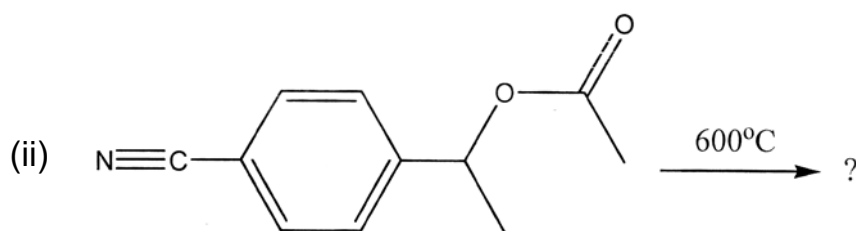
SECTION – C

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

11. Find out the product of the following reaction with Felkin-Anh model.

(a) 

Ph— [structure with Ph, Ph and C=O] $\xrightarrow{\text{LiAlH}_4}$ ?

(b) 

Ph— [structure with SMe and C=O] $\xrightarrow{\text{ZnBH}_4}$ ?

12. (a) Complete the following reactions.

(i) 

[cyclohexene with CO$_2$Et and CO$_2$Et substituents] $\xrightarrow[\text{2) H}_3\text{O}^+]{\text{1) Na-(CH}_3)_3\text{SiCl}}$ ?

(ii) 

[structure with NC, N=N, CN groups] $\xrightarrow[\text{2) Bu}_3\text{SnH}]{\text{1) 66-72°C}}$ ?
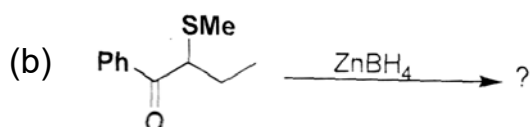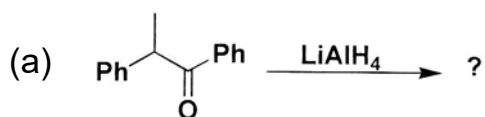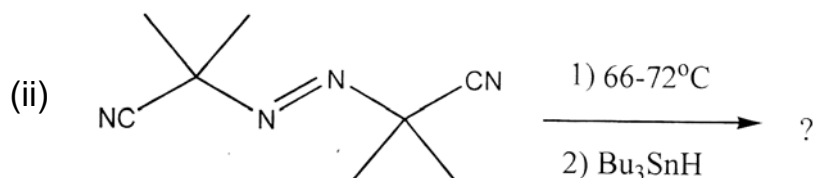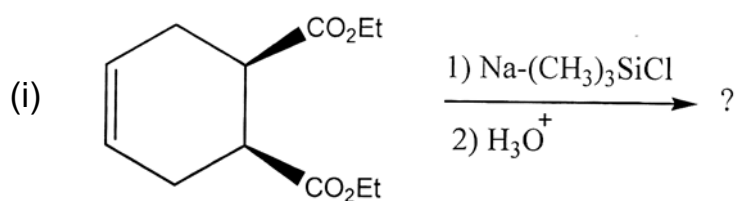
(b) Explain the following reactions. (i) McMurry reaction (ii) Kolbes electrolytic reaction (iii) Ullman reaction.

13. How do solvent and structure of substrate effect on the rate of $S_N1$ and $S_N2$ reactions? Explain.

14. (a) Explain the normal, crossed and directed Aldol condensation reactions with examples.

    (b) Describe the Robinson Annulation reaction.

15. Find the product of the following reactions with stereochemistry point of view.
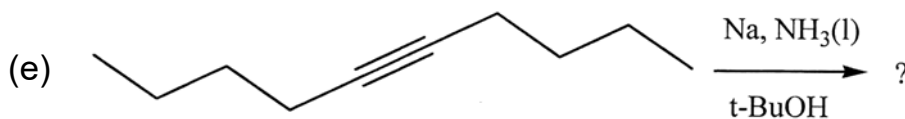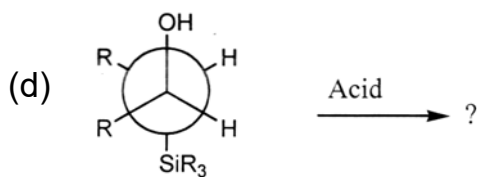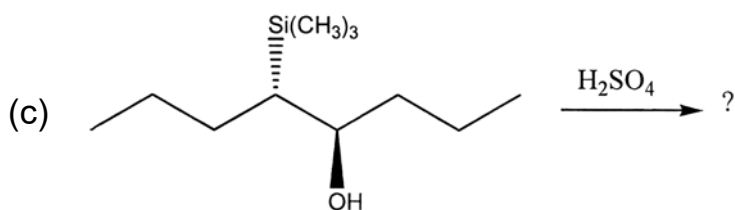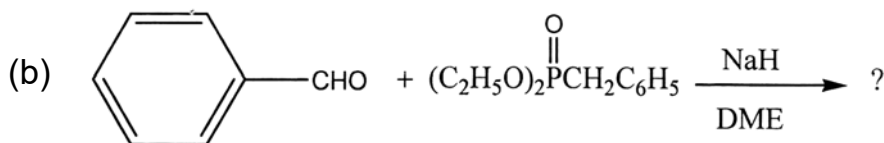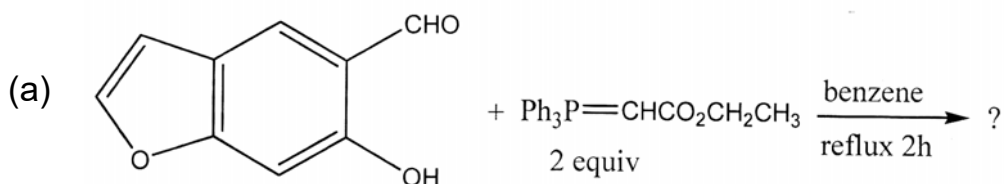
(a)



$+ \ Ph_3P{=}CHCO_2CH_2CH_3$

2 equiv

$\xrightarrow[\text{reflux 2h}]{\text{benzene}}$ ?

(b)



$-CHO \ + \ (C_2H_5O)_2\overset{\overset{O}{\|}}{P}CH_2C_6H_5 \xrightarrow[\text{DME}]{\text{NaH}}$ ?

(c)



$\xrightarrow{H_2SO_4}$ ?

(d)



$\xrightarrow{\text{Acid}}$ ?

(e)



$\xrightarrow[\text{t-BuOH}]{\text{Na, NH}_3(\text{l})}$ ?

**(3 × 10 = 30 Marks)**

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Reg. No. : ...........................

Name : ................................

**First Semester M.Sc. Degree Examination, May 2023**

**Chemistry/Polymer Chemistry/Analytical Chemistry**

**CH 213/ CL 213/ PC 213: PHYSICAL CHEMISTRY – I**

**(2020 Admission Onwards)**

Time : 3 Hours

Max. Marks : 75

SECTION – A

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

1. (a) Define laplacian operator.

   (b) What are hermite polynomials?

   (c) Write the recursion formula.

2. (a) What are surface films?

   (b) What is enzyme catalysis?

   (c) Give the expression for freundlich adsorption.

3. (a) Define fugacity

   (b) State henry's law.

   (c) Give the duhem-Margules equation.

4.  (a)  What are termolecular reactions?

    (b)  Mention are any two relaxation techniques to monitor rapid reactions.

    (c)  What is primary salt effect?

5.  (a)  What are symmetry elements?

    (b)  What is similarity transformation?

    (c)  What are abelian groups?

**(10 × 2 = 20 Marks)**

SECTION – B

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

6.  (a)  Give the important postulates of quantum mechanics.

    (b)  Calculate the lowest energy transition of an electron confined to a 1D-box of infinite potential path.

7.  (a)  Discuss the theories of catalysis.

    (b)  Describe any two instrumental techniques for surface analysis.

8.  (a)  Derive any two Maxwell's relations.

    (b)  Derive Van't Hoff equation.

9.  (a)  Discuss the Lindemann-Christiansen hypothesis for the treatment of unimolecular reactions.

    (b)  With schematic diagram, explain how laser flash photolysis is helpful in monitoring the fast reactions.

10. (a)  Construct the character table for $C_{2v}$ point group.

    (b)  Write the 3x3 matrix representations of all the symmetry elements.

**(5 × 5 = 25 Marks)**

SECTION – C

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

11.  Write the Hamiltonian for a simple harmonic oscillator and get the complete wave functions by solving the schrodinger wave equation.

12.  Discuss the kinetics of Langmuir adsorption isotherm.

13.  (a)  Define chemical potential.

     (b)  Derive Gibbs – Duhem equation

     (c)  Describe ant two methods for the determination of partial molar properties.

14.  How will you obtain the three-halves and one-half order kinetics for a chain reaction? Derive the rate expression and equations for the chain length.

15.  Show that the hybridization in methane is sp$^3$, using group theory.

**(3 × 10 = 30 Marks)**

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**P – 6084**

Reg. No. : ...........................

Name : .................................

### Third Semester M.Sc. Degree Examination, January 2023

### Chemistry/Analytical Chemistry/Applied Chemistry/ Polymer Chemistry/Medicinal Chemistry

### CH/CL/CA/PC/CM 231 : INORGANIC CHEMISTRY III

(Chemistry/Analytical Chemistry/Applied Chemistry/ Medicinal 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 caries **2** marks.

1.  (a)  CO stretching frequency in IR spectra drops as the metal becomes more electron rich. Justify the statement.

    (b)  Formulate neutral, 18 electron complexes of chromium which contain only
        (i)   cyclopentadienyl and nitrosyl ligands
        (ii)  cyclopentadienyl, carbonyl and nitrosyl ligands.

    (c)  Why $Cr(CO)_6$ is stable than $V(CO)_6$ Explain.

2.  (a)  The aquation reaction of $[Co(NH_3)Cl_2]^+$ is faster than that of $[Co(NH_3)_5Cl]^{2+}$. Why?

    (b)  The rate of outer sphere electron transfer from $[Fe(CN)_4]^{4-}$ to $[Fe(CN)_4]^{3-}$ is much faster than that from $[Co(NH_3)_6]^{2+}$ to $[Co(NH_3)_6]^{3+}$. Why?

    (c)  With a suitable example, explain the stepwise and overall formation constants.

**P.T.O.**

3. (a) What are nitrogenases? Give the functions of nitrogenases.

   (b) Oxy form of hemocyanin is blue while the deoxy form is colorless.

   (c) What is the role of Mn in photosynthesis?

4. (a) What are the limitations of Mössbauer spectroscopy?

   (b) What is CD? What is its application in metal complexes?

   (c) How coordinated and uncoordinated nitrate ion can be distinguished by IR Spectroscopy?

5. (a) $^{18}F$ undergoes 10% radioactive decay in 16.5 minutes. Calculate its half life.

   (b) Describe the working of G.M. counter.

   (c) What is a Breeder reactor?

**(10 × 2 = 20 Marks)**

SECTION – B

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

6. (a) How is Ziese's salt synthesized? Write its structure and bonding.

   (b) Discuss the fluxional behavior exhibited by two organometallic compounds.

7. (a) What is macrocylic effect?

   (b) Write down Marcus equation and illustrate its important applications.

8. (a) What stops simple iron-porphyrins from functioning as oxygen carriers? Discuss the role of globin and heme part in cooperatively and reversible uptake of oxygen by hemoglobin.

   (b) What are cytochromes? Give the active site structure of P-450.

**P – 6084**

9. (a) Discuss the applications of NMR for the study of diamagnetic complexes.

   (b) What is the principle of Mössbauer spectroscopy?

10. (a) Explain the nuclear fusion reactions.

    (b) What are magic numbers of the nucleus? Explain the uses of magic numbers.

**(5 × 5 = 25 Marks)**

SECTION – C

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

11. Explain polymerization of olefins using Wilkinson catalyst

12. Account for the photoreactive excited states of Cr (III) complexes. Giving suitable examples discuss the photoaquation reactions of Cr (III) complexes.

13. Describe structure, classification and function of biological iron-sulfur proteins.

14. Write an account of EPR spectroscopy of Cu (II) complexes.

15. Explain the nuclear fission process. How it can be used as a source of energy?

**(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 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 $\pi$-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 "$\beta$" in the following reaction.

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

    (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 $(\lambda)$.

   (b) Complete the following nuclear reaction

   $$^{27}_{13}Al + ^4_2He \longrightarrow \underline{\ \ ?\ \ } + \underline{\ \ ?\ \ }$$

   (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 × 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 $\pi$-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 $\left[BH_3\right]^-$.

15. Discuss the principles of following counting techniques

    (a) G.M. Counter

    (b) Ionization and Scintillation counters.

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**(3 × 10 = 30 Marks)**

Reg. No. : ...........................

Name : .................................

## Third Semester M.Sc. Degree Examination, January 2023

## Chemistry/Analytical Chemistry/Applied Chemistry/Polymer Chemistry/ Medicinal Chemistry

## CH/CL/CA/PC/CM 232 : ORGANIC CHEMISTRY III

**(Chemistry/Analytical Chemistry/Applied Chemistry/ Medicinal 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) How will you differentiate a primary, secondary, and tertiary amine in IR spectrum?

    (b) How the $\lambda$ max value of the $\pi \rightarrow \pi *$ transition of naphthalene varies in octane and in DMS? Give reason.

    (c) Write the fragmentation pattern to account the major peaks of the compounds

       (i)   $CH_3CH_2COOCH_3$          ;   $m/z = 57, 59,$ and $88$

       (ii)  $CH_3OCH_2CH_2CH_3$        ;   $m/z = 31, 45, 59,$ and $74$

2. (a) What is the structure of the compound $C_5H_{10}$ with one $H^1$NMR and one $C^{13}$NMR peaks?

   (b) What is nuclear overhauser effect (NOE)?

   (c) What is the difference between proton decoupled and off resonance decoupled NMR?

3. (a) Write the mechanism of Mannih reaction.

   (b) Cyclopentene on hydroxylation with $OsO_4$ gives only a meso compound – Justify.

   (c) Write the mechanism of oxidation of secondary alcohol to ketone using aluminium isopropoxide.

4. (a) Suggest hydroxyl and carbonyl protecting groups (one each) in synthesis; also suggest method of removal of. These protecting groups after the reaction.

   (b) Give two examples of electrochemical reduction methods for the removal of an organic pollutant in water.

   (c) Explain "synthons" with suitable examples.

5. (a) Which compound in the each of the following pairs would have flow first in a silica gel column? Give reason.

       (i)   benzene or cyclohexane

       (ii)  acetic acid or methyl acetate

   (b) Explain the terms "reverse-phase packing" and "isocratic elution" used in HPLC.

   (c) What is the difference between analytical and preparative chromatography?

**(10 × 2 = 20 Marks)**

**P – 6085**

## SECTION – B

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

6. (a) (i) What happens to the $\lambda$ max values of p-nitrophenol on addition of NaOH and p-nitroaniline on addition of HCl? Explain.

   (ii) Explain very briefly the use of IR spectroscopy in the study of hydrogen bond in compounds.

   (b) (i) Why methane is used as common reagent in chemical ionization technique?

   (ii) Provide the m/z values of any four important fragments in the mass spectrum 2-pentanone.

7. (a) Describe the use of $\delta$ and J values in the structure identification of organic compounds using NMR spectroscopy.

   (b) Deduce the identity of the following compound from the spectral data given.

   $C_4H_8O_2$ : 1H NMR, $\delta$ 1.23 (3H, triplet), 2.00 (3H, singlet),
   4.02 (2H, quartet) (ppm); IR, 2980, 1740 $cm^{-1}$.

8. (a) What is Chichibabin reaction? Discuss its mechanism. Give two examples.

   (b) Write short note on Heck reaction.

9. (a) Illustrate the principle of reactivity *umpolung* with suitable examples.

   (b) Explain the retro synthesis of olefins.

10. (a) Explain the differences between adsorption and partition chromatography.

   (b) Discuss the advantages and limitations of supercritical fluid chromatography.

   **(5 × 5 = 25 Marks)**

SECTION – C

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

11. Write short notes on
    (a) Bathochromic and hypsochromic effects of polar solvents
    (b) Basic factors influencing IR frequencies
    (c) Mc Lafferty rearrangement
    (d) Chemical ionization in mass spectroscopy

12. Explain briefly the following in NMR spectroscopy.
    (a) Diamagnetic anisotropy
    (b) Shift reagents
    (c) Advantages of 2D spectra
    (d) Chemical exchange and double resonance

13. Write short notes on
    (a) Clemmensen reduction
    (b) Shapiro reaction
    (c) Dieckmann condensation
    (d) Simmons-Smith reaction

14. (a) Differentiate
       (i) Stereospecific and stereoselective synthesis
       (ii) Chiral auxiliary and chiral reagents
       (iii) Enantioselective and diastereoselective
       (iv) Absolute and Partial asymmetric synthesis (AAS and PAS)    **4**

    (b) Write short notes on
       (i) Sharpless asymmetric epoxidation
       (ii) Mitsunobu reaction
       (iii) BINAP (2,2'bis(diphenylphosphino)-1,1'-binaphthyl)    **6**

15. Illustrate the importance of choice of solvent, adsorbent and detector in chromatographic separation by giving suitable examples.

———————    **(3 × 10 = 30 Marks)**

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Reg. No. : ..........................

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## Third Semester M.Sc. Degree Examination, January 2023

### Chemistry / Polymer Chemistry / Analytical Chemistry

### CH/CL/PC 232 – ORGANIC CHEMISTRY – III

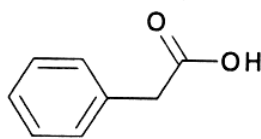### (2020 Admission Onwards)

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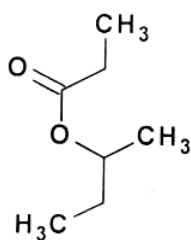
2. (a) What is the theory of NMR spectroscopy?

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

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

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?

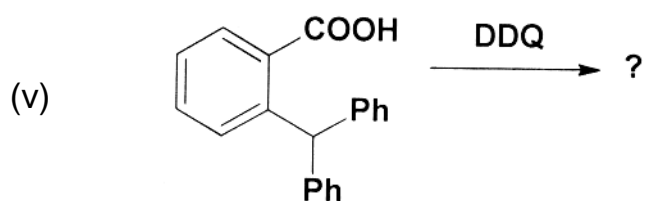                                                    **(10 × 2 = 20 Marks)**
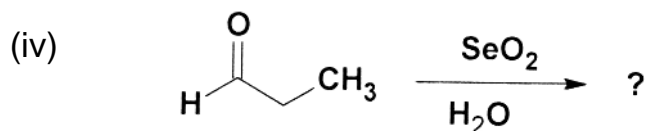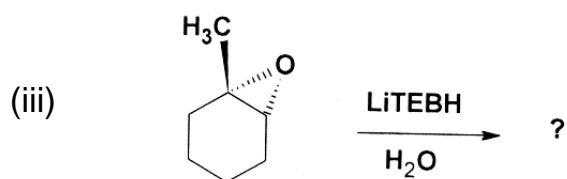

                              SECTION – B

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.

**P – 6081**

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)

$H_3C$—(acetic anhydride) $\xrightarrow{\text{LiAlH}_4}$ ?

(ii)

$H_3C$, $H_3C$ CH(CHO) $\xrightarrow[\text{H}_2\text{O}]{\text{DIBAL - H}}$ ?

(iii)

(spiro epoxide with $H_3C$) $\xrightarrow[\text{H}_2\text{O}]{\text{LiTEBH}}$ ?

(iv)

$H$—CO—CH$_2$—CH$_3$ $\xrightarrow[\text{H}_2\text{O}]{\text{SeO}_2}$ ?

(v)

(benzene ring with COOH and CHPh$_2$ substituent) $\xrightarrow{\text{DDQ}}$ ?
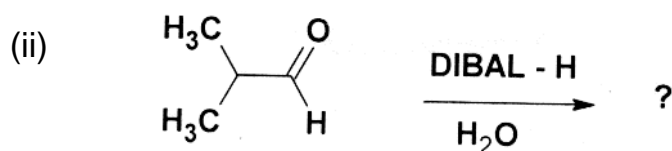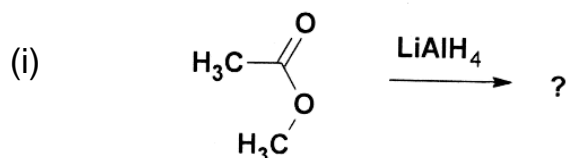
**(5 × 5 = 25 Marks)**

SECTION – C

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

11. Monitor the Hoffmann degradation reaction of $CH_3$-O-$CH_2$CO-$NH_2$ 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 $\times$ 10 = 30 Marks)**

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**P – 6086**

## Third Semester M.Sc. Degree Examination, January 2023

### Chemistry/Analytical Chemistry/Applied Chemistry/Polymer Chemistry/ Medicinal Chemistry

### CH/CL/CA/PC/CM 233 : PHYSICAL CHEMISTRY III

**(Chemistry/Analytical Chemistry/Applied Chemistry/ Medicinal Chemistry (2016-2019 Admission) and Polymer Chemistry (2018-2019) Admission)**

Time : Three 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) Which is more stable $O_2, N_2^+, N_2^-$? Explain.

   (b) Explain method of variation.

   (c) Give the spectroscopic term symbol for $O_2$.

2. (a) What is a global minimum?

   (b) Explain basis set.

   (c) Name some commonly used force field.

3. (a) Briefly describe chemical shift.

   (b) What is doplar effect?

   (c) Give the principle of NQR spectroscopy.

4. (a) Explain statistical deviation.

   (b) State Kopp's law.

   (c) What are the limitations of Einstein's theory?

5. (a) What is the difference between reference electrode and indicator electrode?

   (b) Explain atomiser in ASS

   (c) Give the principle of conductometry.

**(10 × 2 = 20 Marks)**

## SECTION – B

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

6. (a) Apply MO theory on $H_2^+$.

   (b) Explain linear variation functions.

7. (a) Discuss the strength and weakness of Huckel method.

   (b) Construct Z matrix of $H_2O$ and $H_2O_2$.

8. (a) Describe g factor. How can we determine g factor?

   (b) Give the principle of UV spectroscopy. Discuss its applications.

9. (a) Derive electronic partition function for 2D system.

   (b) Explain Debye theory.

10. (a) Discuss hollow cathode lamp.

    (b) Explain inference in AAS.

**(5 × 5 = 25 Marks)**

SECTION – C

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

11. Apply HMO method on benzene system.

12. Explain Ab initio methods.

13. Discuss doplar effect and quadrapole effect.

14. Explain principle of equipartition of energy.

15. Write a note on principle, method and application of polorography.

**(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.

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.

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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