MSC Sem - 1

Paper / Subject: Code: 94603 / Chemistry: Physical Chemistry (Rev)

[Time: 2:30 Hours] [Marks: 60]

Please check whether you have got the right question paper.

N.B.: 1. All questions are compulsory.
2. Figure to the right indicates full marks.
3. Use of non – programmable scientific calculator is allowed.

Useful constants

$c = 2.998 \times 10^{8}$ m.s^{-1}	$e = 1.602 \times 10^{-19}$ C
$R = 8.314$ J.K^{-1}mol^{-1}	$k = 1.3811 \times 10\text{-}23$ J.K^{-1}
$= 2.0$ cal.K^{-1} mol^{-1}	
$h = 6.626 \times 10^{-34}$ Js	$1J = 6.24 \times 10^{18}$ eV
$m_e = 9.110 \times 10^{-31}$ kg	$1eV = 8.06 \times 10^{3}$ cm^{-1}
$N_A = 6.022 \times 10^{23}$ mol^{-1}	1 amu $= 1.66 \times 10^{-27}$ kg

Atomic mass of H = 1, C = 12, N = 14, O = 16, S = 32, Cl = 35.5

1. A) Attempt ***any two*** of the following:

i) What is inversion temperature? Show that Joule Thomson Effect is isoenthalpic. 4

ii) Derive the expression to show the variation of the entropy with temperature at constant pressure and volume. 4

iii) Write the expression for entropy change in the following phase transitions. 4

a. Melting b. Vapourization

c. Sublimation d. Allotropic transformation

iv) Explain the concept of residual entropy with suitable example. 4

1. B) Attempt ***any one*** of the following:

i) Calculate $\mu_{j.t.}$ for a certain gas at 273 K and 100 bars taking Cp as 35.5 JK^{-1}mol^{-1}. The van der Waal's constant 'a' and 'b' are 0.139 Nm^{4}mol^{-2} and 3.92×10^{-5} m^{3} mol^{-1}. 4

ii) Calculate the entropy change for conversation of one mole of steam at 373K to one mole of ice at 273K. Cp of water = 75.6 JK^{-1}mol^{-1}, Molar enthalpy of vaporization = 40.645 KJ^{-1} mol^{-1} and Molar enthalpy of fusion = 6.003 KJ^{-1}mol^{-1} 4

2. A) Attempt ***any two*** of the following:

i) What is meant by normalization of wave function? Normalize the following wave Function. $\psi = A \sin n\pi x/L$ in the limit zero to L. 4

ii) What is linear harmonic oscillator? Derive Hermit equation for one dimensional simple harmonic oscillator. 4

iii) What is the condition for orthogonality of wave function? Show that two normalized wave function ψ_1 and ψ_2 are orthogonal to each other. 4

iv) Starting with equation 4

$$\frac{\partial^2\psi(x,t)}{\partial x^2} = \frac{1}{C^2}\frac{\partial^2\psi(x,t)}{\partial t^2}$$

Setup the time independent Schrodinger equation.

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Q.4 Answer **any two** of the following:

A. Explain the principle of Differential Scanning Calorimetry (DSC) and discuss any one of its application. 10

B. Differentiate between power-compensated and heat-flux DSC instruments.

C. Discuss the factors affecting DSC Curves.

D. Describe the role of multilayered films in automated analysis.

Q.5 Answer **any five** of the following:

A. What are determinate errors? Enlist two determinate types of error. 10

B. What is the meaning of government standards like HALLMARK and AGMARK?

C. Assign oxidation number to each element in $Cr(OH)_4^-$.

D. Solid $BaSO_4$ is dissolved in water at 25 °C. Its solubility is 1.04×10^{-5} mol/dm^3. Calculate the solubility product (Ksp) of the compound.

E. Explain the effect of temperature on the λ_{max} values in the UV-visible spectra.

F. What are the photoconducting transducers in FTIR?

G. Describe the quantity measured for each of the following techniques.

a) TGA b) DTA

H. Discuss the advantages of automated analyses.

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msc - chem - NEP2020 - sem I

Time: 2 Hours Marks-: 50

N.B. -1) All questions are compulsory.

2) Figures to the eight indicate full marks.

Q.1) Answer the following (Any Two) (10)

1) What are three types of sources? Explain each with suitable example.

2) What is a search engine? Discuss any four types of search engine.

3) Write a short note on- Citation index and impact factor of journal.

4) What are the internet and the world wide concept?

Q. 2) Answer the following (Any Two) (10)

1) Define- Accuracy, Precision, Mean, Mode, and Median.

2) What is a scientific method? Give different steps involved in scientific method?

3) Write a short note on- Curve fitting.

4) What is ANOVA? Give its basic principle? Why is ANOVA method used? Give various types of ANOVA.

Q.3) Answer the following (Any Two) (10)

1) Give different types of scientific writing.

2) Discuss outline for writing of scientific papers?

3) Define plagiarism. How can be plagiarism avoided?

4) What is a research? Give various steps involved in scientific research?

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Q.4) Answer the following (Any Two) (10)

1) What are the safe working procedure and protective environment in laboratory?

2) What is chemical waste? Write a short note on- Recycling of laboratory chemicals

3) Discuss the methods for laboratory disposal of explosive?

4) What is a chemical hazard? Explain different types of chemical hazards?

Q.5 Answer the following (Any Five) (10)

1) Define H-index. If a researcher has published 66 articles and out of these 23 articles having minimum 23 citations then what is the H-index of the author?

2) How do you cite publication information?

3) Differentiate between correlation and Regression.

4) What is SI system? Give SI unit of mass?

5) Why publishing research article is important?

6) Write a short note on- Scientific poster.

7) What are the examples of protective clothing?

8) Mention the full form and three types of first aid.

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MSc = organic chemistry = semI NEP 2020

Time: 2 Hours **Marks: 50**

1. Attempt **ANY TWO** of the following.

   i) On the basis of molecular orbital theory explain the structure and bonding in diborane molecule. 5

   ii) On the basis of hybridization explain the structure and bonding of iodine heptafluoride & sulphur tetrafluoride. 5

   iii) Derive the wave functions for sp^2 hybrid orbitals considering sigma bonding only. 5

   iv) Explain the concept of resonance. Draw the resonating structures for carbonate ion. 5

2. Attempt **ANY TWO** from the following.

   i) Derive the matrix representation for translation operation. 5

   ii) Show that C_{2v} point group is an Abelian group. 5

   iii) Define subgroup. Give its characteristics 5

   iv) What are Mullikens notations for irreducible representations? 5

3. Attempt **ANY TWO** of the following.

   i) What is Band Theory? Explain the property of solids as semiconductors and insulators on the basis of Band theory. 5

   ii) Explain the structural features of Rutile (TiO_2) compound. 5

   iii) Discuss with suitable example, the role of rare earth ions in solid state laser materials. 5

   iv) Write a note on,' Biological method for preparation of nanomaterials' 5

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2. B) Attempt ***any one*** of the following:

i) A hockey ball of mass 0.2 kg moving with a velocity of 3×10^3 ms^{-1}. If the ball can be located within an error equal to 600 nm, calculate the uncertainty in momentum of the ball so compared with the momentum of the ball itself. 4

ii) If $\hat{A} = \frac{d}{dx}$ and $\hat{B} = \frac{d^2}{dx^2}$ and f(x) = sinx. Show that, $\hat{A}$ and $\hat{B}$ are commutative or noncommutative. What does it mean when two operators are said to be non-commutative? 4

3. A) Attempt ***any two*** of the following:

i) Write the reaction mechanism for the decomposition of acetaldehyde and using steady state principle show that 4

$\frac{d}{dx}[CH_4] = k[CH_3CHO]^{3/2}$

ii) Explain the Rice – Ramsperger – Kassel (RRK) theory. 4

iii) Explain the mechanism of decomposition of ozone. 4

iv) In the case of the organic decomposition of ethane, use the steady state equations for the reaction scheme and show that the rate of production of ethylene is given by $\frac{d}{dx}[C_2H_4] = k[C_2H_6]$ 4

3. B) Attempt ***any one*** of the following:

i) The following process follows the first order kinetics

$$L \xrightarrow{14d} M \xrightarrow{21d} N$$ 4

where **14d** and **21d** are the half life time of the reaction in days from L to M and M to N respectively. At what stage of time will the concentration of M become maximum?

ii) The rate of formation of C in the reaction, $2A + B \rightarrow C$ is 0.25 mol L^{-1} s^{-1}. State the reaction rate and the rates of consumption of A and B. 4

4. A) Attempt ***any two*** of the following:

i) What is meant by strong electrolyte? Explain electrophoretic effect for conductance of strong electrolytes. 4

ii) Explain in detail the Debye-Falkenhagen effect for the conductance of strong electrolytes. 4

iii) With the help of well labelled diagram explain construction and working of solid oxide fuel cell. 4

iv) Write a note on the electrochemical enzyme – catalysed oxidation of Styrene. 4

MSC-Chemistry Sem-I

TIME: 2 ½ HOURS

MAX.MARKS:60

N.B. 1) All questions are compulsory.
2) Figures to the right indicate full marks.
3) Use of logarithmic table/non programmable calculator is allowed.
4) At. Wts: At. Wts: H=1, C=12, N=14, O=16, Na=23, Al=27, S=32, Cl=35.5, K=39, Ca=40, Ag=108, Ba=137, Pb=207, Mg=24.3, F=19, Cu=63.5, Cr=52, Sn=118.7

Q.1 A) Attempt **Any two** of the following:

a) Define the following terms with respect to performance characteristics of an analytical instrument, **4**
1. Dynamic range 2. Selectivity 3. Sensitivity 4. Precision

b) What are advantages of implementing ISO 9000 series. **4**

c) Define "biosensor" with respect to analytical device. Give classification of transducer. **4**

d) Explain the "piezoelectric effect" that forms the basis of quartz crystal microbalance (QCM) sensor with diagram. **4**

B) Attempt **any one** of the following:

a) Define: Data domain. What is electrical domain and non-electrical domain? **4**

b) Discuss quality audits and quality reviews. **4**

Q.2 A. Attempt **any two** of the following:

a) (i) Assign oxidation number to each element in $Cr(OH)_4^-$ **4**
(ii) Solid BaSO4 is dissolved in water at 25°C. Its solubility is 2.45×10^{-3} g /dm^3. Calculate the solubility product (Ksp) of the compound.

b) Calculate the volume of HCl (density 1.19 gm / cm^3, 42% HCl by weight) required to prepare 10 dm^3 of 0.2N HCl. **4**

c) Determine the mole fraction of both the substances, when 45 g of acetone is mixed with 55 g of methanol. **4**

d) 16.98 g of $AgNO_3$ is treated with 6.5 g of NaCl, producing AgCl. Calculate the amount of AgCl produced, in grams. Which is the limiting reagent? **4**

B. Attempt **any one** of the following:

a) A buffer solution was prepared by mixing 0.05 mole acetic acid with 0.06 mole sodium acetate in distilled water to make 1 dm^3 solution. Calculate the pH of the solution. Given K_a for acetic acid is 1.75×10^{-5}. **4**

b) Calculate the amount of KNO_3 required, in grams , to prepare 250 cm^3 of a 100 ppm solution of KNO_3. Find the concentration of the solution in terms of ppm of K^+. **4**

Q.3 A. Attempt **any two** of the following:

a) With the help of schematic diagram, discuss the instrumentation of the dispersive IR spectrophotometer. **4**

b) Derive Beer Lambert's law and state its limitations. **4**

c) Explain:
i. Optical arrangement of a dual wavelength spectrophotometer. 4
ii. Photo conducting transducers used in IR spectrometer.

d) Discuss the fiber optics used in optical instruments. 4

B Attempt **any One** of the following

a) Simultaneous determination of two elements P and Q spectrophotometrically at two different wavelengths gave the following results: 4
[Given: b= 1cm]

Elements	Concentration (mol dm^{-3})	Absorbance	
		447nm	650nm
P	**2.8×10^{-3}**	**0.645**	**0.180**
Q	**7.2×10^{-3}**	**0.128**	**0.874**
P + Q	-------	**0.427**	**0.412**

Calculate the molar concentration of P and Q.

b) Discuss the different techniques for preparation of solid samples for IR absorption measurements. 4

Q.4 A. Attempt **any two** of the following:

a) What is Differential scanning calorimetry (DSC)? Discuss the principle of heat-flux DSC. 4

b) What is a DSC curve? With a suitable example, discuss the nature of DSC curve. 4

c) Discuss the application of DSC in the study of specific heat, liquid crystals and percentage crystallinity. 4

d) Describe the role of multi-layered films in automated analysis. 4

B. Attempt any one of the following:

a) What is an automatic titrator? What are the benefits of using automatic titrator? 4

b) Discuss the principle of flow injection analysis. 4

Q.5 Attempt **any four** of the following: 12

a) Discuss quantitative method of analysis with respect to standard addition method.

b) Define: 1. Technique 2. Method 3. Procedure

c) 2.94 g of $K_2Cr_2O_7$ is dissolved in acidic medium to prepare 100 cm3 solution. Calculate the normality of the solution. Express the concentration in terms of molarity.

d) Calculate the pH of a 0.1 M NH_4OH solution. Given $K_b = 1 \times 10^{-5}$.

e) What is diffuse reflectance spectroscopy? Explain the diffuse reflectance spectrum.

f) What are the major advantages of an FTIR spectrometer compared with a dispersive instrument?

g) Describe what quantity is measured and how the measurement is performed for each of the following techniques: TGA, DTA and DSC.

h) Draw a block diagram of power compensated DSC. Discuss how the DSC experiment is carried out.

MSc = Sem I = chemistry (NEP 2020)

TIME: 2 HOURS **MAX. MARKS: 50**

NB:

1) **All questions are compulsory.**
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3) **Use of logarithmic table/non-programmable calculator is allowed.**
4) **At. Wts: H=1, C=12,N=14,O=16,Na=23,Al=27,S=32, Cl=35.5, K=39, Ca=40,Ag=108 , Ba=137, Pb=207,Mg= 24.3,F=19,Cu= 63.5, Cr = 52, Sn=118.7 Fe = 55.8**

Q.1 Answer **any two** of the following: 10

A. Discuss performance characteristics of analytical method.

B. Write note on basic safety in laboratory.

C. Give classification of Analytical methods.

D. What is the principle of NABL accreditation?

Q.2 Answer **any two** of the following: 10

A. A buffer solution was prepared by mixing 0.05 mole acetic acid with 0.06 mole sodium acetate in distilled water to make 1 dm^3 solution. Calculate the pH of the solution. [Given Ka for acetic acid is 1.8×10^{-5}].

B. Calculate the volume of HCl (density 1.19 gm / cm^3, 38% HCl by weight) required to prepare 18 dm^3 of 0.02 N HCl.

C. 161 g of ethanol and 145 g of acetone are mixed together. Find the mole fraction of each compound in the mixture.

D. 100 g of Na_2CO_3 reacts with 100 g of HCl. Calculate the amount of NaCl formed, in moles and in grams. Which is the limiting reagent.

Q.3 Answer **any two** of the following: 10

A. Draw a labelled schematic diagram of Michelson's interferometer. Explain its working in FTIR

B. Name the Infra-red (IR) sources and describe any two in detail.

C. In what way the Fourier Transform (FT) instruments differ from the optical instruments?

D. With the help of block diagram describe the dual wavelength spectrophotometer. What type of samples can be analysed by it?

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4. Attempt **ANY TWO** of the following.

i) Explain how absorption spectra and pH method help in detection of complex formation. 5

ii) Derive the expression for stepwise formation constant in complexes. 5

iii) Draw Orgel diagram for d^4 metal ion in octahedral complex. Assign the electronic transitions. 5

iv) Explain the significance of Tanabe-Sugano diagrams in interelectronic repulsions. 5

5. Attempt **ANY FIVE** of the following 10

i) Calculate the formal charge of sulphur in the sulphate ion.

ii) What is hydrogen bonding. Give two examples of molecules which shows hydrogen bonding.

iii) Define group and symmetry elements with examples.

iv) Construct character table for C_2h point group with suitable example.

v) State the principle underlying the preparation of nanomaterial by ceramic method.

vi) Explain in brief the terms: 1. Fermi Energy 2. First Brillouin zone

vii) Give electronic transitions for d^1 and d^3 configurations on the basis of Orgel diagram.

viii) State any four methods of detection of complex formation.

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msc - chem - sem I

[Time: 2 ½ Hours] [Total Marks: 60]

Please check whether you have got the right question paper

NB: 1. **All** questions are **compulsory**
2. **Figures** to the **right** indicate **full** marks.

Q.1 Attempt any **two** of the following:

(A)

(a) What are the kinetic and thermodynamic control of organic reactions? Give suitable examples. 4

(b) Explain the use of the following techniques in determining the mechanism of a reaction: 4
I) Detection and trapping of intermediate.
II) Stereo-chemical evidence.

(c) Discuss primary and secondary kinetic isotope effects using suitable examples. 4

(d) What is specific acid and base catalysis? Illustrate specific base catalysis with a suitable example. 4

(B) Attempt any **one** of the following:

(a) Discuss the Hammond postulates. 4

(b) Arrange the following in increasing order of basicity and justify your answer: Phenol, o-nitrophenol, m-nitrophenol, p-nitrophenol. 4

Q.2 Attempt any **two** of the following:

(A)

(a) Give the AAL^1 mechanism for ester hydrolysis with suitable example. 4

(b) Explain the following term with a suitable example. 4
i) Tele Substitution
ii) Ambident nucleophiles

(c) Draw Frost-Musulin diagram for cyclobutadiene and cyclopentadienyl anion. Show distribution of electron in MO's and comment on its aromaticity. 4

(d) Explain the followings 4
i) Comparative reactivity of 1-Bromopropene and 3-Bromopropene to SN^1 reaction.
ii) Comparative nucleophilicity of methoxide and t-butoxide ion.

(B) Attempt any **one** of the following:

(a) Explain the mechanism of nucleophilic substitution on 4-Nitrochlorobenzene 4

(b) Write a short note on 4
i) Homoaromatic compound
ii) Antiaromatic compound

Q.3 Attempt any **two** of the following:

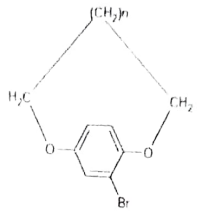
(A)

(a) Explain the chirality of spiranes. Write the structure of pair of enantiomeric spiranes with their configurational descriptors. 4

(b) Explain the stereochemistry of tri and tetra coordinated sulphur compounds. 4

(c) Define pseudoasymmetric centre. Draw structure of two isomeric structures containing pseudoasymmetric centre. Assign configurational descriptors to them. 4

(d) Using substitution addition criterion, identify relationship between H_A and H_B Write stereochemical descriptor to H_A and H_B 4



(B) Attempt any **one** of the following:

(a) Explain the following with suitable example

1) Simple Axis of Symmetry 4

2) Plane of Symmetry

(b) Explain the following with suitable example

1) *Syn and Anti* System. 4

2) Erythro and Threo System

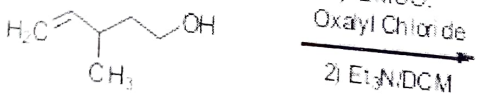
Q.4A) Attempt any **two** of the following:

(a) What is Oppenauer oxidation? Give its Mechanism 4

(b) Explain the mechanism of Wolff Kishner reduction with suitable example. 4

(c) Predict the products in the following reactions: 4

i)



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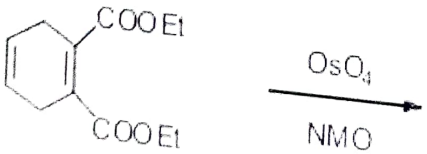

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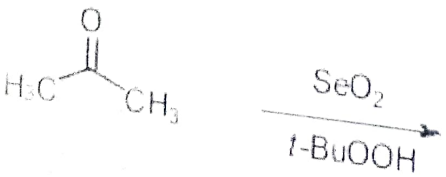

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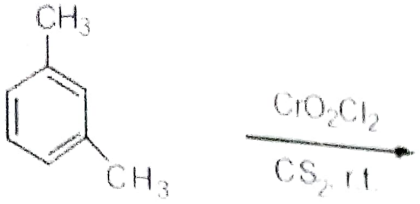


(d) What are L and K selectrides? Give two applications of each. 4

(B) Attempt any **one** of the following:

(a) What is Etard oxidation? Give example with mechanism. 4

(b) Explain Na-liquid NH_3 mediated reduction of aromatic compounds and alkynes. 4

Q.5 Attempt any **four** of the following:

(A) Explain Curtin-Hammett Principle. 3

(B) Discuss the following factors affecting acidity: 3
I) Electronegativity
II) Resonance
III) Hybridization.

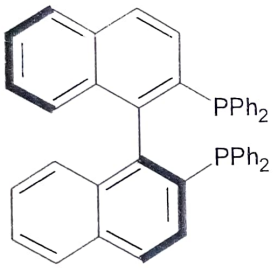
(C) Explain the aromaticity of Pyrrole. 3

(D) Explain the $SN^{2'}$ mechanism with a suitable example 3

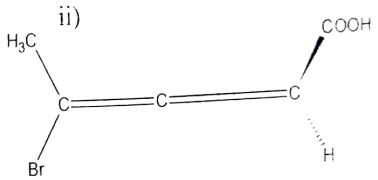
(E) Explain the optical activity of Cyclophanes. 3

(F) Write the configurational descriptor to the following molecules 3

i)



ii)



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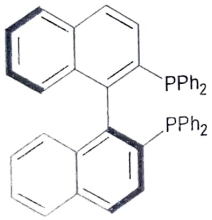
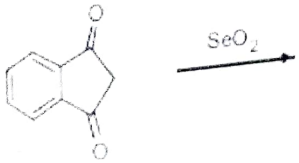


(G) Complete the following reactions. 3

i)



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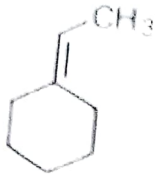
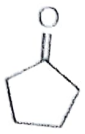
ii)



CrO_3 →

iii)



*m*CPBA OR
Peroxy acids →

(H) What is Collin's reagent? Give one application.

Q.3) **Answer any two of the following:**

a Why inversion of configuration is much more during solvolysis of (I) than (II)? Explain with mechanism. 5

$C_6H_{13}CH(CH_3)Cl$ (I) $C_6H_5CH(CH_3)Cl$ (II)

b Explain aromatic nucleophilic substitution reaction in pyridine with suitable mechanism. 5

c Explain acid catalyzed hydrolysis of ester using A_{AC}^2 mechanism. 5

d Explain aromaticity of the following: 5

i) Thiophene (ii) Pyridine

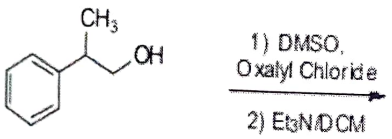
Q.4) **Answer any two of the following:**

a What is Corey-Kim oxidation? Give example with mechanism 5

b Write note on Wolf Kishner Reduction. 5

c Predict the product in the following reactions: 5

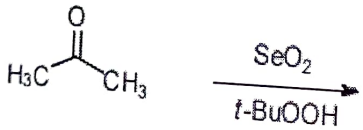
i)



ii)



iii)



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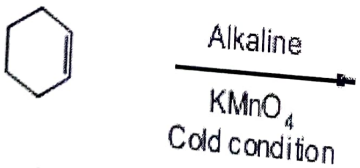

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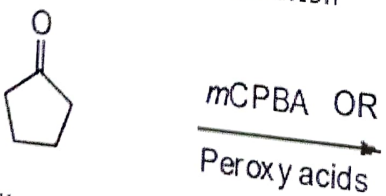


d Illustrate use of the DIBAL-H and K-selectrids in organic synthesis, with two example each. 5

Q.5) Answer **any FIVE** of the following:

a State the principle of microscopic reversibility 2

b Compare acidity of Trifluoroacetic acid and acetic acid 2

c Explain with suitable example improper axis of symmetry 2

d Explain *erythro-threo* system of nomenclature with suitable examples. 2

e What is an antiaromatic compound? Give one example. 2

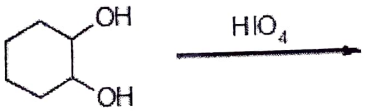
f Why cyclopropenyl cation is called smallest aromatic system? 2

g Complete the following reactions. 2

1)



2)



h Illustrate the use of Red Al in organic synthesis, with two examples. 2

M.Sc Organic Chemistry I - NEP 2020

[Time: 2 hours] [Total Marks: 50]

Please check whether you have the right question paper.

NB: 1. All the questions are compulsory.
2. Figures to the right indicate full marks.

Q.1) Answer any two of the following:

a How do the following techniques help in determining the mechanism of the reaction? 5
i)Product analysis
ii) Trapping of intermediates

b What is general and specific catalysis? Explain its mechanism with suitable examples. 5

c Compare the basicity of pyridine, pyrrole, and piperidine. 5

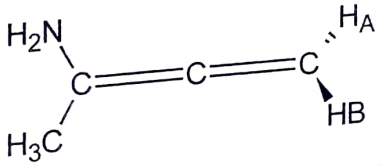
d Give examples and explain the following: 5
i) Primary kinetic isotopic effect
ii) Secondary kinetic isotopic effect

Q.2) Answer any two of the following:

a Draw four stereoisomers of 2,3,4-trihydroxy glutaric acid. Label pseudoasymmetric centre present in the stereoisomers and assign configurational descriptors to the pseudoasymmetric centre. 5

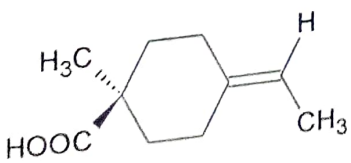
b Explain the stereochemistry of tri coordinated 'C' species namely carbocation, carbanion, carbon free radical 5

c i)State and explain prochiral center with suitable example. 2
ii)Write stereochemical descriptor to H_A and H_B. 3

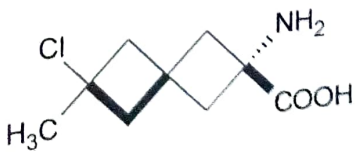


d i)Write the structure of pair of enantiomeric biphenyl with their configurational descriptors. 2
ii)Write the configurational descriptor to the following molecules 3

1)



2)



3)

