MSc - Sem - II

[Time: 2 ½ Hours] [Marks: 60]

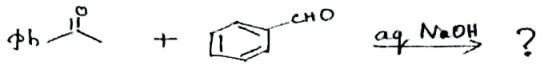
Please check whether you have the right question paper.

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

Q.1) (A) **Answer any two of the following:**

a What is Knoevenagel condensation reaction? Explain its mechanism with a suitable example. 4

b Complete the following reaction and explain its mechanism. 4



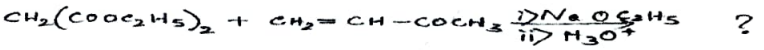
c Explain how solvent polarity affects the rate of alkylation of enolates. 4

d What are enamines? Explain with suitable examples alkylation of enamines. 4

(B) Answer **any one** of the following;

a Discuss the mechanism of Mannich reaction with a suitable example. 4

b Complete the following reaction, name the reaction, and give its mechanism. 4

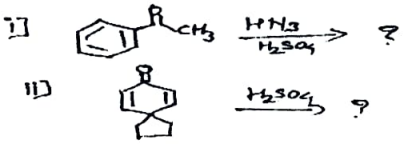


Q.2) (A) Answer **any two** questions out of the following

a What is Baylis-Hilman reaction? Explain its mechanism 4

b What is Curtius rearrangement? Explain its mechanism 4

c Predict the product of the following reactions and give the name of the reactions. 4



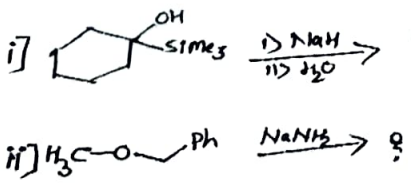
d Complete the following reaction and give its mechanism. 4



(B) Answer **any one** question out of the following

a What is Passerini reaction? Explain its mechanism 4

b Predict the product and name the following reactions 4



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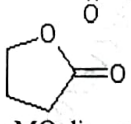
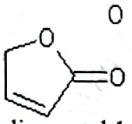
Q.3) (A) Answer any two of the following:

a Draw the π – MO diagrams of diene (1,3-dutadiene) and dienophile (ethylene) showing electron distribution. Label FMOs, show their interaction. 4

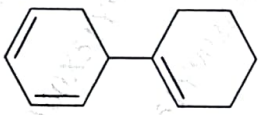
b How are the following compounds distinguished using IR spectroscopy? 4

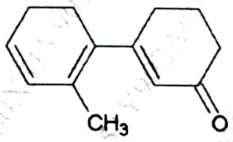
(i) $H_3C-C(=O)-H$ and $H_3C-C(=O)-CH_2$

(ii)  and 

c Draw the MO diagram of butadiene and 1,3,5-hexatriene. Using this diagram explain λ-max of 1,3 butadiene is 217 nm while that of 1,3,5-hexatriene is 254 nm. 4

d Calculate the λmax of the following compounds: 4

i) 

ii) 

(B) Answer any one of the following;

a With the help of suitable example, explain how following factors affect the vibrational frequency. 4

1) Ring size
2) Hydrogen bonding

b Explain donor acceptor interaction in nucleophilic addition reaction on formaldehyde using FMO method. 4

Q.4) (A) Answer any two of the following:

a Write the fragmentation pattern of the following molecules in mass spectroscopy 4

i) 2-Methylbut-2-ene

ii)2-Methylpentane

b Explain the following terms in NMR spectroscopy. 4

i) Karplus equation

ii) Coupling Constant.

c An organic compound with molecular formula $C_6H_{14}O$.IR spectrum gives broad band at 3600 cm-1,PMR spectrum gives δ 0.8 ppm (t) 6H,δ 1.0 ppm (s) 3H , δ 1.5 ppm (q) 4H,δ 1.6 ppm (s) 1H 4

Deduce the structure of the molecule and justify your answer.

d Explain the following terms in Mass spectroscopy with suitable example. 4

i) McLafferty rearrangement

ii) Nitrogen rule

(B) Answer any one of the following:

a Write the number of signals and splitting pattern observed in the NMR spectra of following molecules: 4

i) Butan-2-ol ii) Methylbenzoate

ii) iii) Toluene iv) 2-Methylbutanoic acid

b An organic compound with molecular formula C_6H_7N shows the following spectral data : 4

IR = 1180 cm^{-1},1500cm^{-1}, 3000cm^{-1}, 675cm^{-1} ,730 cm^{-1}

^{1}HNMR = δ 7.5 ppm (m) , δ5.8 ppm (s),

Deduce the structure of the molecule and justify your answer.

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

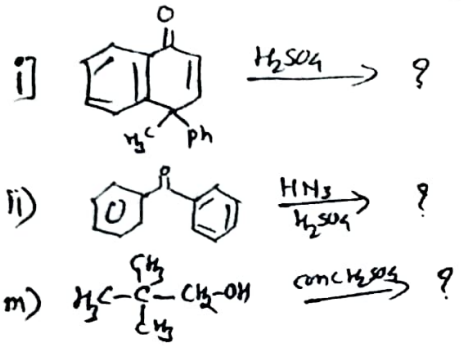
a Complete the following reaction and name the reaction: 3



b Explain in detail the reaction mechanism between acetone and excess of iodine in NaOH. 3

c Explain Tiffeneau- Demjanov rearrangement with a suitable example. 3

d Complete the following reactions. 3



e Define hard and soft nucleophiles. Give one example of each. Comment on the relative energies of their LUMO's 3

f Why benzene shows absorption maxima at 255nm (ε_{max} = 230) whereas aniline shows absorption maxima at 280nm (ε_{max} = 1430)? Justify your answer. 3

g Explain the terms Base peak and Isotopic peaks in Mass spectroscopy. 3

h Explain the term proton coupled and decoupled spectra in 13C NMR spectroscopy. 3

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Paper / Subject Code: 92102 / Chemistry : Paper I - Physical Chemistry

MSC - Sem - II

[Time: 2 ½ Hours] [Marks: 60]

Please check whether you have got the right question paper.

N.B.: 1. **All questions are compulsory.**
2. **Figures 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}
$R = 8.314$ J.K^{-1}mol^{-1}
$= 2.0$ cal.K^{-1} mol^{-1}
$h = 6.626 \times 10^{-34}$Js
$m_e = 9.110 \times 10^{-31}$ kg
$N_A = 6.022 \times 10^{23}$ mol^{-1}

$e = 1.602 \times 10^{-19}$ C
$k = 1.3811 \times 10^{-23}$ J.K^{-1}

$1J = 6.24 \times 10^{18}$ eV
$1eV = 8.06 \times 10^{3}$cm^{-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) Define fugacity. How does it vary with temperature and pressure. 4
   ii) Derive Gibbs Duhem Margules equation. 4
   iii) Explain structure of ADP molecule. Explain the hydrolysis of ATP in biological system with the help of thermodynamics. 4
   iv) Derive an equation for Gibb's adsorption isotherm. 4

1. B) Attempt **any one** of the following:
   i) The partial molar volume of water in a methanol water solution containing 0.61 mole fraction water is 17.2 cm^3/mol. The density of the solution is 0.92 g/cm^3. Calculate the partial molal volume of methanol in the solution. ($R = 8.314$ J mol^{-1} K^{-1}) 4
   ii) Calculate ΔS_{mix} at 298K and 1 atm pressure when 28 g of He (At mass He = 4) is mixed with 100 g of Ne (At mass Ne = 10). 4

2. A) Attempt ***any two*** of the following:
   i) Transform Cartesian coordinates (x,y,z) into polar coordinates (r,θ,Φ) and write the expression for Φ. 4
   ii) Explain the need for an approximate solution to a two-electron system. Show how the problem of two electrons can be reduced to the problem of one electron system. 4
   iii) Derive an expression for the most probable distance of an electron from the nucleus in the ground state of a hydrogen atom. 4
   iv) Write the secular determinant for the benzene molecule. Draw the molecular energy level diagram and indicate HOMO, and LUMO from the diagram. 4

2. B) Attempt ***any one*** of the following:
   i) What are quantum numbers? Explain the significance of magnetic quantum numbers. 4
   ii) An electron with a mass 9.1×10^{-31} kg rotates in a circular orbit with a radius of 0.5 Å.Calculate the energy in eV for n=2. 4

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

i) Derive the parabolic rate law for the reaction of a gas on the surface of solid particles. 4

ii) Explain the kinetics of enzyme inhibition action by uncompetitive inhibition method. 4

iii) Derive an expression for the linear free energy relationship of reactions in solutions. 4

iv) Discuss the kinetics of regulatory enzymes with the help of Hill's equation. 4

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

i) Predict the effect of ionic strength on the rate constant for each of the following reactions. 4

(a) $[Pt(NH_3)_3Br]^+ + CN^- \rightarrow$ Products

(b) $C_{12}H_{22}O_{11} + H^+ \rightarrow$ Products

(c) $[Co(NH_3)_5Cl]^{2+} + Hg^{2+} \rightarrow$ Products

(d) $[NO_2NCO_2C_2H_5]^- + OH^- \rightarrow$ Products

ii) An enzyme hydrolyzed a substrate concentration of 0.03 mmol dm^{-3}, the initial rate was 1.5×10^{-3} mmol $dm^{-3}min^{-1}$and the maximum rate was 4.5×10^{-3} mmol $dm^{-3}.min^{-1}$. Calculate the Michaelis Constant (Km). 4

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

i) Derive an expression for Frenkel defects in ionic crystals thermodynamically. 4

ii) Draw and discuss the phase diagram of solid-gas system involving formation of amino compounds. 4

iii) Draw and discuss the phase diagram of two component systems involving formation of a compound with congruent melting point. 4

iv) Draw and discuss the phase diagram of a three-component system consisting of two pairs of partially miscible liquids. 4

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

i) If the average energy required to create a vacancy in a metal was 1 eV. Calculate the ratio of vacancies in the metal at 727°C and 227°C. $k_B = 8.625 \times 10^{-5}$ eV/K. 4

ii) Calculate the number of phases, the number of components and the number of degrees of freedom in the following system. 4

(a) $CuSO_4.H_2O(s) \rightleftharpoons CuSO_4(s) + H_2O(g)$

(b) One mole of a pure gas enclosed in a cylinder

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

a) Give Kelvin equation. Prove it thermodynamically. 3

b) What do you understand by thermodynamic excess functions? Write an expression for Excess entropy (S^E). 3

c) What are radial probability distribution curves? Sketch radial distribution curves for 1s and 2p orbitals. 3

d) Explain why hydrogen-like atoms represent a two-particle problem. Write the Hamiltonian operator for it. 3

e) Discuss the Lineweaver – Burk plot for an enzyme catalyzed reaction. 3

f) Discuss the factors which affect the reactions in solid state. 3

g) What is line defect? Explain Edge Dislocation. 3

h) Draw phase diagram of a three component system with one pair of partially miscible liquid and explain why tie lines within the binodal curve are neither parallel to each other nor to axis. 3

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Paper / Subject Code: 92126 / Chemistry : Paper II - Inorganic Chemistry

M SC - Sem II

[Time: 2 ½ Hours] [Marks: 60]

Please check whether you have got the right question paper.

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

1. a) Attempt **any two** of the following.
   i) Discuss the mechanism of substitution reaction of octahedral complexes without breaking of metal-ligand bond. **4**
   ii) With respect to Trans effect, explain the effect of the following factors.
   i) Nature of the entering group. ii) Nature of leaving group. **4**
   iii) Explain use of flow methods for determination of rate of very fast reactions. **4**
   iv) Discuss the cis-trans isomerization reaction in a co-ordinate complex. **4**

1. b) Attempt **any one** of the following:
   i) Explain the direct chemical analysis used for the determination of the rate of reaction. **4**
   ii) Explain the mechanism of trans effect in square planar complexes using a suitable example. **4**

2. a) Attempt **any two** of the following.
   i) Assuming that the following complexes obey 16 electron rule, with the help of electron count, identify metal M belonging to 1st transition series . 4
   1) $M(\eta^5\text{-}C_5H_5)(CO)Cl_2$ 2)) $M(CH_3Br)(PPh_3)_3$
   3) $M(\eta^2\text{-}C_2H_2)(CO)_4$ 4)) $M(\eta^6\text{-}C_6H_6)(CO)_3$
   ii) With reference to Schrock Carbene complexes give 4
   1. Any two characteristics 2. One method of preparation 3. One chemical reaction.
   iii) What is an organometallic compound? Give the synthesis of cyclopentadiene complex of Iron. 4
   iv) Explain the structure of bis (triphenyl phosphine) diphenylacetylene Platinum(0) complex. 4

2. b) Attempt **any one** of the following.
   i) How is dibenzene chromium is prepared? Discuss its structure and bonding on the basis of valence bond theory. 4
   ii) Write any one method of preparation of Zeise's salt. Draw its structure and discuss the bonding. 4

3. a) Attempt **any two** of the following.
   i) Explain cell proliferation & cancer. 4
   ii) How mercury enters in water? Give distribution & speciation scheme of mercury in water. 4
   iii) Explain the sources and toxic effects of cadmium. 4
   iv) Explain the sources, biochemical effects & toxicity of arsenic. 4

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3. b) Attempt **any one** of the following.

i) Explain the sources of lead in the environment.

ii) Explain the control and treatment of mercury poisoning.

4. a) Attempt **any two** of the following.

i) Explain structural details of haemoglobin molecule.

ii) Schematically represent cooperative binding mechanism of oxygen with haemoglobin using suitable diagram.

iii) What is hemocyanin? State important features of structure of hemocyanin.

iv) Which are the metal ion carriers in biological system? Discuss the role of Valinomycin as metal ion carrier.

4. b) Attempt **any one** of the following.

i) What is Superoxide dismutase (SOD)? Give stepwise mechanism of activity of SOD.

ii) Distinguish between haemoglobin and myoglobin.

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

a) Based on Taube's classification, Identify Labile and Inert complexes from the following complexes.

i) $[Ti(H_2O)_6]^{3+}$ ii) $[V(H_2O)_6]^{2+}$ iii) $[Cr(H_2O)_6]^{2+}$

b) Identify the products in the following reaction:

i) $[PtCl_4]^{2-} \xrightarrow{PPh_3} A \xrightarrow{Py} B$

ii) $[PtCl_4]^{2-} \xrightarrow{Py} A \xrightarrow{PPh_3} B$

c) Write a note on half sandwich compounds.

d) How is diallyl nickel complex is prepared? Explain its structure.

e) Explain why hexavalent chromium is more toxic than trivalent chromium.

f) Explain biochemical effects of lead poisoning.

g) What is nitrogen fixation? Discuss in brief the role of nitrogenase in nitrogen fixation

h) Write a short note on oxy & deoxy forms of haemoglobin.

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MSC (Research Sem-II Paper IV

(8)

Paper / Subject Code: 92178 / Chemistry : Paper IV - Analytical Chemistry

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.

Q.1 A) Attempt **any two** of the following: 8

a) Discuss the reasons of broadening of chromatographic peaks?

b) Write a note on "Optimization of chromatographic conditions".

c) Give the classification of chromatographic techniques based on physical state of mobile and stationary phases involved.

d) What is HETP? How is it related to column efficiency?

B) Attempt **any one** of the following: 4

a) Describe: "fluorescence detector" used in HPLC. Give its applications.

b) Explain the use of mass spectrometer as detector in chromatography.

Q.2 A) Attempt **any two** of the following: 8

a) With the help of schematic diagram, discuss the X-ray tube used in X-ray instruments.

b) With a suitable diagram describe the construction and working of "Time Of Flight"(TOF) mass analyzer. Compare between magnetic sector mass analyzer and TOF.

c) Enlist any four applications of isotopic dilution analysis.

d) With respect to isotope dilution method, discuss the single dilution method.

B. Attempt **any one** of the following: 4

a) Discuss Fast Atom Bombardment Sources (FAB) used in mass spectrometer. Write any two drawbacks of FAB.

b) Draw a schematic diagram of various components of a mass spectrometer and write the function of each component.

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

a) Draw a schematic diagram of scanning electron microscope (SEM). How is it used to obtain SEM images? 8

b) What is Transmission electron microscope (TEM)? Discuss the different lens used in TEM.

c) Discuss the applications of electron spectroscopy for chemical analysis (ESCA).

d) With a schematic diagram, explain the different components of an ICP torch.

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

a) Discuss the principle Scanning Tunneling Microscope (STM). 4

b) Compare the techniques: ESCA and Auger electron spectroscopy.

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

a) Write short note on solid state electrodes. State any one application of solid state electrodes. 8

b) Discuss effect of complex formation on the polarographic wave.

c) Discuss the instrumentation for coulometry at controlled potential.

d) What is electrogravimetry? Give applications of elecrogravimetry.

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

a) Determine the diffusion current for a Nickel solution, if diffusion coefficient for Ni having concentration of 3mM is $0.69 \times 10^{-5} cm^2 s^{-1}$. Flow rate of Hg is 4 mgs^{-1} and drop time is 4 s. 4

b) A constant current of 0.800A is used to deposit copper at the cathode and oxygen at the anode of an electrolytic cell. Calculate the number of grams of Cu deposited in 15.2 min, assuming no other redox reaction (1Faraday = 96500 C, molar mass of Cu = 63.54).

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

a) Integrator output for the separation of hydrocarbons by capillary column GC-FID.

Analyte	Retention time (min)	Area	Peak width at the base (in units of minutes)
Ethyl Benzene	13.359	510009	0.090
o-xylene	13.724	618229	0.087

Calculate: Calculate k', α for any two adjacent compounds.

b) Discuss in brief "Chiral Chromatography".

c) What are X-rays? Discuss the Bragg's law for diffraction of X-rays.

d) Give quantitative applications of mass spectrometry.

e) Differentiate between ICP-AES and AAS.

f) With the help of schematic diagram, describe an electron gun used in instruments for auger electron spectroscopy.

g) Discuss desired characteristics of ion selective electrodes.

h) Discuss wire net cylindrical cathode used in electrogravimetry and state any one advantage.

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(11)

msc – chem – NEP2020 – sem II

(2 hours) Total Marks: 50

N.B: **1) All questions are Compulsory.**
2) Figures to the right indicate full marks.

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

A) Describe the mechanism of "inner sphere" electron transfer reaction in octahedral complexes. 5

B) Concerning the Trans effect, explain the effect of the following factors.
i) Nature of the entering group. ii) Nature of leaving group. 5

C) Explain the following factors affecting the rate of reaction.
1. Temperature. 2. Catalyst. 5

D) Discuss the cis-trans isomerization reaction in a co-ordinate complex. 5

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

A) What is an organometallic compound? Give the synthesis of cyclopentadiene complex of Iron. Draw its structure. 5

B) State 16 electron rule. With the help of electron count, show which of the following complexes obey the rule?
1) $[Rh\ Cl\ (PPh_3)_3]_2$) 2) $[\ (\eta^5\text{-}C_5H_5)\ Mn\ \eta^6 - C_6H_6)]$ 3) $[Ir\ (CO)\ (Br)\ (PPh_3)_2]$
4) $[\ Pt\ Cl_4]^{2-}$

C) Describe the preparation of Zeise's salt. Explain its structure and bonding on the basis of valance bond theory. 5

D) Explain the preparation and chemical properties of alkene derivatives of Platinum and Palladium. 5

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

A) Explain the speciation by chromium. Hexavalent chromium is more toxic. Explain? 5

B) What is biochemical methylation. Illustrate how mercury gets propagated in the food chain. 5

C) State different sources of lead. Explain the toxic effects of lead. 5

D) Describe the case study of Ita-itai disease. 5

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

A) Explain structural details of hemerythrin. 5

B) Schematically represent oxygen dissociation curve with respect to cooperative binding of oxygen with haemoglobin. 5

C) What is nitrogen fixation? Explain the mechanism of nitrogen fixation using suitable chemical reactions. 5

D) Which are the metal ion carriers in biological system? Discuss the role of Valinomycin as metal ion carrier. 5

Q 5. Attempt any **five** of the following: 10

A) Based on Taube's classification, Identify Labile and Inert complexes from the following complexes.

i) $[V(NH_3)_6]^{2+}$ ii) $[Cr(H_2O)_6]^{2+}$

B) Identify the products in the following reaction:

i) $[PtCl_4]^{2-} \xrightarrow{PPh_3} A \xrightarrow{H_2O} B$

C) Explain the preparation of Fischer Carbenes.

D) Draw the structure of Tricarbonyl (η4 butadiene) Iron (0). Explain its silent features.

E) Describe uses of I^{123} as radio diagnostic aid.

F) Explain different sources of copper poisoning.

G) Explain catalytic activity of monooxygenase enzyme in brief.

H) Distinguish between haemoglobin and myoglobin.

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56232 - Subcode
Analytical chem II

(13)

MSC - organic chem - NEP2020 - Sem II

Duration - 2 Hours Max Marks 50

N.B. 1. All questions are compulsory.
2. Figures to the right indicate marks.

Q.1 Attempt **any two** of the following. 10

A. What is the difference between the columns, C8 and C18 used in an HPLC system?

B. The retention time of two components on column were found to 3.28 min and 5.26 min respectively. Calculate (i) HETP for each peak (ii) Resolution. If the width of the two peaks is 0.46 and 0.57 min., respectively and the time for mobile phase was 0.17min with the length of the column as 24.1cm.

C. What are different ways of optimization of chromatographic conditions. Discuss in details.

D. Give ideal properties of the detectors to be used in GLC and GSC.

Q.2 Attempt any **two** of the following. 10

A. With the help of schematic diagram, describe lithium drifted silicon detector used in X-ray spectroscopy.

B. Write qualitative and quantitative applications of X-ray fluorescence spectroscopy.

C. Name ion sources used in molecular mass spectrometry. Discuss any one in details with its advantages.

D. Explain principle and theory of neutron activation analysis.

Q.3 Attempt **any two** of the following. 10

A. Discuss the principle of the scanning tunneling microscope (STM).

B. Draw a schematic diagram of scanning electron microscope (SEM) and discuss the process of obtaining SEM images.

C. With respect to transmission electron microscope (TEM), discuss:
i. Electron gun ii. Condenser lens and iii. Objective lens

D. Explain the appearance and temperature profile of the inductively coupled plasma source used in atomic emission spectrometer.

Q.4 Attempt **any two** of the following. 10

A. Write short note on enzyme-based biosensors with example.

B. Discuss effect of complex formation on the polarographic wave.

C. What is electrogravimetry? Discuss the factors that control the physical properties of electrolytic precipitates in electrogravimetry.

D. Calculate the time needed, in minutes, for a constant current of 0.96 A to deposit 0.5 g of Co(II) as elemental cobalt on the surface of a cathode. (1 Faraday =96500 C, molar mass of cobalt = 58.93)

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Q. Write any five of the following.

A. Mention any two applications of Electronic detector.

B. Name the detectors used in HPLC and mention its use.

C. Describe powder method used in X-ray diffraction analysis.

D. Draw a schematic diagram of "Time of Flight Mass analyzer".

E. Write the mathematical expression for magnification achievable in scanning electron microscope (SEM) images and explain the terms involved.

F. Mention the limitations of atomic absorption spectrometry (AAS).

G. State any two desired characteristics of ion selective electrodes.

H. State any two features of controlled potential coloumetry.

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(15)

MSC - NEP2020 - chem - sem II

[Time: 2 hours]

[Total Marks: 50]

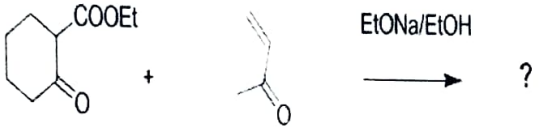
Please check whether you have the right question paper.

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

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

a Explain Knoevenagel amine catalysed condensation and give its mechanism with a suitable example **5**

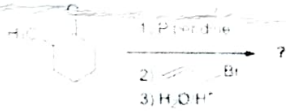
b Predict the products and give the mechanism of the following reaction **5**



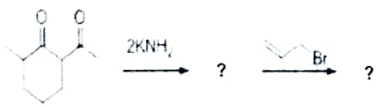
c Discuss the mechanism of Mannich reaction with a suitable example. **5**

d Complete the following reactions: **5**

1.



2.

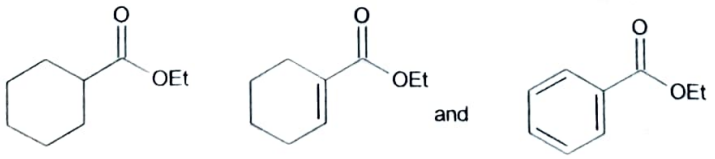


Q.2) Answer any two of the following: **10M**

a Draw the π – MO diagrams of diene (1, 3-dutadiene) and dienophile (ethylene) showing electron distribution. Label FMOs, show their interaction **5**

b How the following compounds are distinguished using IR spectroscopy? **5**

(i)



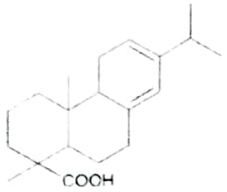


c Draw the MO diagram of ethene and butadiene. Using this diagram explain λ-max of ethene is 170 nm while that of 1, 3 butadiene is 217 nm. **5**

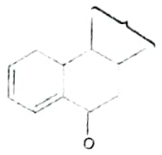
X51Y9B58CBX51Y9B58CBX51Y9B58CBX51Y9B58CB

d Using Woodward Fischer rules Calculate the λmax of the following compounds: 5

i)



ii)



Q.3) Answer any two of the following: 10M

a What is Curtius rearrangement? Explain its mechanism. 5

b Explain Passerini reaction with its mechanism. 5

c Explain Dienone-Phenol rearrangement with suitable example. Explain its mechanism. 5

d What is Baylis-Hilman reaction? Explain its mechanism. 5

Q.4) Answer any two of the following: 10M

a Predict the number of signals and splitting pattern of the protons in the following molecules (PMR spectra): 5
i) t-butyl alcohol ii) Isopropyl alcohol

b Give the fragmentation pattern of the following molecules: 5
i) Pentanal ii) n-Butylbenzene

c An organic compound A (Molecular formula: $C_9H_{10}O_2$) exhibits the following spectral data: 5
IR: 1745cm^{-1}(s), 1225cm^{-1}(br, s), 749cm^{-1}(s), 697cm^{-1}(s)
^{1}H NMR = δ 1.96 (3H, s); 5.00 (2H, s); 7.22 (5H, s)
Deduce the structure of the compound.

d Explain the following with respect to NMR spectroscopy: 5
i) Karplus curve and its significance
ii) Spin-spin coupling

Q.5) Answer any FIVE of the following; **10M**

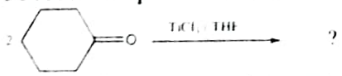
a Discuss in brief stability of enolate ions with suitable example. 2

b Explain the reaction of acetophenone with excess iodine and NaOH. 2

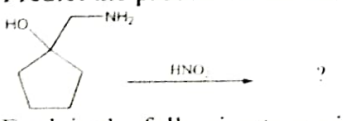
c Define hard and soft electrophiles. Give one example of each 2

d Explain the term combination bond w.r.t. IR spectroscopy 2

e Predict the product of the following reaction and give name of the reaction. 2



f Predict the product of the following reaction and give name of the reaction. 2



g Explain the following terms in mass spectrometry: 2
i) Base peak
ii) Isotopic abundance

h Why is TMS used as a reference standard in NMR spectroscopy? 2

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Paper / Subject Code: N562 /2 / Physical Chemistry-IV

msc – chem – sem II – NEP zero

[Time: 1hr] [Marks:25]

Please check whether you hav 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 scien ific calculator is allowed.

Useful constants

$c = 2.998 \times 10^{8}$ m.s^{-1}
$R = 8.314$ J.K^{-1}mol^{-1}
$= 2.0$ cal.K^{-1} mol^{-1}
$h = 6.626 \times 10^{-34}$ Js
$m_e = 9.110 \times 10^{-31}$ kg
$NA = 6.022 \times 10^{23}$ mol^{-1}

$e = 1.602 \times 10^{-19}$ C
$k = 1.3811$ x 10-23 J.K^{-1}
$1J = 6.24 \times 10^{18}$ eV
$1eV = 8.06 \times 10^{3}$ cm^{-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) Derive thermodynamically the Kelvin equation of vapour pressure of droplets 04
   ii) What is meant by the term excess functions? Write an expression for 04
   a) Excess entropy b) Excess enthalpy
   iii) What is ATP and draw its structure? How is ATP synthesized from ADP? 04
   iv) At NTP 16g of O_2 was mixed with 14g of N_2. Calculate Δ_{mix} G and Δ_{mix} S 04

2. A) Attempt ***any two*** of the following:
   i) Derive the parabolic rate law equation for the reaction of a gas on the surface of solid particles. 04
   ii) Discuss the kinetics of regulatory enzymes. 04
   iii) Derive Lineweaver-Burk and Eadie analysis of the rate data of enzyme catalyzed reaction. 04
   iv) An enzyme hydrolysed a substrate concentration of 0.02 mmol dm^{-3}, the initial rate was 1.7 x 10^{-3} mmol dm^{-3} min^{-1} and the maximum rate was 5.5 x 10^{-3} mmol dm^{-3}.min^{-1}. Calculate the Michaelis constant (K_m). 04

3. A) Attempt ***any three*** of the following:
   i) Derive an equation showing change in fugacity with respect to pressure 03
   ii) Write the postulates BET Adsorption isotherm. 03
   iii) Explain the structure of ATP molecule with diagram giving one example of biochemical reaction involving ATP. 03
   iv) Discuss the factors which affect the reactions in solid state. 03
   v) Derive an expression for the linear free energy relationship of reactions in solution. 03
   vi) Predict the effect of ionic strength on the rate constant for each of the 03

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following reactions.

i) $[PtCl_4]^{-2} + OH^- \rightarrow$ Product

ii) $[Cr(urea)_6]^{+3} + H_2O \rightarrow$ Product

iii) $Fe^{+2} + [Co(C_2O_4)_3]^{-3} \rightarrow$ Product

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