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

A. Mention any two applications of thermionic 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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(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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[Time: 1hr] [Marks:25]

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} | $k = 1.3811$ x 10-23 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}
$NA = 6.022 \times 10^{23}$ 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) Derive thermodynamically the Kelvin equation of vapour pressure of droplets 04
   ii) What is meant by the term excess functions? Write an expression for a) Excess entropy b) Excess enthalpy 04
   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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[Time: 2 hours] **[Total Marks: 50]**

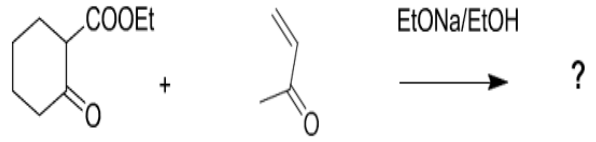
Please check whether you have the right question paper.

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**

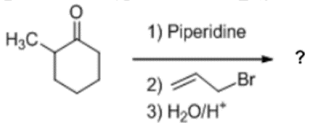
b Predict the products and give the mechanism of the following reaction **5**



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

d Complete the following reactions: **5**

1.



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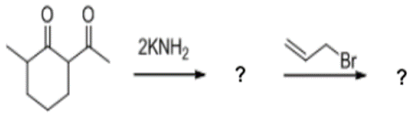
2.

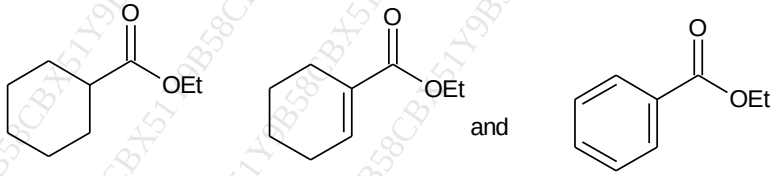


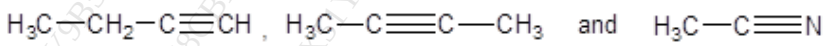
Q.2) **Answer any two of the following:** **10M**

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**

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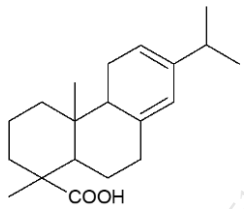
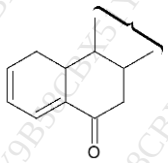
d Using Woodward Fischer rules Calculate the λmax of the following compounds: **5**

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)
^1H 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

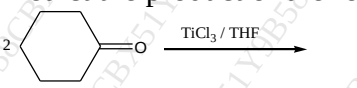
a Discuss in brief stability of enolate ions with suitable example. **2**

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

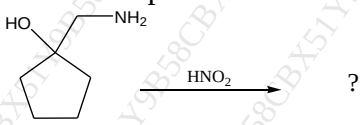
c Define hard and soft electrophiles. Give one example of each **2**

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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