[Time: 2 and 1/2 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 (A)	Attempt any **two** of the following:		
(a)	Derive expressions for the wave function of sp^3 hybrid orbitals using the concept of hybridization.		4
(b)	Explain the bonding in SF_6 molecule on the basis of molecular orbital theory. Draw the molecular orbital diagram showing the distribution of electrons in various molecular orbitals.		4
(c)	What is resonance energy? Draw all possible resonating structures for nitrate ion. Calculate the formal charges for all the atoms in the ion.		4
(d)	What are van der Waals forces? Discuss any two types with suitable examples.		4
(B)	Attempt any **one** of the following:		
(a)	On the basis of Valence Bond Theory, explain the structure and bonding of ClF_3 and PF_5.		4
(b)	Construct a labelled molecular orbital diagram of Vanadium molecule. Explain the magnetic behaviour of the molecule.		4
Q.2 (A)	Attempt any **two** of the following:		
(a)	Construct character table for H_2O point group		4
(b)	On the basis of SALC, draw Molecular Orbital diagram for ammonia molecule.		4
(c)	Define subgroups. Give subgroups of C2v point group.		4
(d)	Derive the matrix representation for rotational operation.		4
(B)	Attempt any **one** of the following:		
(a)	Discuss the criteria for a set of elements to form a group by giving suitable example.		4
(b)	Write a short note on irreducible representations.		4
Q.3 (A)	Attempt any **two** of the following:		
(a)	Describe the properties of conductors and semiconductors on the basis of Band theory.		4
(b)	Explain Langmuir-Blodgett method of preparation of nanomaterials.		4
(c)	Draw the structure of Rutile compound. State the features of the structure.		4
(d)	What are the principles underlying ceramic method and precursor method for preparation of inorganic solids?		4
(B)	Attempt any **one** of the following:		
(a)	Comment on concept of First Brillouin zone in solids.		4
(b)	Schematically represent formation of bands in solids using Band Theory.		4

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Q.4A)	Attempt any **two** of the following:	
(a)	State the Jahn Teller theorem. Discuss the interpretation of ESR Spectra of octahedral complex of Cu (II).	4
(b)	With respect to complex formation, explain the following evidence: 1) pH metric study. 2)dissolution of insoluble precipitate	4
(c)	Draw the orgel diagram for the complex ion $[CrF_6]^{3-}$ and assign the electronic transitions.	4
(d)	"The measurement of molar conductance of aqueous solution of cobalt amines compounds helps Werner to assigned correct formulae. Justify the statement.	4
(B)	Attempt any **one** of the following:	
(a)	Describe the potentiometric method for determination of formation constant in complexes.	4
(b)	Draw the Orgel diagram for $[Ni(H_2O)_6]^{2+}$. Assign the electronic transitions.	4
Q.5	Attempt any **four** of the following:	
(A)	Draw the Lewis dot structure of SCN- ion. Give all possible resonating structure and calculate the formal charge. Predict the most stable structure.	3
(B)	HF has a smaller heat of vaporization than water. Explain.	3
(C)	Explain group multiplication table for water molecule.	3
(D)	Define group, sub group and point group with example.	3
(E)	Define the terms : 1. Forbidden gap 2. Fermi Energy 3.Semiconductor	3
(F)	Give merits and demerits of microwave method in preparation of nanomaterials.	3
(G)	^{31}P NMR spectra shows 1 peak for trans $[PtClBr(PR_3)_2]$ & 2 peaks for the cis $[PtClBr(PR_3)_2]$. Justify.	3
(H)	Write a note on Racah parameter.	3

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[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}	$k = 1.3811$ 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
$m_e = 9.110$ x10^{-31} kg	$1eV = 8.06 \times 10^{3}$ cm^{-1}
$N_A = 6.022 \times 10^{23}$ mol^{-1}	1 amu = 1.66×10^{-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 x 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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2. B) Attempt ***any one*** of the following:

i) A hockey ball of mass 0.2 kg moving with a velocity of 3 x10^3 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, A and 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 4

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

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

4. 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

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

i) Calculate the mean ionic activity coefficient of $AlCl_3$ in aqueous solution containing 0.02m $AlCl_3$ and 0.04m KCl at 298K. (Given: A = 0.509 at 298 K) 4

ii) Calculate the resting membrane potential for the following: 4

Ion Species	Intracellular concentration in mM	Extracellular concentration in mM
K^+	0.0002	5
Na^+	250	10

(Given that $\frac{2.303RT}{F}$ at $298K = 61$)

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

a) Derive the following Maxwell's relation, $\left[\frac{\partial T}{\partial V}\right]_S = -\left[\frac{\partial P}{\partial S}\right]_V$ 3

b) Standard molar entropies depend upon structure of the substance. Give reason. 3

c) What is Hermitian operators? 3

d) Write a note on magnetic quantum number. 3

e) Explain three explosion limits of H_2 and O_2 reaction. 3

f) Explain the principle of microscopic reversibility. 3

g) What is fuel cell? Write any two applications of phosphoric acid fuel cell. 3

h) Write Debye-Huckel-Onsager equation and explain its validity for aqueous solutions. 3

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[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 (A)	Attempt any **two** of the following:	
(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: I) Detection and trapping of intermediate. II) Stereo-chemical evidence.	4
(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 (A)	Attempt any **two** of the following:	
(a)	Give the AAL^1 mechanism for ester hydrolysis with suitable example.	4
(b)	Explain the following term with a suitable example. i) Tele Substitution ii) Ambident nucleophiles	4
(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 i) Comparative reactivity of 1-Bromopropene and 3-Bromopropene to SN^1 reaction. ii) Comparative nucleophilicity of methoxide and t-butoxide ion.	4
(B)	Attempt any **one** of the following:	
(a)	Explain the mechanism of nucleophilic substitution on 4-Nitrochlorobenzene	4
(b)	Write a short note on i) Homoaromatic compound ii) Antiaromatic compound	4
Q.3 (A)	Attempt any **two** of the following:	
(a)	Explain the chirality of spiranes. Write the structure of pair of enantiomeric spiranes with their configurational descriptors.	4

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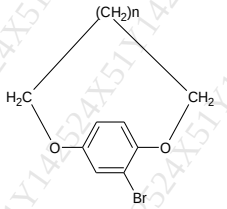
(b) Explain the stereochemistry of tri and tetra coordinated sulphur compounds. 4

(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 4

1) Simple Axis of Symmetry

2) Plane of Symmetry

(b) Explain the following with suitable example 4

1) *Syn and Anti* System.
2) Erythro and Threo System

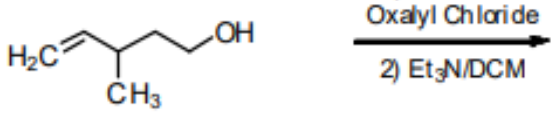
Q.4A) Attempt any **two** of the following:

(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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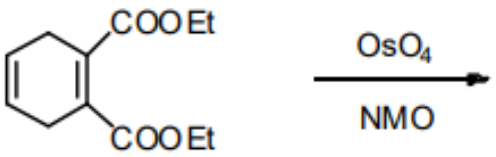

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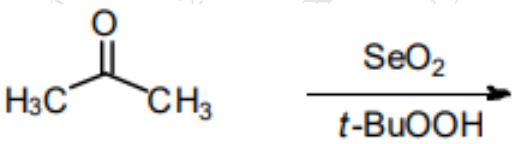

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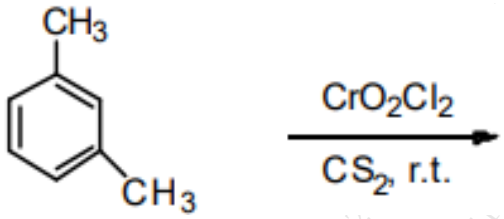
iv)



(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.

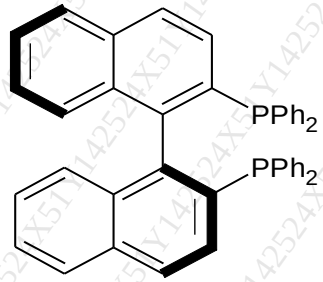
(C) Explain the aromaticity of Pyrrole. 3

(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)



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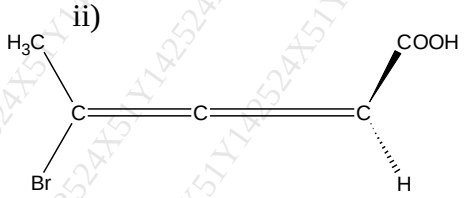

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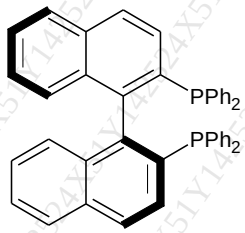
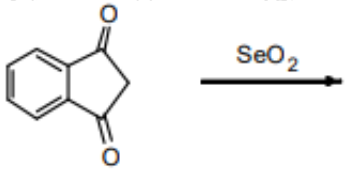


(G) Complete the following reactions. 3

i)



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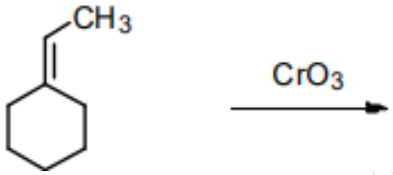
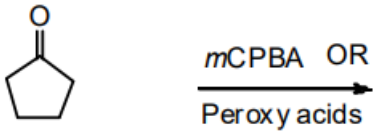
ii) 

iii) 

(H) What is Collin's reagent? Give one application. 3

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TIME: 2 ½ HOURS **MAX.MARKS:60**

NB:

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: 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 , Ag = 108 , Mn = 55**

Q 1 A	Attempt **any two** of the following:		
a.	What are determinate errors? How to minimize determinate errors?		4
b.	Describe the calibration curve method for quantitative analysis of unknown sample.		4
c.	What are OECD principles of Good Laboratory Practices?		4
d.	What is six sigma approach for total quality management? Explain.		4
Q 1 B	Attempt **any one** of the following:		
a.	Write note on cost and benefits of introducing quality system.		4
b.	Explain the figure of merits in analytical determination.		4
Q 2 A	Attempt **any two** of the following:		
a.	i.	Solid AgCl is dissolved in water at 25°C. Its solubility is 1.43 x 10^{-3}g /dm^3. Calculate the solubility product (K_{sp}) of the compound.	4
	ii.	Calculate the amount of succinic acid required to prepare 250 cm^3 of a 0.1 N solution of succinic acid in water.	
b.	100 g of Na_2CO_3 reacts with 100 g of HCl. Which is the limiting reagent. Calculate the amount of NaCl formed, in moles and in grams.		4
c.	A buffer solution was prepared by mixing 0.05 mole of Formic acid with 0.06 mole of sodium formate in distilled water to make 1 dm^3 solution. Calculate the pH of the solution. Given Ka for formic acid is 1.8 x 10^{-4}.		4
d.	Determine the mole fraction of both the substances, when 45 g of acetone is mixed with 55 g of methanol.		4
Q 2 B	Attempt **any one** of the following:		
a.	Calculate the weight of compound required to prepare 500 cm^3 of a 50 ppm K^+ solution using (i) KCl (ii) KNO_3		4
b.	25 cm^3 of a solution of $Ba(OH)_2$ required 45.8 cm^3 of 0.25 M HCl for complete neutralization. i. Write the equation of the reaction. ii. What is the molarity of the $Ba(OH)_2$ solution.		4

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Q3 A Attempt **any two** of the following:

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

b. Discuss the fiber optics used in optical instruments. 4

c. Derive Beer Lambert's law and state its limitations. 4

d. Explain: 4

i. Optical arrangement of a dual wavelength spectrophotometer.

ii. Photoconducting transducers used in IR spectrometer.

Q 3 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}**	**0.666**	**0.180**
Q	**7.2×10^{-3}**	**0.130**	**0.874**
P + Q	-------	**0.440**	**0.412**

Calculate the molar concentration of A and B.

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

b. Discuss the instrumentation of power compensated DSC. 4

c. What is an automatic titrator? Write the advantages of using automatic titrator. 4

d. Describe the application of flow injection analysis for the colorimetric estimation of chloride. 4

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

a. Discuss the factors affecting the DSC curves. 4

b. What are thermal methods? Discuss the principle of heat-flux DSC. 4

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Q5 Attempt **any four** of the following:

a.	Discuss the types of quality standards for quality systems in laboratories.	3
b.	Define: 1. Determination 2. Protocol 3. Analysis	3
c.	Determine oxidation number of Cl in (i)$Ca(ClO_2)_2$ (ii) $KClO_3$ (iii) Cl_2	3
d.	Calculate the amount of $K_2Cr_2O_7$ that is required to prepare 1dm^3 of a 100 ppm solution with respect to Cr^{+6}. How much volume of this solution will be required to prepare 5 dm^3 of a 100 ppb solution?	3
e.	What is diffuse reflectance spectroscopy? Explain the diffuse reflectance spectrum.	3
f.	What are the major advantages of an FTIR spectrometer compared with a dispersive instrument?	3
g.	Differentiate between TGA and DTA.	3
h.	Describe what quantity is measured and how the measurement is performed for each of the following techniques: TGA, DTA and DSC.	3

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