2009

M.Sc. Part–II Examination

CHEMISTRY

PAPER—V

Full Marks : 75

Time : 3 Hours

The figures in the right-hand margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Illustrate the answers wherever necessary.

(Physical Special)

Answer any *five* questions taking at least *two* from each group.

Group—A

1. (a) (i) Define (1) Absolute error, (2) relative percentage error.

(ii) Round-off the following number to three significant figures : 0·03258. $1\frac{1}{2}+1\frac{1}{2}+2$

(b) Let x_T and x_A denote respectively the true and approximate values of a number. Find the absolute error, relative error and percentage error in x_A when

$x_T = \frac{1}{3}$, $x_A = 0{\cdot}333$. 5

(c) Evaluate f(3·8) using 5

x	0	1	2	3	4
f(x)	1	1·5	2·2	3·1	4·3

(Turn Over)

2. (a) Derive the matrix representations of $\hat{L}_x$ and $\hat{L}_y$ operators using $l = 1$ for the basis function. 5+5

(b) Find out the eigen values and eigen vectors of the matrix $\begin{bmatrix} 7 & -3\sqrt{3} \\ -3\sqrt{3} & 13 \end{bmatrix}$. 5

3. (a) Find out the normalised eigen function of $\hat{S}_x$ and $\hat{S}_y$ operators. 4

(b) Derive the expression for $\hat{S}^2 D$. 6

(c) Write a note on branching diagram. 5

Or

(a) What is interpolation? Establish Newton's forward interpolation formula. 7

(b) Solve by Gauss Elimination method : 8

$$\begin{aligned} x_1 - x_2 - x_3 &= 1 \\ 2x_1 - 3x_2 + x_3 &= 1 \\ 3x_1 + x_2 - x_3 &= 2 \end{aligned}$$

4. (a) Show that $K_{ij} \le J_{ij}$. 5

(b) Derive Roothaan's equation in matrix form FC = SCE the terms having the usual meaning. 10

5. (a) For a given value of internuclear distance R(a.n) derive the overlap integral (S_{ab}) between two H-atoms (a, b). Given $1S_a = \frac{1}{\sqrt{\pi}} c^{-r_a}$, $1S_b = \frac{1}{\sqrt{\pi}} c^{-r_b}$. 6

(b) Using Hückel theory for heteromolecules verify that in formaldehyde the CO polarity is C^-O^+ in the π^{2*} state. 9

Group—B

6. (a) State and prove Eckart's theorem for the ground state. 5

(b) Derive the general expression for the Hückel MO's and energies in linear polyenes by analytical method. Apply the method to calculate the ground state energy of allyl radical. 10

Or

Starting from the expression for energy associated with a closed shell atom of 2N electrons using a single determinantal wavefunctions, obtain the Hartree-Fock equation in the pseudo-eigen value form. 15

7. (a) Describe the steps involve to obtain the symmetries of the vibrational modes of a linear molecule using sub-group method.

(b) Use both cartesian and internal co-ordinate system to obtain the symmetries of vibrational modes in ML_5. Comment on your result. 5+10

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_{v'}$			
A_1	1	1	1	1	1	z		x^2+y^2, z^2
A_2	1	1	1	−1	−1	R_z		
B_1	1	−1	1	1	−1			x^2-y^2
B_2	1	−1	1	−1	1			xy
E	2	0	−2	0	0	(x, y)	(R_x, R_y)	(xz, yz)

8. (a) Use group theoretical principle to find the Raman and IR activity of the vibrational modes of NH_3. 10

C_{3v}	E	$2C_3$	$3\sigma_v$				
A_1	1	1	1	z		x^2+y^2, z^2	
A_2	1	1	−1	R_z			
E	2	−1	0	(x, y)	(R_x, R_y)	(x^2-y^2, xy)	(xz, yz)

(b) Write a short note on tetragonal distortion in octahedral complexes. 5

9. (a) Write short note on superconductor. 6

(b) Find out the concentration of Frenkel defect in crystal. 5

(c) How would you identify a face centred cubic lattice by calculating geometrical structure factor. 4

10. (a) Discuss the mechanism of the formation of V-centre with a suitable example. 5

(b) Find out the conditions for occuring maximum diffraction according to the theory of Von-Laue. 10

(Inorganic Special)

Answer any *five* questions taking at least *two* from each group.

Group—A

1. (a) Establish the relation

$$\vec{\mu}_l = \sqrt{l(l+1)}\left(\frac{eh}{4\pi mc}\right)$$

where the terms are of their usual meaning. 5

(b) Proof that the energy difference between two successive J levels is the product of λ and large of the two J values. (Where the terms are of their usual meaning) 6

(c) Explain why the bis (diazoaminobenzenato) Copper (II) is diamagnetic. 4
(diazoaminobenzene = $C_6H_5 - NH - N = N - C_6H_5$)

2. (a) How would you monitor acid hydrolysis of $[Cr(NH_3)_5S_2O_3]^+$ in presence of 0·05M $HClO_4$? 5

(b) Outline the Salient features of "Marcus Theory". 5

(c) Explain "Ray-Dutt" mechanism of racemization. 5

3. (a) What is Koopman's theorem? 3

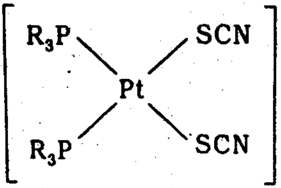
(b) The compound $PFCl_4$ can exist in two isomer, NQR spectroscopy predicts one of them in solid state. Discuss. 3

(c) How many peaks are observed in ^1H NMR of BH_4^-. Explain. 5

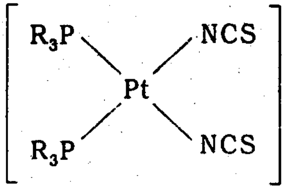
(d) ^{31}P resonance P_4S_3 consists of two peaks with intensity ratios of 3:1. The more intense peak is a doublet and the less intense is a quadruplet. Predict the structure of P_4S_3 from the above informations. 4

4. (a) Which of the following is the most likely structure for pentacyanocobalt (III)-μ-cyanopentaamminecobalt (III).
$[(NH_3)_5Co—CN—Co(CN)_5]$ or $[(NH_3)_5Co—NC—Co(CN)_5]$
Why? 3

(b) Which one of the following [(A) or (B)] is more stable and why? 3



(A)



(B)

(c) Draw all possible isomers of [Co(Br)(CN)(Cl)(NH_3)(en)]. 4

(d) The hydrated chromium chloride that is available commercially has the overall composition $CrCl_3.6H_2O$. On boiling a solution, it becomes violet and has a molar electrical conductivity similar to that of $[Co(NH_3)_6]Cl_3$. In contrast $CrCl_3.5H_2O$ is green and has a lower molar conductivity in solution. If a dilute acidified solution of the green complex is allowed to stand for several hours, it turns violet. Interpret these observations with structural diagrams. 3

(e) What do you mean by "polytopal isomerism"? 2

5. (a) Use group theoretical principal to find the state of hybridization of the central metal atom in $[Co(NH_3)_6]^{3+}$. 6

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1		
E_g	2	−1	0	0	2	2	0	−1	2	0		$(2z^2-x^2-y^2)$ (x^2-y^2)
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	R_x, R_y, R_z	
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1		(xz, yz, xy)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	−1	−1	1	−1	1	−1	−1	1		
E_u	2	−1	0	0	2	−2	0	1	−2	0		
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1		

(b) Construct the sigma bonding LGO, MO and the MO energy level diagram of the complex $[Co(NH_3)_6]^{3+}$. 9

Group—B

6. (a) What do you mean by "multiplet width" ? Deduce the expression for the magnetic moments for the cases where the "multiplet width" is large as compared to kT. 1+8

   (b) Show superexchange phenomenon through sigma and π-overlap. 3

   (c) What is the utility of Pascal's constants ? 3

7. (a) Starting from tetrachloroplatinate ion, how would you prepare various isomeric forms of $[Pt\,Cl\,Br(NH_3)_2]$? Give outline only. 5

   (b) Explain "Trans-effect" and "Trans-influence". 5

   (c) Write a note on "isotopic effect" on reaction rates. 5

8. (a) What is dpph ? Why it is used as a standard in esr experiment ? 3

   (b) How many lines are expected from the esr spectrum of (i) $\dot{C}H_3$; (ii) napthyl radical ? 3+3

   (c) Octahedral Ni(II) complex are often found to be esr inactive, while Ni(III) complexes always show esr spectra. Explain. 6

9. (a) Predict the ^{19}F NMR spectrum of SiF_6^{2-}. 4

   (b) Explain fluxional behaviour of $B_3H_8^-$ by ^{11}B NMR. 4

   (c) The chemical shift of Mössbaure spectra mainly affected by electron density at concerned nucleus. Explain with proper example. 4

   (d) What is Doppler effect in Mössbaure spectroscopy ? 3

10. (a) Use both cartesian and internal co-ordinate system to obtain the symmetry of vibrational modes in Cis-ML_4X_2. Comment on your results. 8

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

(b) Use group theoretical principle to find the IR and Raman activity of the vibrational modes of H_2O. 7

(Organic Special)

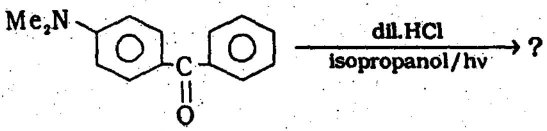
Answer any *five* questions
taking at least *two* from each group.

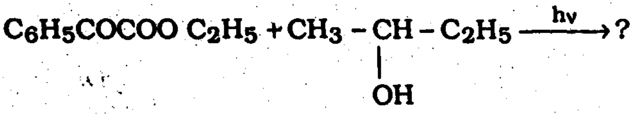
Group—A

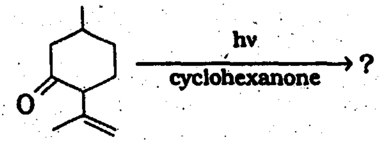
1. (a) Quantum yield for benzpinacol formation is 1. How can this information be used for elucidation of the mechanism of the reaction? 4

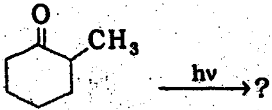
(b) Explain the following statements :
"Benzophenone undergoes photoreduction in presence of isopropanol but Michler's Ketone does not absorb under the same condition." 5

(c) Predict the product/s of the following reaction with mechanism (attempt any *three*) : 3×2

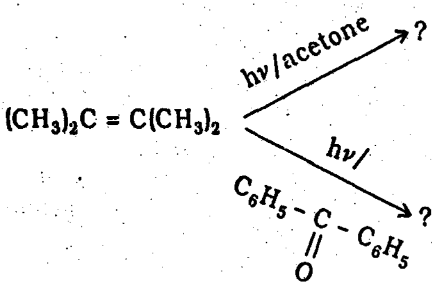
(i) 

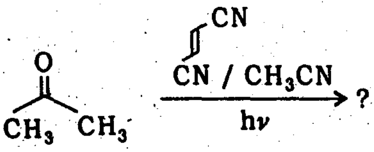
(ii) 
$C_6H_5COCOO\,C_2H_5 + CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-C_2H_5 \xrightarrow{h\nu} ?$

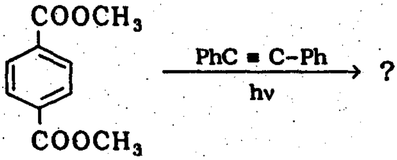
(iii) 

(iv) 

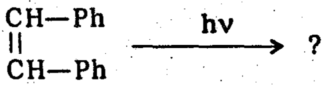
2. (a) What is Paterno-Büchi addition reaction ? Explain the reaction with suitable example and also predict the product of the following vecutin with mechanism, (attempt any *two*) : 3+(3×2)

(i) 

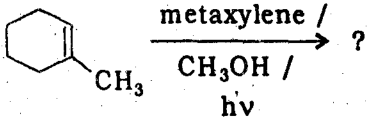
(ii) 

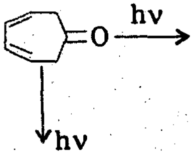
(iii) 

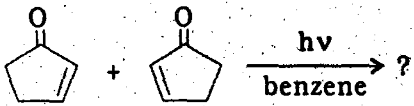
(b) Predict the product/s of the following reactions (attempt any *three*) : 3×2

(i) 

$$\begin{matrix}\text{CH—Ph}\\ \|\\ \text{CH—Ph}\end{matrix} \xrightarrow{h\nu} ?$$

(ii) 

(iii) 

(iv) 

3. (a) Upon subjecting both the *threo-* and *erythro-* isomer of 3-phenyl-2butyl tosylate to acetolysis, the former gives racemic and the latter chiral acetate. How does this phenomenon is explained in terms of the formation of a phenonium ion intermediate? How does the formation of phenonium ion is established from the curved Hammett plot obtained upon plotting the logarithms of rate constants of the acetolysis of 3-aryl-2-butyl brosylates against the *sigma-* values of the substituents on the aromatic ring. 9

(b) Why the *rho-* value for the ionization of substituted benzoic acid in ethanol is twice its value in water? 3

Or

Explain why the negative slope of a Hammett plot should indicate that the reaction is facilitated by electron donation by the substituents and a positive slope would indicate that the reaction is facilitated by electron withdrawal. 3

(c) How are *sigmazero* value of substituents are calculated ? What are the difficulties in using these values ? 3

Or

How are *sigma I* values of substituents are calculated.

4. Answer any *three* of the following questions : 3×5

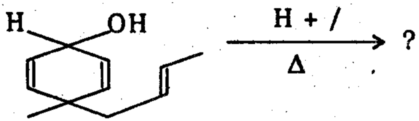
(a) Explain why alkaline hydrolysis of ethyl esters of benzoic acids carrying *meta-* and *para-* substituents gives a linear Hammett plot but the hydrolysis of the same esters with 99.99% H_2SO_4 gives a non-linear Hammett plot.

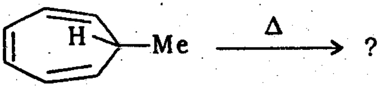
(b) What is the conceptual basis of Yukawa-Tsuno equation ?

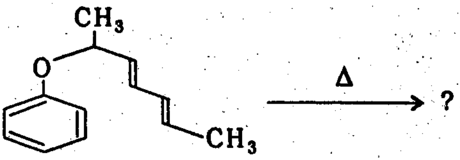
(c) Explain why a curved Hammett plot is obtained when the logarithms of rate constants of semicarbazone formation at pH4 of substituted benzaldehydes are plotted against the *sigma* values of the substituents.

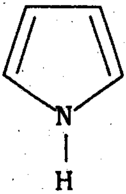
(d) Explain why the points due to *p*-NMe_2 and *p*-OMe deviate from the linear Hammett plot obtained when rate constants of the solvolysis of *t*-cumyl chlorides are plotted against the *sigma*-values of the substituents present in the aromatic ring.

5. (a) What is sigmatropic reaction of i, j shift ? Explain with examples. Hence predict the products of the following reaction, indication frontier orbital interactions, (attempt any *two*) : 3+(3×2)

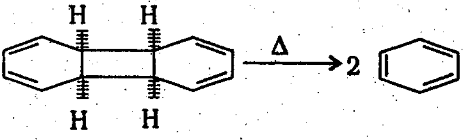
(i) 

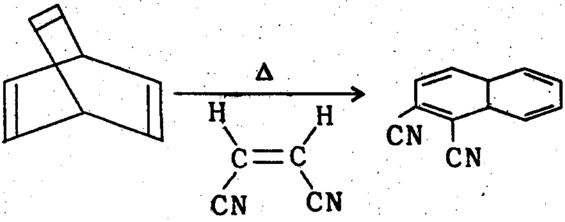
(ii) 

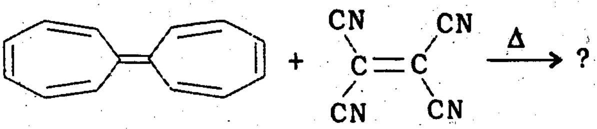
(iii) 

(iv)  $+ \text{EtOOC}-C\equiv C-\text{COOEt} \xrightarrow{h\nu} ?$

(b) Carry out the following conversions with mechanism (attempt any *two*) : 3×2

(i) 

(ii) 

(iii) 

Group—B

6. (a) Complete the following reaction sequence based on explanation in terms of stereoelectronic and steric effects, wherever necessary. 7

$$\text{1 – Benzoylcyclohexene} \xrightarrow{\text{PhMgBr}} (A) + (B) \xrightarrow{Ac_2O} ?$$

$$(A) + (B) \xrightarrow{H_3O^+} (C) \xrightarrow[80^\circ C]{Br_2 + AcOH} ?$$

(b) Deduce from the first principle the Curtin-Hammett principle (taking help of a potential energy diagram) for a case where the less stable conformer gives rise to the predominant product. Illustrate with an example. 8

7. (a) Write correctly the conformations of perhydrodiphenic acid diastereomers and explain their relative stability. Outline the stereochemical reasoning leading to the relative stereochemistry of those with transoid backbone configuration. 8

(b) By application of Octant rule predict and designate the absolute configuration of the chiral centres of (+)-*trans*-9,10-dimethyl-2-decalone which shows positive Cotton effect. What changes would you observe in the ORD curves of its epimeric 1-bromo derivatives? 5+2

8. Answer any *three* of the following : 5×3

(a) Elucidate the absolute configuration of the following compounds by application of the relevant rules. Attempt any *two* :

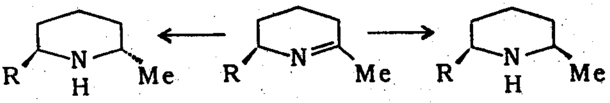
(i) (–)-1-Bromo-3-methylallene.

(ii) (+)-α-Chloro butyric acid.

(iii) Pentahelicene showing +CE in the CD spectrum.

(b) Explain the formation of the diastereomers obtained by the $NaBH_4$ reduction of cholestan-2-one with the help of the *Felkin model* of the transition state. Give the approximate percentages of the diastereomers formed.

(c) How were the following conversions done? Explain in terms of steric and stereoelectronic effects involved. Indicate the natural product, and write its name.



$R = n - C_{11}H_{23}$

(d) Predict the sign of the Cotton effect that the following steroid derivative will exhibit in its CD spectrum. Name the rule you have apply ; show the nature of the CD curve, the units of the two axes, and the position of the λmax.

1α, 2β-Dibenzoyloxycholestane

(e) (i) How can you effect *complete* conversion of the more stable diastereomer of 2-ethyle-4-*t*-butylcyclohexanone into the less stable one. Explain.

(ii) Comment on the relative stability of the conformers of 1, 4-diphenyl-*cis*-6-methylcyclohexene.

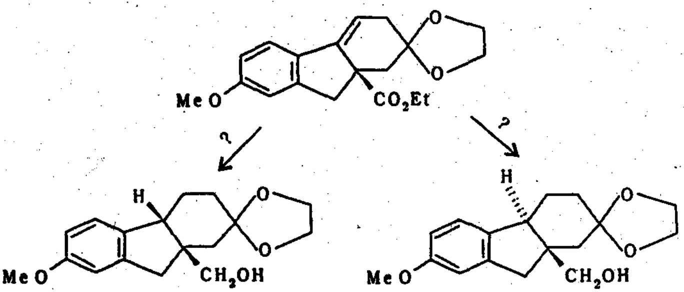
9. (a) Write down the flipped conformers of 9(*R*), 10(*S*)-9-mythyl-*cis*-2-decalone(A). Find out the signs of the torsion angles of the ring junctions directly from the conformations (by application of a relevant rule), and hence label the steroid and nonsteroid forms. Explain why the forms are named so. 2+2+2

(b) Assuming that the steroid conformation is the predominant one, predict the sign of the cotton effect that compound(A) will exhibit, after finding out the sign of the Cotton effect that each conformer will exhibit, by application of the octate rule. 5

(c) Upon kinetically controlled bromination with bromine in acetic acid *cis*-2-decalone forms predominantly the axial 1-bromo derivative—explain this fact in terms of the mechanism and steric strains involved. 4

Or

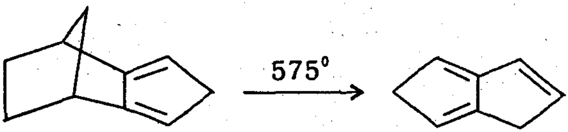
How do you achieve the following transformations :



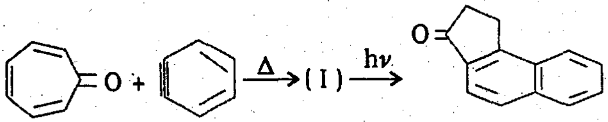
4

10. (a) Suggest machanisms of the following reactions and explain. 2+3

(i)

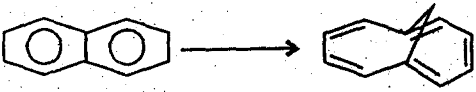


(ii)

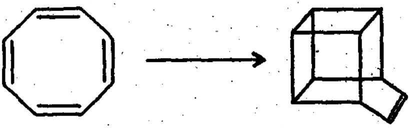


(b) Synthesise the following compounds using at least one pericyclic reaction at one of the steps : 3+3

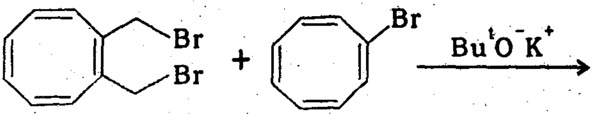
(i)



(ii)



(c) Write structure of (II) and explain : 3



$\xrightarrow{Bu^tO^-K^+}$ $C_{18}H_{14}$ (II)

(d) What is meant by Tandem reaction ? Cite an example. 1