M.Sc. 4th Semester Examination, 2011

CHEMISTRY

(*Inorganic Special/Organic Special/ Physical Special*)

PAPER—CH-2201

The figures in the right-hand margin indicate marks

(*Inorganic Special*)

Full Marks : 40

Time : 2 hours

Answer any **four** questions

1. (*a*) "Materials having no permanent magnetic dipoles are called antiferro-magnetic." Justify or criticize. 3

   (*b*) Explain the terms "susceptibility" and "permeability" in magnetism. 2 + 2

   (*c*) Explain the diamagnetic nature of the bis(diazoaminobenzenato) copper (II) complex. 3

(*Turn Over*)

2. Derive Curie equation. State the conditions to obey Curie law. 8 + 2

3. (*a*) How enthalpy and entropy of activation of a substitution reaction provide useful information about the mechanism? 4

(*b*) Write down the Marcus-Hush relation for the cross reaction given below with proper significance of the terms involved: 6

$$[Fe(CN)_6]^{4-} + [Mo(CN)_8]^{3-} \rightarrow [Fe(CN)_6]^{3-} + [Mo(CN)_8]^{4-}$$

4. Derive classical theory of diamagnetism (Langevin theory). 10

5. (*a*) Rate constants and entropy of activation values for substitution reaction of $[Ru(H_2O)_6]^{3+}$ are given below:

Entering ligand	Rate constant ($M^{-1}S^{-1}$)	Entropy of activation ($J\ mol^{-1}\ k^{-1}$)
Imidazole	1860	–20
SCN^-	270	–18
CH_3CN	30	–24

(*Continued*)

How the above data provide an idea about the mechanism of substitution reaction? 4

(*b*) Explain the mechanism of outer sphere electron transfer for the $[Ru(NH_3)_6]^{2+}/[Ru(NH_3)_6]^{3+}$ system. 6

6. (*a*) What are paramagnetic and diamagnetic materials? Give examples. Discuss the temperature variation of paramagnetic and diamagnetic susceptibility of materials. 5

(*b*) Write short note on "Spin-orbit interaction". 5

7. (*a*) Write down the pseudo first order rate equation for the following reaction: 4

$[Pt(biPy)(Cl)_2] + Py \rightarrow [Pt(biPy)(Py)(Cl)]^+$
(biPy = 2, 2′ bipyridine).

(*b*) Write down the plausible mechanism of the following reactions: 6

$$\textit{trans}\text{-}[Pt(en)_2(Cl)_2]^{2+} + {}^*Cl^- \longrightarrow \textit{trans}\text{-}[Pt(en)_2({}^*Cl)(Cl)] + Cl^-$$

(*Organic Special*)

Full Marks : 40

Time : 2 hours

Answer any five questions taking at least two from each Group

GROUP – A

1. Acetolysis of *threo* 3-phenyl-2-butyl tosylate gives racemic product, while the *erythro* isomer of the same compound gives chiral acetate. How does the above observation can be accounted for in terms of a phenonium ion intermediate? How does the formation of phenonium ion is established from the curved Hammett plot obtained upon plotting of the logarithms of the titrametric rate constants of the acetolysis of 3-aryl-2-butyl brosylates against the *sigma* values of the substituents on the aromatic ring? 8

2. (*a*) Reaction of diphenylmethyl chloride with ethanol has a *rho* value of –5·09. How does it help to choose between the two alternative mechanistic pathways that this reaction might follow? 4

(*b*) Why a curved Hammett plot is obtained when the logarithms of rate constants of semicarbazone formation of substituted benzal dehydes at pH_4, are plotted against the *sigma* values of the substituents. 4

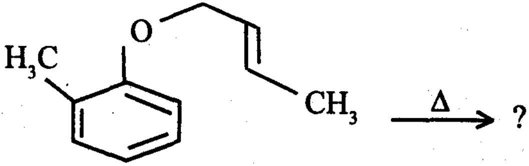
3. How are *sigma I* values of substituents are calculated ? In the base-induced dehydrobromination of aryl ethyl bromides, a good linear correlation is obtained only when *sigma minus* values of the substituents on the aromatic ring are used account for the above observation. 3 + 5

4. (*a*) Write down the modified version of Yukawa - Tsuno equation. The $r^{+/-}$ values of the Yukawa - Tsuno equation for the solvolysis of *t*-cumyl chloride in 90% aqueous acetone and acetolysis of neophyl brosylate are 1·00 and 0·54 respectively. What light do these values throw on the two transition states ? 4

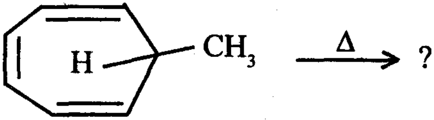
(*b*) What is the difference in the methods of separation of polar and mesomeric effects of substituents by extended Hammett approach and dual substituent parameter approach ? 4

5. (*a*) What is *i*, *g* shift in sigmatropic reaction and hence predict the product/s of the following reactions indicating frontier orbital interactions (attempt any *two*) : 1 + 2 × 2

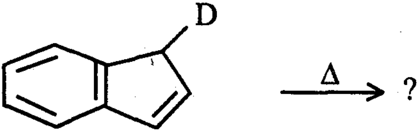
(*i*)



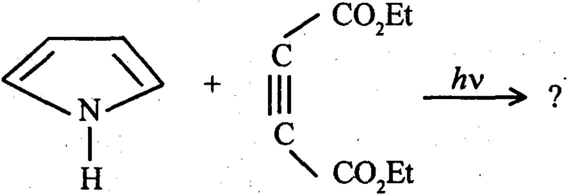
(*ii*)



(*iii*)



(*b*) What is supra and antara mode in cycloaddition reaction and hence predict the product of the following reaction ? 1 + 2



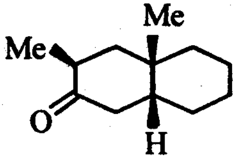
GROUP – B

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

7. (*a*) Draw the two conformers of *cis-cisoid-cis*-perhydrophenanthrene. Comment on its optical activity, and its relative enthalpy ($\Delta\Delta H^{\circ}$) with respect to the *trans-transoid-trans* isomer. 4

(*b*) Explain with the help of the Felkin model of the transition states the formation of the diastereomers obtained by the $NaBH_4$ reduction of cholestan-2-one, and justify the approximate percentages of the diastereomers formed. 4

8. Predict the sign of the Cotton effect that the steroid form of the compound (1) and its epimeric 1-bromo derivatives would exhibit. Name the compound mentioning the absolute configuration of its chiral centers. Why compound (1) possesses an anancomeric conformation. 6 + 1 + 1



(1)

9. (*a*) Elucidate the absolute configuration of the following compounds by application of the relevant rules. Name. Answer any *two* : 3

(*i*) (+)-2-Bromobutanoic acid

(*ii*) (+)-1-Bromo-1-phenyl-3-methylallene

(*iii*) (–)-Pentahelicene.

(*b*) Predict the sign of the Cotton effect that 6β, 7β-dibenzoyloxycholestane would exhibit. Show the nature of the CD curve, the units of the two axes and the position of the λ_{max}. Who discovered the rule that you are applying here ? 5

10. (*a*) Explain why the points due to *p*-NO_2 and *p*-CN deviate from the linear Hammett plot when the pK_a values of the substituted phenols are plotted against the *sigma*-values of the substituents ? 4

(*b*) Explain the terms *m* and *Y* in Grunwald-Winstein equation. Why is the equation more successful in dealing with solvent effects in reactions that follow S_N1 mechanism in comparison to those that S_N2 follow S_N2 mechanism ? 4

(*Physical Special*)

Full Marks : 40

Time : 2 hours

GROUP – A

Answer any one of the following

1. (*a*) Is there any basic difference between variation principle and perturbation theory ? Discuss briefly about the same. 5

(*b*) Any trial function is not suitable for variational calculation. Show with derivation the same for the ground state. 5

2. Calculate the ground state energy of Helium atom using the variational principle. 10

Or

Consider the $^1P_1$ state of Helium atom and discuss how the degeneracy is lifted by the application of a magnetic field in the *Z*-direction as a perturbation.

GROUP – B

Answer any **one** of the following

3. Apply Hückel theory to calculate the MO's and MO energies of butadine in the ground state. 10

4. Discuss the basis for π-electron approximation for molecules containing both sigma and pi-electrons. 10

Or

How the MO's and MO energies of hetero molecules containg π-electrons on the hetero atoms are calculated by Hückel theory taking formaldehyde as an example? 10

GROUP – C

Answer any **one** of the following

5. (*a*) Derive the expression for occurring diffraction maxima according to Laue's diffraction method. 7

(*b*) What is a diode and how does it work? 3

6. (*a*) Between atomic scattering factor and geometrical structure factor which one is better for determination of crystal structure and why ? 5

(*b*) What is 'V_2' centre and narrate the mechanism of formation of a V_2 centre using a suitable example ? 5

GROUP – D

Answer any **one** of the following

7. (*a*) Obtain the symmetry of vibrational modes of ammonia. 5

(*b*) Use group theory, to justify the IR and Raman activity of the vibrational modes of ammonia. Following is the character table of C_{3v} point group. 5

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	$(X, Y), (R_X, R_Y)$	$(X^2-Y^2, XY), (XZ, YZ)$

8. Sketch the MO diagram of formaldehyde. Use group theoretical principle to justify, which one of the following transition in formaldehyde is electronically allowed.

$$n \rightarrow \pi^* \ , \quad \pi \rightarrow \pi^*$$

Following is the character table of C_{2v} point group: 2 + 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