M.Sc. 4th Semester Examination, 2010

CHEMISTRY

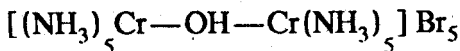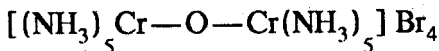PAPER — CH - 2201

Full Marks : 40

Time : 2 hours

The figures in the right-hand margin indicate marks
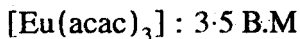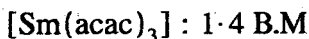
(*Inorganic*)

Answer any *four* questions

1. (*a*) Which one of the following two complexes will
have more superexchange interaction and why ? 3

$$[(NH_3)_5 Cr—O—Cr(NH_3)_5] Br_4$$

$$[(NH_3)_5 Cr—OH—Cr(NH_3)_5] Br_5$$

(*b*) Explain the following magnetic moment data
(at 27° C) :   5

$$[Sm(acac)_3] : 1·4 \ B.M$$

$$[Eu(acac)_3] : 3·5 \ B.M$$

(c) What is the value of magnetic dipole moment associated with a loop carrying current ? 2

2. (a) Distinguish between ferromagnetic, ferrimagnetic and antiferromagnetic materials. Give an example for each class of material. 4 + 1

(b) Explain the diamagnetic nature of bis (diazoaminobenzenato) copper (II) complex. 4

(c) What is Bohr magneton ? 1

3. Write short notes on : 3 + 3 + 4

(a) Intra and intermolecular antiferromagnetism.

(b) Direct metal-metal interaction.

(c) Lande interval rule.

4. (a) Derive an expression for magnetic moment for a substance whose multiplet width small as compared to kT. 7

(b) Explain the origin of diamagnetism in a free atom. 3

(Continued)

5. (a) What are "complementary" and "non-complementary" electron transfer processes ? Give examples.   5

   (b) How would you distinguish between "outer sphere" and "inner sphere" electron transfer mechanisms ?   5

6. (a) What are "labile" and "inert" complexes ? How they are related with thermodynamically "stable" and "unstable" complexes.   2 + 2

   (b) Which one of the following two complexes react faster ? Give reasons.   4

   $$[Fe(H_2O)_6]^{2+} \text{ and } [Fe(H_2O)_6]^{3+}$$
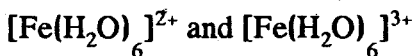
   (c) What is the significance of the following facts taken together for the mechanism of substitution at Co (III) in aqueous solution ?

   (i) The rate of aquation are always given by the following expression :

   $$rate = K_{aq}[Co(NH_3)_5 X]^{2+}$$

(*ii*) No direct replacement of X^- by Y^- is ever observed. Instead, water enters first and is subsequently replaced by Y^-.   2

7. (*a*) Base hydrolysis of $[Co(NH_3)_5 Cl]^{2+}$ is about 10^6 times faster than acid hydrolysis. Explain.   5

(*b*) State the principles of "Murcus theory".   5

(*Organic*)

Answer *five* questions, taking at least *two* from each Group

GROUP—A

1. (*a*) The parabolic Hammett plot obtained when $\log k/k_0$ in the reaction between substituted benzyl chlorides, carrying *para-* and *meta-* substituents in the benzene ring and aniline (where k and k_0 are the rate constants of substituted and unsubstituted benzyl chloride respectively) are plotted against σ values of the substituents indicates a change in the nature of the transition state with change of substituents. Elucidate.   4

(*Continued*)

(b) What idea do you get about the transition state from the fact that you need to use σ^+ values of the substituents in order to get a linear Hammett plot with a negative slope in the Beckmann rearrangement of acetophenone oximes, carrying *para-* and *meta-* substituents in the benzene ring, in 98% sulfuric acid ?   4

2. (a) Explain why the Hammett plot obtained when pK_{BH^+} in the ionization of substituted anilines is linear but the points due to $p-NO_2$ and $p-CN$ deviate from the straight line but the points due to $m-NO_2$ and $m-CN$ do not deviate.   4

(b) Solvolysis of both the compound A and B (O Bs = brosylate) were subjected to Yukawa – Tsuno equation and the $r^{+/-}$ values of 1·00 and 0·54 were obtained. How does this observation indicates a difference in the nature of the respective transition states.   4
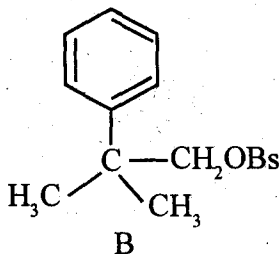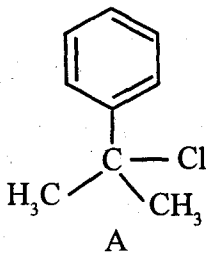
3. Indicate the difficulties in using dielectric constant as a solvent parameter with suitable examples. What is the basis of Grunwald - Winstein solvent parameter Y ? Why the use of this parameter in S_N2 type reactions give unsatisfactory results ? 8

4. What is the conceptual difference between Extended Hammett Approach and Dual Substituent Parameter Treatment for separation of polar and mesomeric effects exerted by a substituent ? The following DSP equations are obtained in the dediazotization of aromatic diazo compound carrying *meta-* and *para-*substituents in the benzene ring:

For *meta-*substituents:

$$\log (k/k_0) = -4,5\sigma_1 - 1\cdot8\,\sigma_R^+$$
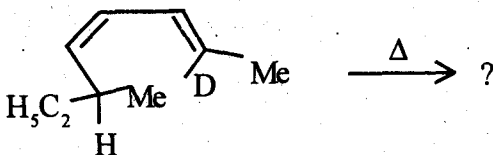
For *para-*substituents:

$$\log (k/k_0) = -3,7\sigma_1 + 2\cdot4\,\sigma_R^+$$

How do these equations rationalize that the dediazotization follow S_N1 pathway ? 8
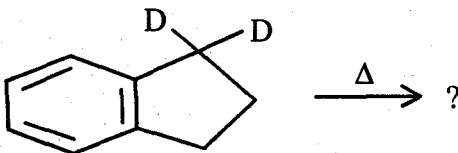
5. Predict the product/s of the following reactions indicating frontier orbital interactions in each case (F.O.I) (attempt any *four*) : 8
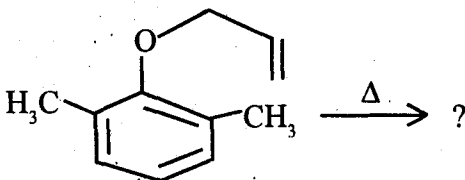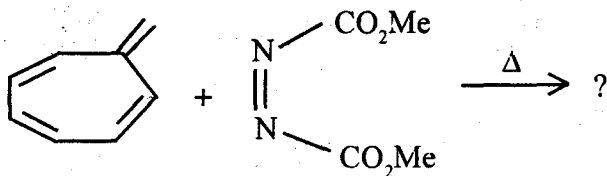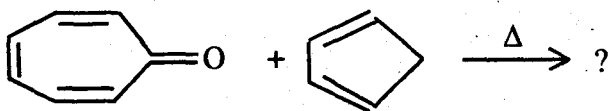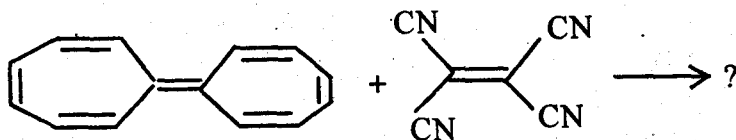
(*i*)

(*ii*)

(*iii*)

(*iv*)

(v)

(vi)

GROUP—B

6. Outline the stereochemical reasoning leading to the relative stereochemistry of the perhydrodiphenic acid diastereomers with *cisoid* backbone configuration. How will you correlate these compounds with the corresponding perhydro-phenanthrene isomers. $6 + 2$

7. (a) Predict the products of the following reactions indicating the predominant one in each case by application of Felkin – Ahn model: case (i), $R = Et$ and case (ii), $R = \underline{t}\text{-Bu}$, 5

$$PhCHRCHO + \underline{t}\text{-Bu}\, C(OLi) = CH_2 \longrightarrow$$
Any enantiomer.

(*Continued*)
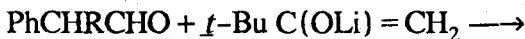
(*b*) Write down the salient points of the *axial haloketone rule*. 3

8. (*a*) Predict the sign of the cotton effect that the nonsteroid form of the following compound (A) and its epimeric 3-bromo derivatives would exhibit. Name the compound, mentioning the absolute configuration of its chiral centers. 5

Me   (A)
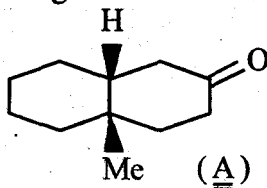
(*b*) Predict the sign of the Cotton effect that 3p, 4α–di–*p*–dimethylaminobenzoyloxycholestane would exhibit. Show that nature of the CD curve, units of the two axes and the position of the λ_{max}. 3

9. Attempt any *two* : 4 × 2

(*a*) What will happen when compounds (B) and (C) are treated with a strong base ? Name the compounds. Comment on the optical activity of the corresponding hydrocarbons. 4

(B) O   O (C)
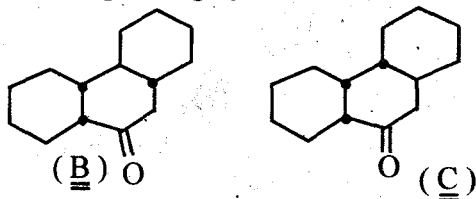
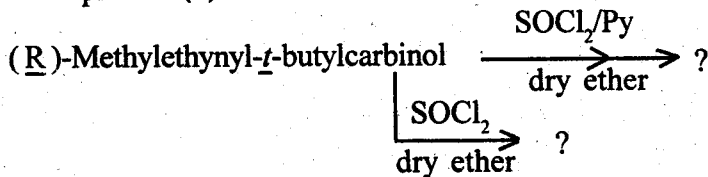(b) Elucidate the absolute configuration of the following compounds by application of the relevant rules. Name the rules. $1 + 1\frac{1}{2} + 1\frac{1}{2}$

   (i) (+)-Hexahelicene

   (ii) (-)-1-Chloro-1-Phenyl-3-ethylallene

   (iii) (+)-2-Chloropropionic acid.

(c) Show the mechanism of the following reactions and specify the absolute configuration of the product(s):   4

(R)-Methylethynyl-*t*-butylcarbinol $\xrightarrow[\text{dry ether}]{\text{SOCl}_2/\text{Py}}$?

$\xrightarrow[\text{dry ether}]{\text{SOCl}_2}$?

(*Physical Special*)

Answer any *four* questions, taking *two* from each Group

GROUP—A

Answer any *two* of the following

1. (a) Give a brief introduction of two approximate methods in quantum mechanics.   5

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

2. (a) Using the trial function $\psi = e^{-cr}$ calculate the ground state energy of H-atom. 5

(b) Derive the secular determinant as encountered in linear variational theorem. 5

3. (a) Calculate the ground state energy of an anharmonic oscillator whose potential energy is

(i) $U(X) = \dfrac{1}{2} KX^2 + \dfrac{1}{6} K_2 X^3$

(ii) $U(X) = \dfrac{1}{2} KX^2 + \dfrac{1}{6} K_2 X^3 + \dfrac{1}{24} K_3 X^4$.

Comment on the result. 5

(b) Derive the expression of total π-electronic energy in terms of charge density and bond order. 5

4. (a) Derive the energy levels and general expression for the MO's in linear polyenes. 5

(b) Derive the n th order perturbation equation for non-degenerate cases. 5

GROUP—B

Answer any *two* of the following

5. (a) Show that the perturbation energy upto third order can be obtained for a knowledge of wavefunction upto 1st order. 5

(b) Derive $E_k^{(1)}$ and $C_{kj}^{(1)}$. 5

6. (a) State and explain the working principle of a semiconductor. 5

(b) How would you distinguish a body centered cubic lattice and a face centered cubic lattice by calculating geometrical structure factor. 5

7. (a) When KCl crystal is heated in air, no colour is observed but when it is heated in K vapour it shows violet colour. Explain the phenomenon. 5

(b) Does the F-absorption frequency depend on the interionic distance ?   2

(c) Given the density of KBr is 2·75 g/cc and that the length of an edge of a cubic unit cell is 654 pm. Determine how many formula units of KBr there are in a unit cell. Does the unit cell have a NaCl or a CsCl structure ?   3

8. Use Cartesian co-ordinate as well as internal co-ordinate approach to obtain the symmetry of vibrational modes in ClF_3. Find the symmetry of pure and mixed vibrational modes of ClF_3. Following is the character table for C_{2v}.   4 + 4 + 2

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$		
A_1	1	1	1	1	T_z	X^2, Y^2, Z^2
A_2	1	1	-1	-1	R_z	XY
B_1	1	-1	1	-1	$T_X R_Y$	XZ
B_2	1	-1	-1	1	$T_Y R_X$	YZ