M.Sc. 4th Semester Examination, 2013

CHEMISTRY

PAPER—CEM-401

Full Marks : 40

Time : 2 hours

The figures in the right-hand margin indicate marks

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

Illustrate the answers wherever necessary

(*Physical Special*)

GROUP – A

Answer any *one* of the following : 10 × 1

1. State and prove Eckart's theorem for the ground state of a system. 10

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

GROUP – B

Answer any *one* of the following : 10×1

3. (*a*) Calculate using Hückel theory, the charge densities of different carbon atom of butadiene. 5

(*b*) Calculate the bond orders in butadiene. 5

4. (*a*) Derive the *n*th order perturbation equation for the non-degenerate system. 5

(*b*) Show that the third order perturbation energy can be calculated from first order perturbation wave-function only. 5

Or

(*a*) Explain the working principle of an diode with an suitable example. 6

(*b*) Define and derive the expression of geometrical structure factor. 4

GROUP – C

Answer any *one* of the following : 10 × 1

5. (*a*) Prove that :

$$\sigma = \frac{ne^2\tau}{2m}$$

where the symbols have their usual meanings. 7

(*b*) Tantalum-forms a body-centered cubic unit cell with $a = 330{\cdot}2$ pm. Calculate the crystallographic radius of tantalum atom ? 3

6. (*a*) What is 'R_2' centre and narrate the mechanism of formation of a 'R_2' centre using a suitable example. 6

(*b*) Define Hall effect and Hall mobility ? 2 + 2

GROUP – D

Answer any *one* of the following : 10 × 1

7. Use Cartesian co-ordinate as well as internal co-ordinate method to obtain the vibrational

modes in ML_5 (Square pyramidal). Comment on your results : 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*) What is direct product representation ? How does it help in determining the zero and non-zero value of transition moment integral. 5

(*b*) Obtain vibrational modes in HCN using integration method. Hence find the IR and vibrational Raman activity of those modes. 5

$C_{\infty v}$	E	$2C_\alpha^\theta$	.....	$\alpha\sigma_v$	
A_1	1	1	.....	1	z
A_2	1	1	.....	−1	R_z
E_1	2	$2\cos\theta$	.....	0	$(x, y), (R_x, R_y)$
E_2	2	$2\cos 2\theta$	.....	0	
E_3	2	$2\cos 3\theta$	.....	0	

(*Organic Special*)

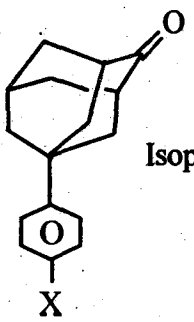
Answer any *five* questions taking at least **two** from each Group

GROUP – A

1. (*a*) State and illustrate (using orbital pictures) taking (*R*)-EtCHMeCOPh as an example the Felkin-Anh model (acyclic) of stereo-selective nucleophilic (RMgBr) addition leading to Cram product as major diastereomer. 3

(*b*) How *anti*-Cram product can be obtained as major diastereomer from the same set of reactants as in (*a*) ? Explain your answer. 2

(*c*) Explain the product ratio of the following reactions in terms of a suitable model : 3



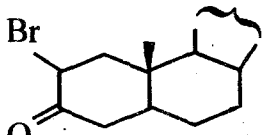
$NaBH_4$ / Isopropyl alcohol → (*Z*)-Alcohol + (*E*)-Alcohol

When X = Cl	minor	major
When X = OH/NH_2	major	minor

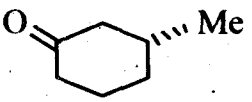
2. Comment on the following : 4 x 2

(*i*) The 2-bromo-3-ketosteroid (A) [Partial structure shown], known to have axial Br, shows a positive cotton effect ORD curve.

(*ii*) (*R*)-3-Methylcyclohexanone(B) shows a positive cotton effect ORD curve.



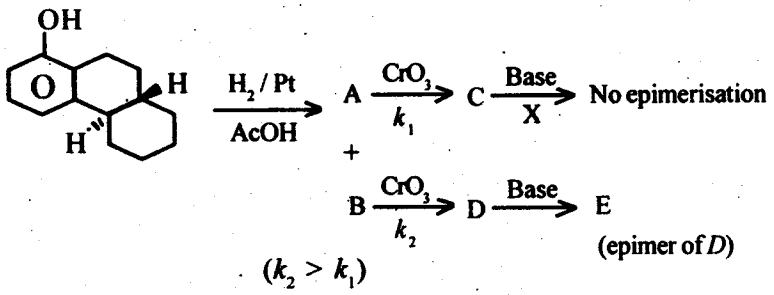
(A)



(B)

3. (*a*) Comment on the chirality, stability and sign of torsion angles of ring junction in the central ring of (*i*) *cis*-syn-*cis* and (*ii*) *trans-anti-trans* isomers of perhydro-anthracene. 4

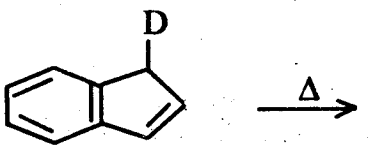
(*b*) Identify the compounds *A* - *E* (Conformational structure) in the following transformations : 4



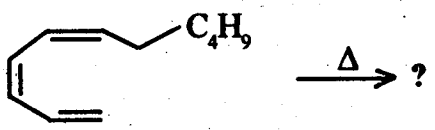
4. What is (*i*, *j*) sigmatropic shift ? Predict the product/s of the following reaction indicating Frontier-Orbital-Interaction (Attempt any *three*) :

$2 + 3 \times 2$

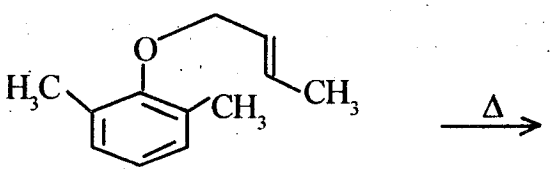
(*i*)



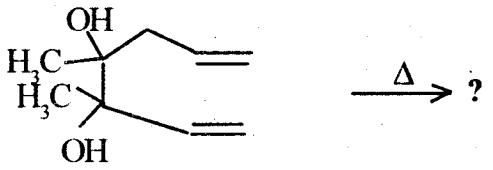
(*ii*)



(*iii*)



(*iv*)



GROUP – B

5. Answer the following questions : 4 × 2

(*a*) How can you explain that upon quenching the acetolysis of *threo*-3-phenyl -2-butyl tosylate after 1·5 times its half life, the remaining start material that recovered is optically inactive ?

(*b*) The parabolic Hammett plot obtained in the reaction :

$$p\text{–X} - C_6H_4CH_2Cl + C_6H_5NH_2$$

upon plotting $\log k / \log k_0$ against σ values of X indicates a change in the transition state. Elucidate.

6. Account for any *two* of the following : 4 × 2

(*i*) The value of ρ (5·09) of the reaction of diphenyl methyl chloride with ethanol indicates that the reaction is more likely to proceed *via* S_N1 rather than S_N2 pathway.

(*ii*) A positive slope in a linear Hammett plot indicates that the reaction is favoured (higher yield and / or faster rate when the reacting molecile carries an electron acceptor substituent while a negative slope indicate that the reaction is facilitated when the reacting molecule carries an electron donor substituent.

(*iii*) In the base induced dehydrobromination of aryl ethyl bromides a linear Hammett plot requires the use of σ^- rather than σ.

7. What is Yukawa-Tsuno equation, both in its original and in its collective form ? What is the conceptual basis of calling it a "sliding scale" ? How does the $r^{+/-}$ values of the thermally induced Beckmann Rearrangement of acetophenone oxime picryl either and the same rearrangement

of acetophenone oxime in 94·5% sulfuric acid indicate that both the reactions proceed via similar intermediates ? 8

8. Discuss the principle behind the deduction of Taft's Dual Substituent Parameter treatment in Correlation Analysis. How are the anomalies observed while correlating $\log k / \log k_0$ values with σ values of the substituents in the dediazoniation of *m*– and *p*– substituted arly diazonium compounds can be explained by using Dual Substitute Parameter Treatment. 8

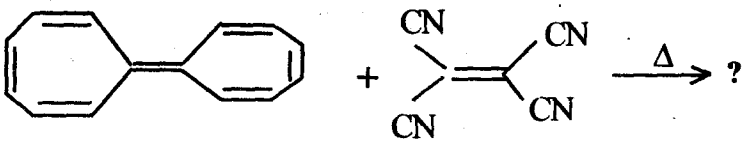
Or

Define "supra" and 'antara' facial cycloadation reaction with a suitable example. Predict the products of the following reactions (attempt any *three*) : $2 + 3 \times 2$

(*i*)  $+ EtO_2C-C\equiv C-CO_2Et \xrightarrow{h\nu}$

(*ii*) $CH_2=CH-\underset{\displaystyle OH}{\underset{|}{CH}}-C(CH_3)_2-CH_2-CH=CH_2 \xrightarrow[CuCl]{h\nu}$

(*iii*)



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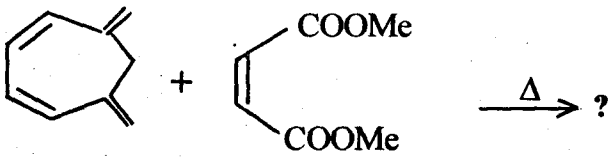

(*Inorganic Special*)

Answer any *four* question 10×4

1. (*a*) The number of *f*-electrons in Eu^{3+} and Am^{3+} is same, but they have different magnetic moment value. Explain. 2

(*b*) Use Hund's rules to determine the values of S, L, and J in the ground state of an P_m^{3+} ion. Calculate the Lande' g-factor, total magnetic moment, and the magnetic moment along the field direction. 1 + 3

(*c*) Define paramagnetic and diamagnetic substances on the basis of their values of magnetic susceptibility and intensity of magnetization. 3

(*d*) What do you mean by "magnetically dilute system" ? 1

2. (*a*) Why is Mn^{2+} the only ion among the divalent first transition series metal ions whose magnetic moment is predicted by the μ_J equation ? 2

(*b*) Discuss the magnetic properties of the lanthanide ions and give a comparison of the magnetic properties of the lanthanide and actinide ions. 4 + 2

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

3. (*a*) Electron transfer reaction between $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ is much faster than between $[CO(NH_3)_6]^{3+}$ and $[CO(NH_3)_6]^{2+}$ Explain. 3

(*b*) Explain why substitution reaction of $[Cr(CO)_6]$ is very slow, but substitution reaction of isoelectronic complex $[V(CO)_5(NO)]$ is very fast. 3

(*c*) Assign inner and outer sphare reaction mechanism for the reaction between $[CO(NH_3)_5Cl]^{2+}$ and Cr^{2+} in acidic solution. Justify that this reaction follow inner sphare reaction mechanism. 3 + 1

4. (*a*) What is the difference between the magnetic field strength H and magnetic induction B ? How are they related to each other ? 2

(*b*) Write short notes on : 5 + 3

(*i*) Spin-orbit interaction

(*ii*) Ferrimagnetism.

5. (*a*) Among the metal ions Ni(II), Pd(II) and Pt(II), only Pt(II) shows significant trans effect-comment. 2

(*b*) The ratios of the constants for reduction of $[CO(edta)Cl]^{2-}$ and $[CO(edta)(H_2O)]^{-}$ by various reductants at 25°C are given below. Comment about the inner or outer sphare nature of these reactions. 2

Reductant	K_{cl}/K_{aqua}
$[Fe(CN)_6]^{4-}$	33
$Ti\,3^{+}$	31
Cr^{2+}	2×10^3
Fe^{2+}	$>3\times10^2$

(*c*) In acidic solution of $[CO(NH_3)_5(CO_3)]^{+}$ is converted to its corresponding aqua complex for removal of CO_2, but when the reaction is carried out in presence of H_2O^{18}, no O^{18} is found in the product. Explain. 3

(*d*) Give general expression for base hydrolysis reaction and comment on the order of the reaction. Write D-CB mechanism for $[CO(NH_3)_5Cl]^{2+}$. 1 + 2

6. (*a*) What do you mean by "multiplet width" ? Derive an expression for magnetic moment for a substance whose "multiplet width" is large in comparison with kT. 1 + 6

   (*b*) Define "Curie law" and "Curie-Weiss law". What is the significance of Weiss constant ? 2 + 1

7. (*a*) Write the mechanism for all types of dissociative reactions of coordination compounds. Derive rate law expression for any one of these dissociative reaction. 3 + 2

   (*b*) Write the generalize mechanism for inner sphare electron transfer reaction. What is the main evidence of this reaction ? 3

   (*c*) Comment about the stereochemical nature of square planar ligand substitution reaction. 2