M.Sc. 4th Semester Examination, 2015

CHEMISTRY

PAPER – CEM-401

Full Marks : 40

Time : 2 hours

The figures in the right hand margin indicate marks

(*Inorganic Chemistry Special*)

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

GROUP –A

1. (*a*) Explain the Curie law and Curie-Weiss law. Indicate the significance of the Weiss constant. 2 +1

   (*b*) Discuss the phenomenon of antiferromagnetism. How does an antiferromagnetic substance differ from a diamagnetic substance ? 3

(*c*) Calculate the allowed values of magnetic moment along the field axis of an atom which has $J = 2$ and $g = 2$. 2

2. (*a*) What is Lande interval rule ? Establish this rule. 1 + 2

(*b*) What do you mean by "multiplet width" ? Establish magnetic moment equation for a system which has multiplet width large as compared to kT. 1 + 4

3. (*a*) Establish the paramagnetic susceptibility equation for solid substances. 6

(*b*) Define the terms : 1 + 1

(*i*) Magnetically concentrated system.

(*ii*) Anomalous magnetic moment.

4. (*a*) Explain the diamagnetic nature of bis (diazoamino benzenato) copper (II) compound. 2

(*b*) The number of *f*-electron in Sm^{3+} and Pu^{3+} is same, but they have different magnetic moment value. Explain. 2

(*c*) Write short notes on : 2 + 2

(*i*) Intra and inter molecular antiferro-magnetism

(*ii*) Super exchange.

GROUP –B

5. (*a*) Derive the dissociative mechanism for L_5MX complex where five coordinated intermediate have appreciable life time. Derive rate law, considering *Y* as attacking molecule. If $K_2[Y]$ is very large or very small what will be the effect on rate law. 3 + 2 + 1

(*b*) What is stoichiometric mechanism ? In the reaction of $[Co(NCS)(NH_3)_5]^{2+}$ with $Fe(H_2O)_6]^{2+}$ in water is it possible to identify $[Fe(NCS)(H_2O)_5]^{2+}$ as an intermediate ? Explain. What are the final products of this reaction ? 2

6. (*a*) Rate constant for acid aquation of $[Co(NH_3)_5X]^{n+}$ are

Complex	$k\ (s^{-1})$
$[Co(NH_3)_5(OP(OMe)_3)]^{3+}$	$2{\cdot}5 \times 10^{-4}$
$[Co(NH_3)_5(NO_3)]^{2+}$	$2{\cdot}4 \times 10^{-5}$
$[Co(NH_3)_5I]^{2+}$	$8{\cdot}3 \times 10^{-6}$

and anation by Y^- of $[Co(NH_3)_5H_2O]^{3+}$ are

Y^{n-}	$k\ (s^{-1})$
H_2O	100×10^{-6}
N_3^-	100×10^{-6}
SO_4^{2-}	24×10^{-6}

Comment on the rate constant variation in these two cases. By predict the mechanism the reactions will proceed ? 4

(*b*) Explain the octahedral ligand substitution for (A) $[Fe(H_2O)_6]^{3+}$ and (B) $[Fe(H_2O)_5(OH)]^{2+}$ complex

Y^{n-}	$k\,(M^{-1}s^{-1})$ A	$k\,(M^{-1}s^{-1})$ B
SO_4^{2-}	$1{\cdot}1 \times 10^5$	$2{\cdot}3 \times 10^3$
Cl^-	$5{\cdot}5 \times 10^3$	4·8
Br^-	$2{\cdot}6 \times 10^3$	1·6

Compare the rate constant data for A and B, based on the charge with proper explanation. 4

7. (*a*) Base hydrolysis of $[Co(NH_3)_5Cl]^{2+}$ obeys the rate expression

$$\text{Rate} = k\,[Co(NH_3)_5Cl]^{2+}\,[OH^-]$$

(*i*) Propose a suitable mechanism for it and explain by giving geometrical structure of each step.

(*ii*) Derive rate law for it.

(*iii*) Comment on the rate of reaction. 3 + 3 + 1

(*b*) What is trans effect ? 1

8. (*a*) Base hydrolysis of $[Co(NH_3)_5X]^{n+}$ in the presence of NaSCN gives

n^+	X^-	Total % of SCN^-
+3	$OP(OMe)_3$	17·5
+3	$OSMe_2$	17·9
+2	OSO_2CF_3	13·6
+2	OSO_2CH_3	13·4
+1	OSO_3	6·8

Explain why the total % captured by NCS^- is constant for complexes of a particular charge? 2

(*b*) Discuss 'Outer sphere and inner sphere mechanism' for complexes with suitable example. 3

(*c*) The ratios of the rateconstant for reduction of $[Co(EDTA)Cl]^{2-}$ and $[Co(EDTA)H_2O]^{1-}$ by various reductants at 25°C are given

below. What can you say about the inner or outer sphere nature of the reactions ? 3

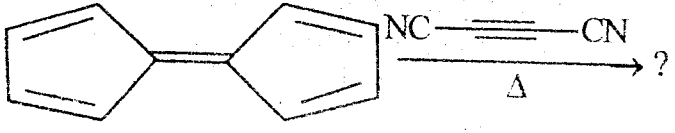
Reductants	k_{Cl}/k_{aq}
$[Fe(CN)_6]^{4-}$	33
Ti^{3+}	31
Cr^{2+}	2×10^3
Fe^{2+}	3×10^2

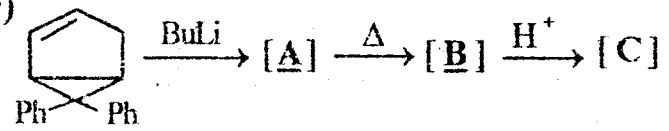
(Organic Special)

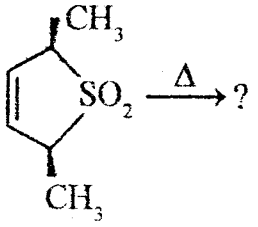
Answer any **five** questions taking at least **two** from each Group

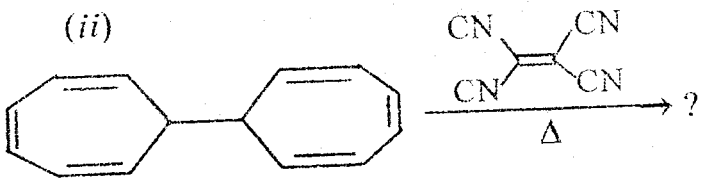
GROUP – A

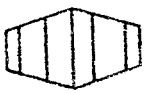
1. (*a*) Predict the product/s of the following pair of reaction indicating mechanistic path way with frontier orbital interactions in each case ;

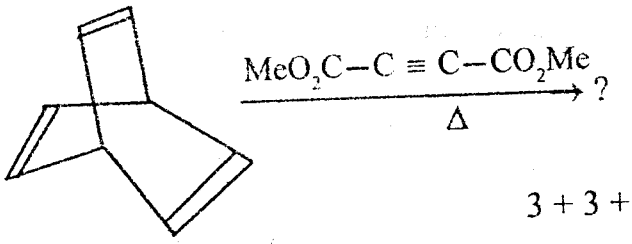
(*i*) 

(*a*) 

(*b*) 

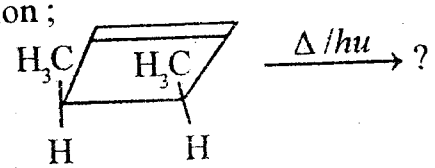
(*ii*) 

(*b*)  Identify the product of the following reaction :



3 + 3 + 2

2. (*a*) Predict the product of the following reaction both in thermal and photochemical condition ;



and explain that 'electrocyclic ring opening' reaction is 'Cycloaddition'. Rationalise on the basis of Frontier-Orbital Interaction (F.O.I).

(*Continued*)

(*c*) $CH_3CHO + C_6H_5NHOH + C_6H_5CH =$

$$CH_2 \xrightarrow[\Delta]{80^\circ C} ?$$

Or

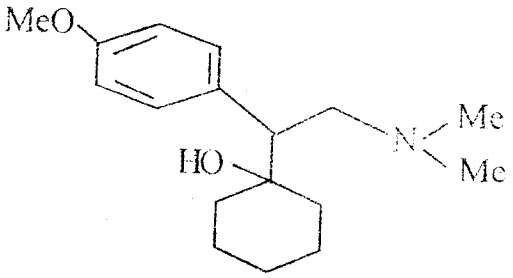
$$C_6H_5N_3 + MeO_2C.C \equiv C.CO_2Me \xrightarrow{\Delta} ?$$

4. (*a*) How and why Hammett equation deviates in case of a reaction series of substituted phenol. Calculate the strength of acidity of *p*-nitrophenol with phenol, whose $p = 2{\cdot}1$ and $\sigma_{pNO_2} = +{\cdot}78$.

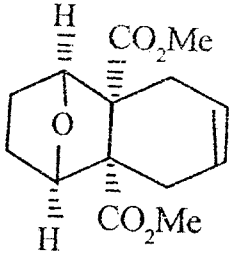
(*b*) *m* or *p* nitro ethyl benzoate was hydrolyzed (base catalyzed) 63·5 faster than ethyl benzoate. What would be the rate of hydrolysis of *p*-methoxy ethyl benzoate relative to ethyl benzoate in the same reaction condition ? 4 + 4

5. Describe the synthesis of the following compounds with proper retrosynthetic analysis (attempt any *four*) : 2 × 4

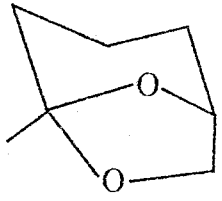
(*i*)



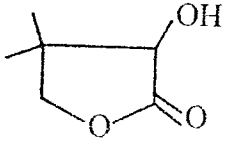
(*ii*)



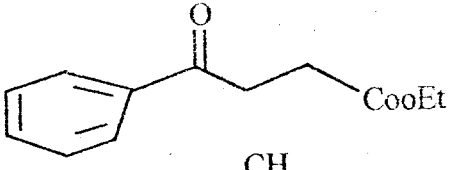
(*iii*)



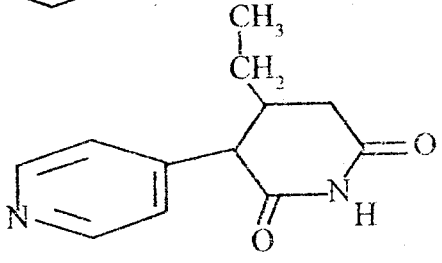
(*iv*)



(*v*)



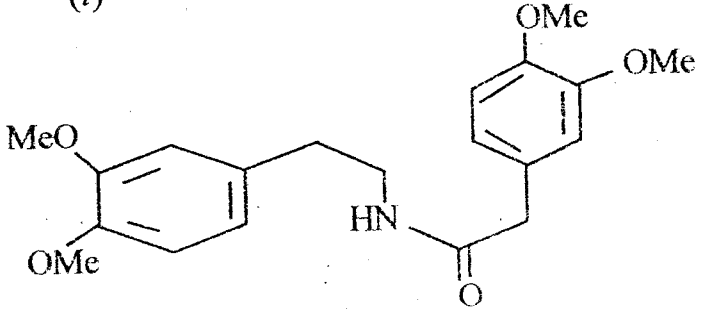
(*vi*)



GROUP –B

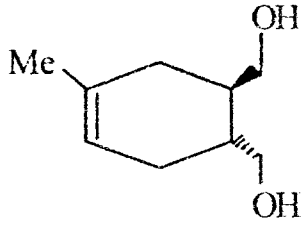
6. (*a*) What is 'Functional Group Interconversion' ? Illustrate the use of Functional Group Interconversion in the retrosynthetic analysis of the following compounds. 2 + 3 + 2

(*i*)



(*Continued*)

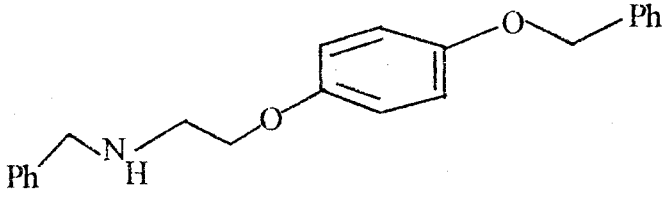
(*ii*)



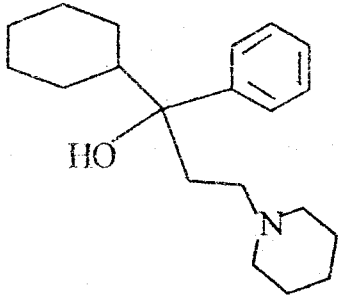
(*b*) Give an example of a donar synthon. 1

7. (*a*) Illustrate with example that disconnection of 1, 6-dicarbonyl compounds involve 'reconnection'. 2

(*b*) How would you design the synthesis of the following compound avoiding disconnection that causes chemoselective problems ? Give explanations. 3

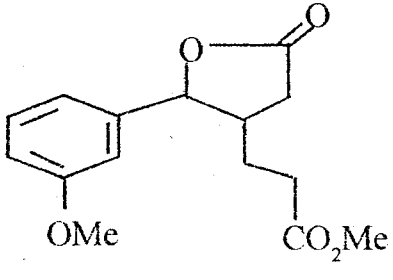


(*c*) Show the synthesis of the following target molecule by both convergent and linear route with retrosynthetic analysis. 3

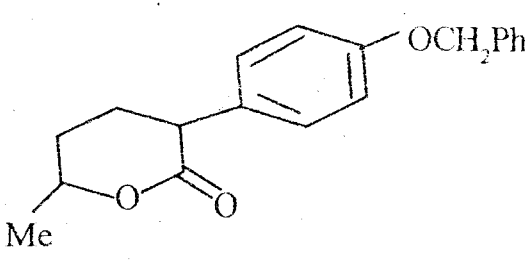


8. Work backwards using the principle of retrosynthetic analysis to find out simple starting materials for the synthesis of the following compounds. 3 + 3 + 2

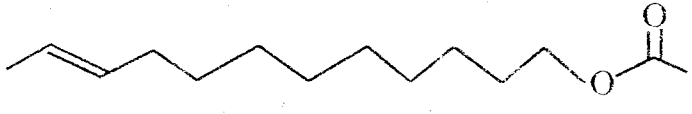
(*i*)



(*ii*)



(*iii*)



9. (*a*) If three reaction series have ionisation constants K, K' and K", how they can be correlated with one standard reaction and therefore derive Hammett equation. 4

(*b*) Acid catalysed esterification of benzoic acid in CH_3OH at 25°C, $p = -0{\cdot}52$. What would be the effect of introducing $-NO_2$ group at para and ortho position ($\sigma_{NO_2} = +0{\cdot}71$). Explain with mechanism. 4

10. (*a*) The following reaction :

$$Aro^- + EtI \xrightarrow[EtOH]{OH^-} Aro^{-\delta} .... Et .....I^{-\delta} \longrightarrow AroEt + I^-$$

has $p = -0{\cdot}99$. What would be the effect of NO_2 or $-NH_2$ in the ring ? 4

(*b*) The methoxy group (–OMe) has $\sigma_m = +0{\cdot}12$ and $\sigma_p = -0{\cdot}27$. What effect it exerts in electrophilic substitution. 2

(*c*) "All the halogens (F, Cl, Br and I^-) show substitutent constant values positive ." – Explain its effect in aromatic substitution. 2

(*Physical Special*)

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

GROUP – A

Answer any *two* questions

1. Discuss clearly the linear variational theorem and write down the essential steps for its application. 10

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

3. Introducing perturbation theory derive the n-th order perturbation equation. 10

4. Establish the justification of Sigma-pi separability in the pi-electron approximation in the molecular orbital calculations. Calculate Coulson's Free Valence indices F_1 and F_2 of butadiene.

(Given $C_{11} = C_{22} = -C_{23} = 0{\cdot}37$

$C_{12} = C_{21} = C_{13} = 0{\cdot}60$

Explain the significance of the result. 4 + 4 + 2

GROUP – B

Answer any *two* of the following :

5. (*a*) Derive the Laue's equations to obtain the directions of diffraction maxima.

(*b*) Gold crystallizes as a fcc lattice. Calculate the surface number density of gold atoms in the 100 planes. Take the length of the unit cell to be 407·9 pm. 8 + 2

6. (*a*) How the *F*-Centers are formed according to the model suggested by de Boer ?

(*b*) What is a 'R_2' centre ?

(*c*) Explain the working principle of a diode according to band theory. 3 + 2 + 5

7. The six normalised octahedral hybrid orbitals h_1, h_2, h_3, h_4, h_5 and h_6 comparising linear combination of atomic orbitals of the central atom of an octahedral complex, span the IRs, A_{1g} (basis '*S*'), E_g (basis d_{z^2}, $d_{x^2-y^2}$) and T_{1u} (basis p_x, p_y, p_z) of the octahedral point group. Find out the quantitative composition of the hybrid orbitals. 10

8. Use both Cartesian co-ordinate and internal co-ordinate system to obtain the vibrational modes of ML_5 (Square pyramidal). Comment on your result. Character table of of C_{4v} point group in given below : 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)