Total Pages—16 **PG/IVS/CHEM-401/12**

M.Sc. 4th Semester Examination, 2012

CHEMISTRY

PAPER – CEM- 401

Full Marks : 40

Time : 2 hours

The figures in the right hand margin indicate marks

(*Organic Special*)

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

GROUP – A

1. Answer any *two* of the following questions :

   (*a*) How can you explain that in the acetolysis of *erythro*-3-phenyl-2-butyl tosylate the rate constant obtained by titrating the *para*-tolune sulfonic acid formed is five times the rate constants when the reaction is followed polarimetrically. 4

(*Turn Over*)

(*b*) Account for the following observations (any *one*): 4 × 1

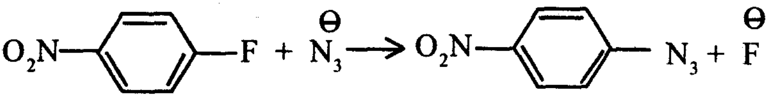
(*i*) The value of ρ in the ionization of *p*-or *m*- substituted benzoic acid in water at 25°C is unity by convention however its value becomes double when the reaction is carried out in ethanol.

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

2. (*a*) Explain the following observation (any *one*): 4 × 1

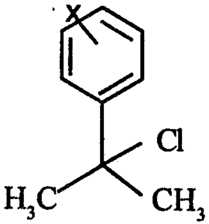
(*i*) A linear Hammett plot is obtained in the alkaline hydrolysis of *p*- and *m*-substituted benzoic acid esters while the Hammett plot of similar esters in 99·9% H_2SO_4 consists of two straight lines of positive and negative slopes meeting at zero.

(*ii*) Although the values of dielectric constants of methanol and *N* .*N* dimethyl formamide are close, the rate of the following reaction is 10^4 times faster in the latter solvent :

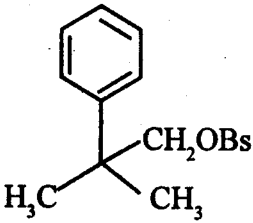


(*b*) What conclusion do you draw about the rate determining step and the nature of the transition step from the obligation to use σ^+ rather than σ in order to have a linear Hammett plot with negative slope in the Beckmann transformation of acetophenone oxime in concentrated sulfuric acid. 4

3. What is Yukawa-Tsuno equation, both in its original and in its collective form ? How does the term $r^{\pm}$ in the collective form of Yukawa-Tsuno equation indicate that this equation involves a sliding scale ? How do the values of ρ and $r^{\pm}$ obtained in the acetolysis of *t*-cumyl chloride and neophyl brosylate obtained from Hammett and Yukawa-Tsuno equation



t-cumyl chloride



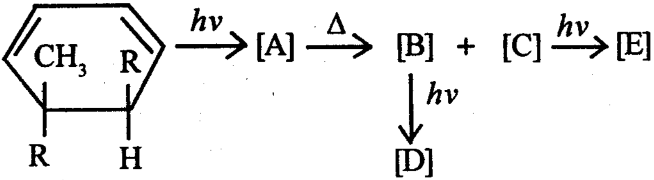
neophyl brosylate

ρ	−4·5	−3·38
$r^{\pm}$	1·00	0·54

respectively suggest that in this case $r^{\pm}$ is a better indicator of the transition state than ρ. 8

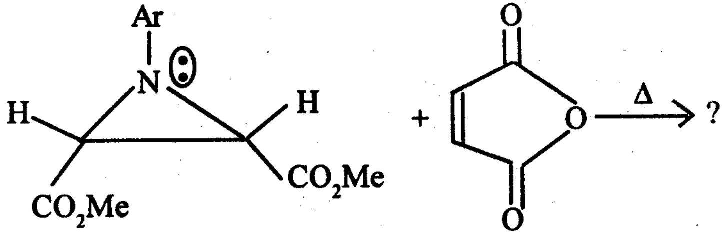
4. Describe Grunwald and Winstein equation of solvent effect in a reaction. What are its limitations ? How was it revised ? 8

5. (*a*) Complete the following transformation,



Identify *A* , *B*, *C*, *D* and *E*. 6

(*b*) 2



GROUP – B

6. (*a*) Predict the products of the following reactions *indicating the predominant one in each case* by application of Felkin-Ahn model.

$\mathrm{Ph\,CH\,R\,CHO} + t\text{-}\mathrm{Bu\,C(OLi)} = \mathrm{CH_2} \rightarrow$

case (*i*) R = Et and case (*ii*) R = *t*-Bu. 5

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

7. (*a*) Outline the mechanism of the multistep *Birch reduction* of 4-*t*-butylcyclohexanone; explain 99% *stereoselectivity* of this reaction. 4

(*b*) Elucidate the *absolute configuration* (*R, S*) of the following compounds by application of the *relevant rules*. Attempt *any two* : 4

(*i*) (−)-α-Chlorobutyric acid

(*ii*) (+)-1, 1′-Binaphthyl (designate its *helicity* also)

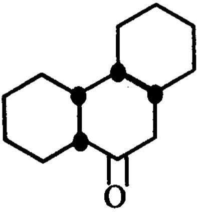
(*iii*) (+)-1-Chloro-3-methyl-3-phenylallene.

8. (*a*) Predict the *sign of the Cotton effect* that the following steroid derivative will exhibit in its CD spectrum Name the rule you have applied. Show the nature of the CD curve, the units of the two axes and the position of the $\lambda_{\max}$.

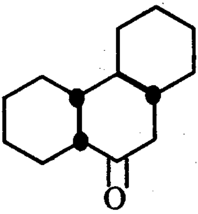
3β, 4β-Di-*p*-dimethylaminobenzoyloxycholestane 5

(*b*) Define molar rotation and deduce its unit which is 10 deg $cm^2\,mole^{-1}$ 3

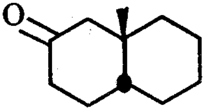
9. (*a*) Name the compounds (**A**) and (**B**). What will happen when these compounds are treated with strong base. Give reasons. Comment on the optical activity of (**A**) and (**B**), and the corresponding hydrocarbons. 5



(**A**)



(**B**)

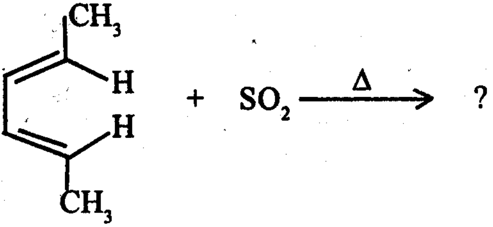


(**C**)

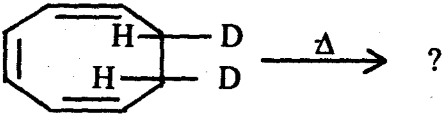
(*b*) Name the compound (**C**). Assuming that the steroid conformation is the predominant one, predict the sign of the cotton effect that the compound (**C**) will exhibit. 3

10. Predict the products of the following with frontier orbital interactions (any *four*) : 2 × 4

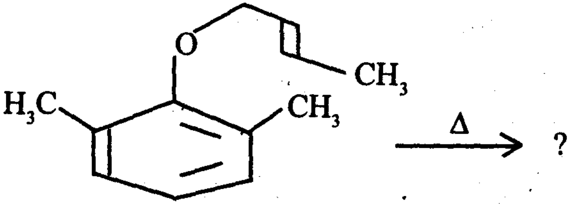
(*i*)



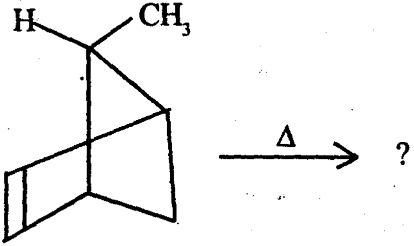
(*ii*)



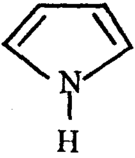
(*iii*)



(*iv*)



(*v*)



$+ \ EtO_2C-C\equiv C-CO_2Et \xrightarrow{h\nu} [?] \xrightarrow{\Delta} [?]$

(*Inorganic Special*)

Answer any *four* questions

1. (*a*) Indicate the differences between antiferromagnetic spin-spin exchange and spin pairing. 2

(*b*) What are the Neel temperature and the Curie temperature ? State the significance of these temperatures. 3

(*c*) Define the terms : 3

(*i*) Magnetically dilute system

(*ii*) Magnetically concentrated system

(*iii*) Anomalous magnetic moment.

(*d*) What are the distinguishing features of ferromagnetism ? 2

2. (*a*) Often, the magnetic moment of a first transition series metal complex approaches μ_s. Explain. 2

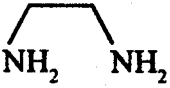
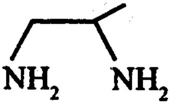
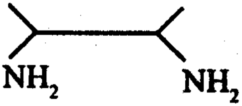
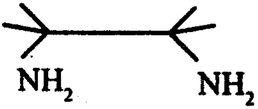
(*b*) Distinguish between ferromagnetism and antiferromagnetism. Give examples. 3

(*c*) What do you understand by quenching of orbital angular momentum ? Explain why octahedral

Ni(II) and tetrahedral Co(II) complex will have the magnetic moment higher than the spin only value. 1 + 3

(*d*) Give the relation between magnetic susceptibility, magnetization and magnetic field. 1

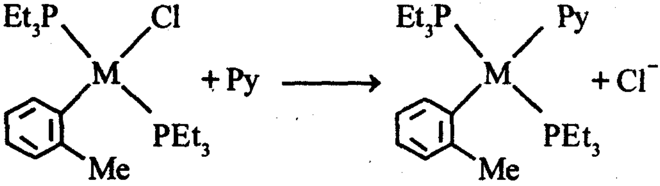
3. (*a*) For *trans*-$[Co(AA)_2Cl_2]^+$, the rate of aquation reaction follows the given order : 3

AA	$k \times 10^4\ sec^{-1}$
	0.32
	0.62
	42
	330

Justify the trend.

(*b*) Solvent exchange reaction of octahedral Cr(III) and Co(II) complexes are extremely slow. Explain. 4

(*c*) For the following reaction, justify the trend of K_y values : 3



M	k_y(mol^{-1} sec^{-1})
Ni (II)	33
Pd (II)	0·58
Pt (II)	$6{\cdot}7 \times 10^{-6}$

4. (*a*) What is Lande interval rule ? Establish this rule. 4

(*b*) Write short notes on : 2 + 3

(*i*) Spin-state equilibrium

(*ii*) Super-exchange.

(*c*) What is the dimension of magnetic susceptibility ? 1

5. (*a*) Give an account of the origin of atomic magnetism. 4

(*b*) Explain the Curie law and the Curie-Weiss law. Indicate the significance of the Weiss constant. 4

(*c*) Explain the diamagnetic nature of $[Mn_2(CO)_{10}]$. 2

6. (*a*) What are the basic mechanistic aspects of inner and outer sphere electron transfer reactions ? 3

(*b*) Explain the following data : 4

Reactants	Rate Constant ($mol^{-1}\ sec^{-1}$)
$[Fe(Phen)_3]^{2+} + [Fe(Phen)_3]^{3+}$	3×10^7
$[Co(NH_3)_6]^{2+} + [Co(NH_3)_6]^{3+}$	10^{-9}

(*c*) The rate constant for the electron transfer reaction $[Co(NH_3)_6]^{3+} + [Cr(H_2O)_6]^{2+}$ is $\sim 10^{-3}\ mol^{-1}\ sec^{-1}$. When one NH_3 is replaced by Cl^-, the rate becomes $6 \times 10^5\ mol^{-1}\ sec^{-1}$. Explain. 3

7. (*a*) $[Co(NH_3)_5(H_2O)]^{3+}$ readily forms $[Co(NH_3)_5(ONO)]^{2+}$ in $HNO_2 - NO_2^-$ buffer medium. Suggest a plausible mechanism for the conversion. 4

(*b*) $[Co(NH_3)_5(CO_3)]^+$ undergoes rapid aquation reaction. Explain with plausible mechanism. 3

(*c*) The hydrolysis of $[Fe(bipy)_3]^{2+}$ is acid dependent. Justify. 3

(*Physical Special*)

Answer any *four* questions

GROUP – A

Answer any *one* of the following

1. Calculate the ground state energy of H-atom using the variational principle. 10

2. Describe the essential features of Extended Hückel theory and show that, it can be used to calculate its equilibrium geometry of a molecule. 10

GROUP – B

Answer any *one* of the following

3. Calculate the delocalization energy and transition energy of longest wave length of butadiene using Hückel theory. 10

4. Show with derivation how the polarity of formaldehyde is changed from ground. State to doubly excited state of formaldehyde. 10

Or

Consider the $^1P_1$ state of He atom and show how the degeneracy is lifted by the application of a magnetic field in the *z*-direction. 10

GROUP – C

Answer any *one* of the following

5. (*a*) Why does the resistivity of Hg become almost zero when it is cooled at the temperature of liquid He ? 5

(*b*) Gold crystallizes as face centered cubic lattice and chromium crystallizes as body centered cubic lattice – Justify. 5

6. (*a*) When KCl crystal is heated with excess K, a violet color is observed; but the intensity of the color decreases when the crystal is cooled at 38 K. – Explain both the phenomena. 4 + 3

(*b*) Europium, which crystallizes as a body centered cubic lattice, has a density of 5·243 g. cm^{-3} at 20 °C. Calculate the crystallographic radius of a europium atom at 20 °C. 3

GROUP – D

Answer any *one* question of the following

7. How does group theoretical principle help in determining the zero and non-zero value of transition moment integral ?

Use group theory to obtain the symmetry species of vibrational modes in water. Show, whether those modes will show IR activity or not. 4 + 6

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

8. Use group theoretical principle to obtain the state of hybridization of central metal atom in [$PtCl_4$]$^{2-}$. Obtain the hybrid orbitals as the linear combination of atomic orbitals. 5 + 5

D_{4h}	E	$2C_4$	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
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	R_Z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		$X^2 - Y^2$
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		XY
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_X, R_Y)	(xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	Z	
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1		
E_u	2	0	−2	0	0	−2	0	2	0	0	(X, Y)	