2016

M.Sc. 4th Seme. Examination

CHEMISTRY

PAPER—CEM-401

Full Marks : 40

Time : 2 Hours

The figures in the margin indicate full marks.

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

Illustrate the answers wherever necessary.

(*Physical Special*)

Answer any *four* questions,
taking *two* questions from each group.

Group—A

1. The unperturbed wave functions of a two fold degenerate system are $\psi_{n_1}^{(0)}$ and $\psi_{n_2}^{(0)}$. And the energy is $E^{(0)}$.

Deduce the expression of energies and wave functions upto first order correction when the system is subjected to weak perturbation, H′ (independent of time). 5+5

2. A one-dimensional Harmonic Oscillator is subjected to a perturbing potential. $H' = bx$, where 'b' is a constant.

   Obtain an expression for its first as well as second order correction to its n^{th} state energy. 2+8

3. State and prove Eckart's theorem. Use $\phi(x) = e^{-\alpha x^2}$ as a trial wave function for a linear Harmonic Oscillator and hence obtain its ground state energy and wave function (normalized) using variational principle. 4+6

4. Use Huckel theory for linear conjugated system to obtain the energies wave functions of the π-M.O of allyl radical. Calculate the charge densities on each carbon atom and the bond order between adjacent carbon atom of allyl radical. 6+2+2

5. Use degenerate perturbation theory to explain the possible splitting of n = 2 level of hydrogen atom in the presence of a homogeneous electric field, E. 10

Group—B

6. Write down the steps involved for the determination of symmetry of vibrational modes of linear molecule using Integration method.

   Determine the symmetry of the vibrational modes of HCN.

   Character table of $C_{\alpha v}$ point group is given below. 3+7

$C_{\alpha v}$	E	$2C_{\alpha}^{\theta}$	$\alpha\sigma_v$	
A_1	1	1	1	z
A_2	1	1	−1	R_z
E_1	2	2 Cosθ	0	(x, y) : (R_x, R_y)
E_2	2	2 Cos2θ	0	
E_3	2	2 Cos3θ	0	

7. Use group theoretical principle to obtain the state of hybridization of central atom in BF_3 and also obtain the hybrid orbitals as the linear combination of atomic orbitals.

Character table of D_{3h} point group is given below. 5+5

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	−1	1	1	−1	R_z	
E'	2	−1	0	2	−1	0	(x, y)	(x^2-y^2, xy)
A_1''	1	1	1	−1	−1	−1		
A_2''	1	1	−1	−1	−1	1	z	
E''	2	−1	0	−2	1	0	(R_x, R_y)	(xz, yz)

8. (a) Prove that

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

where the symbols have their usual meanings.

(b) What is meant by 'actomic scattering factor' ? Draw and explain the atomic scattering factor curves for K^+ and Cl^-.

(c) Calculate the geometrical structure factor (F_{hkl}) for face centered cubic lattice. 4+(1+2)+3

9. (a) How the F' centers are formed from F center ? Why the F' centers are unstable than F center ?

(b) What are 'V_2' centers ? Explain the mechanism of formation of a 'V_2' center.

(c) Calculate the Fermi energy of a silver metal, given that the atomic mass of silver is 107.868 g mol^{-1}, density of the metal is 10.5 g cm^{-3}. (2+1)+(1+3)+3

10. (a) Prove that the concentration of Frenkel defect (n) is directly proportional to $(NNi)^{1/2}$.

(b) Why the resistivity of Hg vanish completely below 4.2K ?

(c) Define Exciton.

(d) 'Phonon has momentum' — justify. 4+3+2+1

(Organic Special)

Answer any *five* questions,
taking at least *two* from each group.

Group—A

1. What would be the effect of introducing electron withdrawing and/or electron donating group in carbazone formation of substituted aromatic aldehyde under the following conditions :

   (i) pH = 1.75, p = 0.91 in 25% EtOH at 25°C

   (ii) pH = 7.0, p = 0.07 in neutral solution 25°C

   (iii) pH = 4.0, p = 1, p = 0 in 25% EtOH at 25°c

   Show the Hammett plot in each case indicating the rate determing step of the mechanism of semicarbazone formation. 3+1+4

2. (a) "In case of hydrolysis of ethyl benzoate in 99.9% H_2SO_4, a non-linear Hammett plot is obtained 'p' value (1.4) with electron withdrawing group and 'p' value (–3.2) with electron donating group." Predict the mechanism of hydrolysis of methyl benzoate in each case.

   (b) The saponification (alkaline hydrolysis) of methyl benzoate has p = 2.229. What would be the effect of introducing electron withdrawing group in the rate of

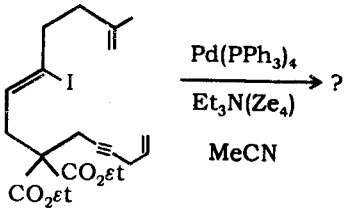
reaction. Show the mechanistic path way of hydrolysis indicating rate determing step. 4+4

3. (a) What is migratory insertion ? Show a migratory insertion with an example. 2

(b) Write down the product of the following reaction and show the important steps. (any *three*) 3×2

(i) $Me_3C- \equiv N \xrightarrow[\text{(ii) } Me_3C-C\equiv N \text{ (iii) } HCl,\ H_2O]{\text{(i) } CP_2Ti=} ?$

(ii)



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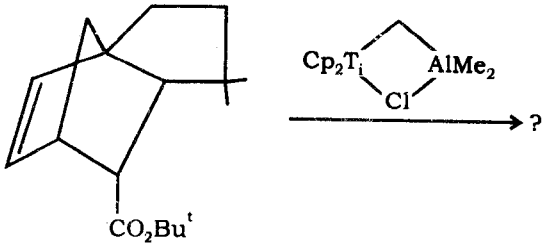
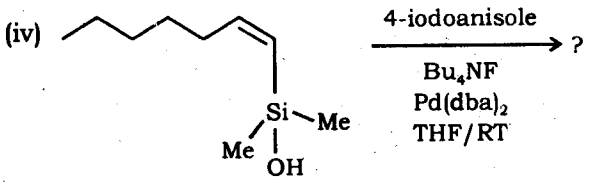
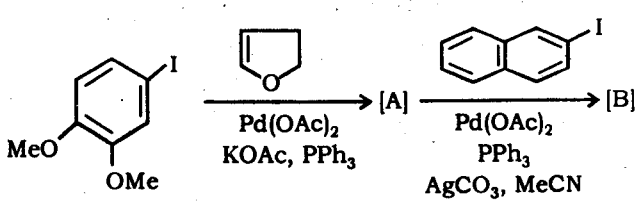
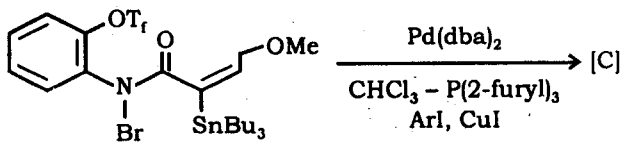


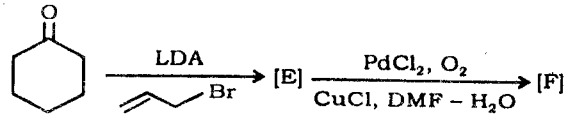
(iv) 

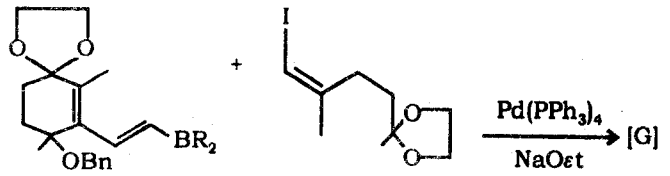
4. Identify A, B, C, D, E, F, G and H. 1×8

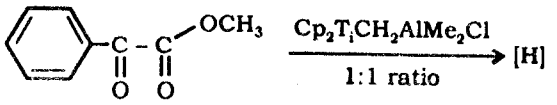
(a) 

(b) 

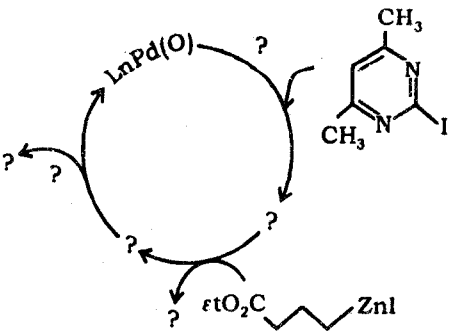
(c) $CH_2CH_2 - CH_2 - \overset{\overset{O}{\|}}{C} - Br \xrightarrow{(Ph_3P)_3RhCl}$ [D]

(d) 

(e) 

(f) 

5. Complete the following cycles :

(a) 

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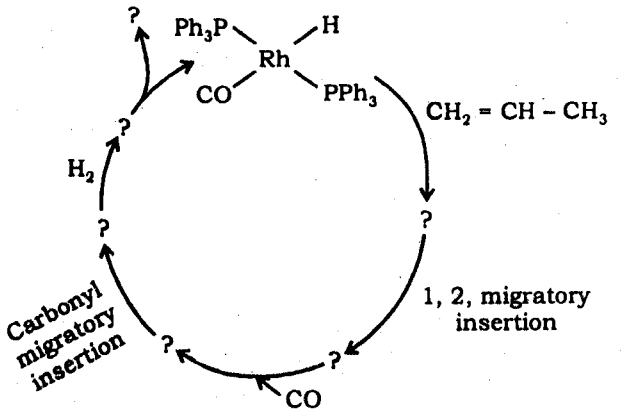
(b)



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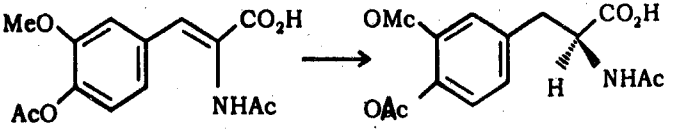
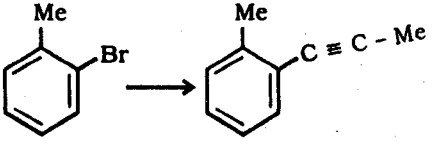
Group—B

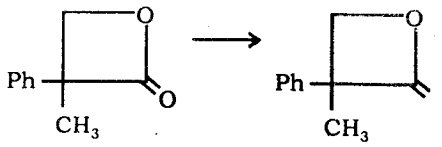
6. (a) Indicate appropriate reagents in each case. 1×4

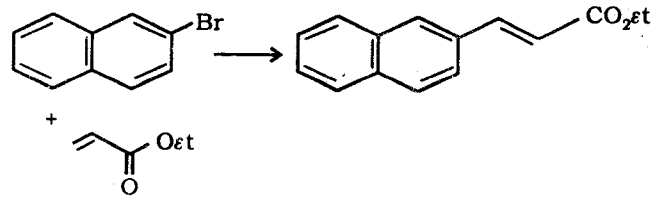
(i)



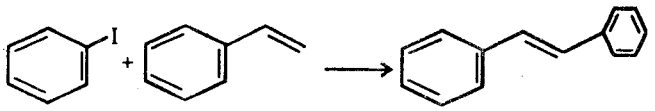
(ii)



(iii) 

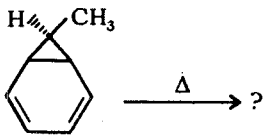
(iv) 

(b) (i) Transition metal complex exhibit special bonding with alkene — explain. 2×2

(ii) 

For the following transformation a base is needed explain why ?

7. Predict the products of the following reactions indicating Frontier-Orbital interactions in each case : 4×2
(Attempt any *four*)

(i) 

(iii) The following reaction proceeds with the mechanism as below :

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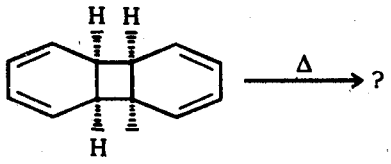
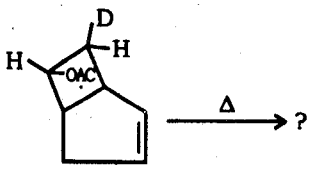
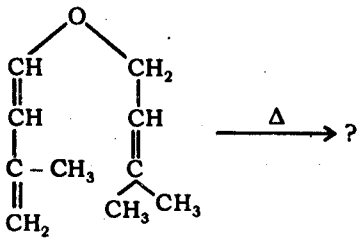
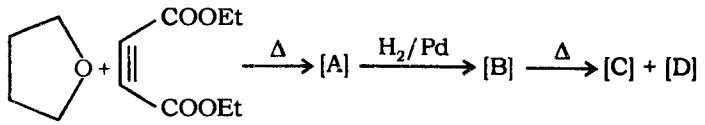
(ii) 

(iii) 

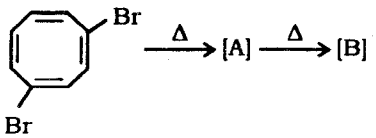
(iv) $Ch_2 = CH - \underset{\underset{OH}{|}}{CH} - C(CH_3)_2 - CH_2 - CH = CH_2 \xrightarrow[CuCl\,(cat)]{hv} ?$

(v) 

8. (a) What is (i, j) shift in sigmatropic reaction ? Define 'Supra' and 'antarafaial' migration with example ? Hence predict the product of the following reaction indicating Frontier Orbital interaction (F.O.I) :

(iii) 

Or



3+2+3

(*Inorganic Special*)

Answer any *five* questions, taking at least *two* from each group.

Group—A

1. (a) What do you mean by "magnetization" ? 2

(b) Use Hund's rules to determine the values of S, L and J in the ground state of a Dy^{3+} ion. Calculate the Lande' g-factor, total magnetic moment, and the magnetic moment along the external magnetic field direction. 4

(c) How does an antiferromagnetic substance differ from a diamagnetic substance ? 2

Explain indicating reasons in each case.

2. (a) What are the distinguishing features of ferro-magnetism ? 2

(b) What do you mean by "magnetically concentrated substance" ? 1

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

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

3. Derive the expression for volume susceptibility of diamagnetism. 8

4. Write short notes on :

(i) Direct metal-metal interaction. 2

(ii) Intra and intermolecular antiferromagnetism. 3

(iii) Spin-orbit interaction. 3

Group—B

5. (a) Derive the rate equation for associative mechanism for L_5MX complex where seven coordinated intermediate has appreciable life time. Consider Y as attacking molecule. 5

(b) What is the intimate mechanism (I) ? What are the differences between I_a and I_d mechanisms. 1+2

6. (a) Rate of anation of $[Ti(H_2O)_6]^{3+}$ by Y^{n-} at 13°C are given below :

Y^{n-} (N = 0)	$k(M^{-1} s^{-1})$	Y^{n-} (N = 0)	$k(M^{-1} s^{-1})$
$ClCH_2CO_2H$	6.7×10^2	NCS^-	8.0×10^3
CH_3CO_2H	9.7×10^2	$ClCH_2CO_2^-$	2.1×10^5
H_2O	8.6×10^3	$CH_3CO_2^-$	1.8×10^6

Comment on the variation of rate constants. In which mechanism the reactions will proceed ? 4

(b) Anation of $[Cr(NH_3)(H_2O)]$ is proceed through interchange mechanism. The entering groups, rate constants and activation parameters (at 50°C) are given below.

Entering ligant	$10^4 k(s^{-1})$	$\Delta H^{\#}(kJ/mol)$	$\Delta S^{\#}(Jmol^{-1}k^{-1})$
NCS^-	6.12	102	12
$HC_2O_4^-$	6.2	112	39
$C_2O_4^{2-}$	6.2	104	33
H_3PO_4	1.45	–	–
$H_2PO_4^-$	1.45	–	–
$[Co(CN)_6]^{3-}$	2.5	103	26
H_2O (exchange)	13.7	97	0

What do these data suggest about the intimate mechanism of these reactions ? 4

7. (a) Kinetic parameters for the K_2 path for the reaction

$[Pd(L)Cl]^+ + I^- \longrightarrow [Pd(L)I]^+ + Cl^{-1}$ at 25°C are given below :

L	$K_2(M^{-1}S^{-1})$	$\Delta V^{\#}$ (cm^3/mol)
dien	4446	–10.3
1, 4, 7-Me_3 dien	3542	–18.9
1, 4, 7-Et_3 dien	932	–11.1
1, 1, 4-Et_3 dien	21.2	–11.3

Suggest a mechanism with proper explanation. 4

(b) For the reaction

$[Pt(NH_3)_4]^{2+} + {}^{15}NH_3 \longrightarrow [Pt^{15}NH_3(NH_3)_3]^{2+} + NH_3$

the exchange of $^{15}NH_3$ is studied in aqueous solutions having $0.050 < [NH_3] > 0.50$, the rate law was found to be, rate = $(k_1 + k_2 [^{15}NH_3]) [Pt(NH_3)_4]^{2+}$, $k_1 = 3.9 \times 10^{10} S^{-1}$ and $k_2 = 9.5 \times 10^{-10}\ M^{-1}S^{-1}$.

(i) What does these data suggest about the exchange mechanism ?

(ii) Calculate the half life for ammonia exchange in 1.0M NH_3. 2+2

8. (a) Activation parameters for [illegible] reactions by V^{2+} are as follows :

Complex	$\Delta H^{\#}$ (kJ/mol)	$\Delta S^{\#}$ (J/molK)
$CoF(NH_3)_5]^{2+}$	46.4	-77.4
$CoCl(NH_3)_5]^{2+}$	31.4	-120
$CoBr(NH_3)_5]^{2+}$	30.1	-115
$CoI(NH_3)_5]^{2+}$	30.5	-103
$Co(N)_3(NH_3)_5]^{2+}$	48.9	-58.5
$Co(SO_4)(NH_3)_5]^{2+}$	48.5	-54.8

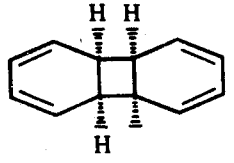
Assign proper mechanism for these reactions. 4

(b) Rate constants for some redox reactions at 25°C are given below :

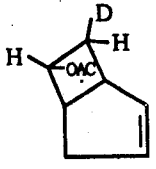
Reaction	Product	$k(M^{-1}s^{-1})$
$CoNCS(NH_3)_5]^{2+} + [Cr(H_2O)_6]^{2+}$	$[Cr(SCN)(H_2O)_5]^{2+}$	19
$CoN_3(NH_3)_5]^{2+} + [Cr(H_2O)_6]^{2+}$	$[CrN_3(H_2O)_5]^{2+}$	3×10^5
$CoSCN(NH_3)_5]^{2+} + [Cr(H_2O)_6]^{2+}$	71% $[Cr(NCS)(H_2O)_5]^{2+}$ 29% $[Cr(SCN)(H_2O)_5]^{2+}$	1.9×10^5

What can you say about the nature of the reactions ?

4

(ii) 

$\xrightarrow{\Delta}$?

(iii) 

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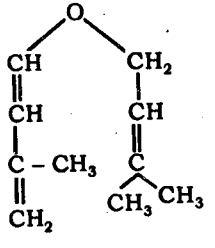
(v) 

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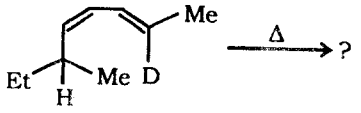
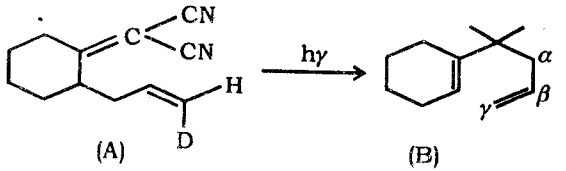


(b) Designate the expected position of '<u>D</u>' in the product ('<u>B</u>'). Do you expect '<u>D</u>' at 'α' or 'γ' position or both in the following photochemical reaction ?



(A) (B)

1+2+2+3

9. (i) Define 'Substituent constant' (σ) of Hammett equation.

(ii) What would be the effect in aromatic substitution reactions of the following groups having substitution constant (σ) values as :

$-OMe : \sigma_m + 0.12, \sigma_p = -0.27$

$-NO_2 : \sigma_m + 0.71, \sigma_p = +0.78$

Explain indicating reasons in each case.