

2017

M.Sc. 4th Semester Examination

CHEMISTRY

PAPER—CEM-402

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 *one* question from each group.

Group—A

Answer any *one* question.

1. (a) Explain what is meant by phenomenological co-efficients and discuss the significance of the cross co-efficients L_{ij} .

(Turn Over)

- (b) Explain what is meant by entropy production. Obtain the expression for the entropy production due to flow of matter. 3+(3+4)
2. (a) Obtain the expression for the entropy production for a flow in a system when an applied electrical field causes a pressure difference ΔP .
- (b) Write down the relations which relate an osmotic effect to a streaming effect. 8+2

Group—B

Answer any one question.

3. (a) What do you understand by the term 'lattice defect'? Why is it required in a perfect crystal? Show that the Frenkel defect is directly proportional to $(N N_i)^{1/2}$; where N is the number of ions and N_i is the number of interstitial sites.
- (b) How is a 'F' centre formed? Why is it unstable? (1+1+5)+(2+1)
4. (a) Define ' V_2 ' Centre? Discuss the mechanism of formation of a ' V_2 ' centre with a suitable example.

(b) Prove that

$$F_{hke} = \sum_{i=1}^N f_j e^{2\pi i(hl_j + kv_j + lw_j)}$$

Where the symbols have their usual meanings. (1+5)+4

Group—C

Answer any *one* question.

5. (a) Which type of average molecular weight is determined by sedimentation equilibrium method? Describe a suitable method for determination of average molecular weight of polymer by sedimentation equilibrium method.
- (b) The molar mass \bar{M}_w of haemoglobin is $64,450 \text{ gmol}^{-1}$. If it contains 0.35 mass percent of Fe, what is its minimum molar mass? Also, calculate the number of Fe atoms present in haemoglobin. (1+6)+3
6. (a) Describe the thermodynamics involved in Flory - Huggins model for a polymer solution.
- (b) What is Einstein - Smoluchowski equation? 8+2

Group—D

Answer any one questions.

7. (a) Why Hg becomes a super conductor below 4.2 K ?
- (b) Why the conductivity of a semiconductor increases with increase in temperature ?
- (c) Define Hall mobility ?
- (d) The density of LiF is 2.601 g/cc. The (III) first order reflection in the X-ray diffraction from LiF occurs at $8^{\circ}44'$ when X-rays of wavelength 70.8 pm are used. If there are four LiF molecules per unit cell, calculate Avogadro's number. LiF crystallizes in the cubic system. Li = 6.939, F = 18.998. 3+2+2+3
8. (a) Define partial structure factor of a polymer.
- (b) Why proteins and nucleic acids are called polymer ?
- (c) How are the different types of average molecular weight of a real polymer sample related to each other ?

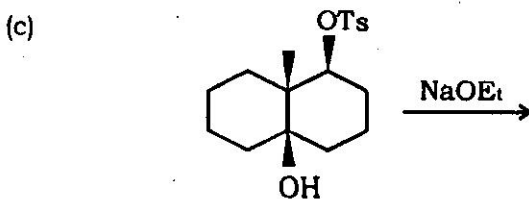
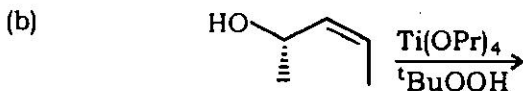
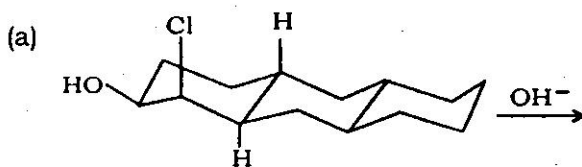
- (d) Calculate the vapour pressure lowering, the boiling point elevation and osmotic pressure of a 1.0 mass percent solution of polystyrene ($\bar{M}_n = 50.0 \text{ kg mol}^{-1}$) in toluene ($\bar{M}_m = 92.15 \text{ g mol}^{-1}$) at 25°C and comment on your result. At 25°C , for toluene $K_b = 3.33 \text{ K m}^{-1}$ and the vapour pressure of pure toluene is 3760 Pa. 2+2+2+4

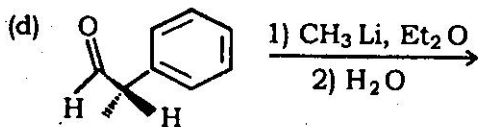
(Organic Special)

Answer any *five* questions,

1. Draw the 3d structures for the following conformers and show in them different steric interactions including their optical properties
 - (a) cis-transoid-cis perhydroanthracene
 - (b) trans-cisoid-cis perhydrophenanthrene
 - (c) 9,10 - dimethyl cis decalin
 - (d) trans-transoid-trans diphenic acid

2. Give the products of the following reactions. Where more than one product is likely to be formed in significant yield, indicate which will be the major product and also predict the mechanism of the reaction involved.





8

3. Write in brief with one example in each case :

(a) Allylic 1,2-strain

(b) 2-alkylketone effect

(c) 3-alkylketone effect

(d) Allylic 1,3-strain

8

4. Write in brief about the following terms : (Any Four) :

4×2

(a) ORD

(b) CD

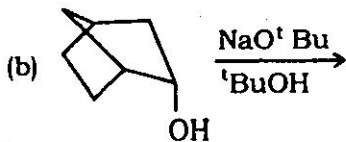
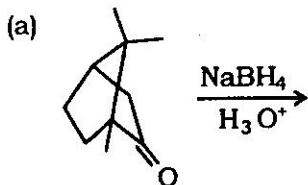
(c) Cotton Effect (CE)

(d) Predict as per octant rule, positive or negative, of
9-Methyl-deca-3-ones

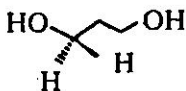
(e) Felkin Model

5. Write all the possible stereoisomers of perhydrophenanthrenes and correlate them with perhydrodiphenic acids by epimerization protocols. 8

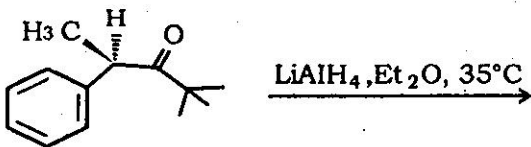
6. Predict the product with appropriate mechanism and product's stereochemistry : 4×2



7. (a) Assign Pro-R and Pro-S to the enantiotopic protons of the following compound. 4×2



- (b) Predict the product with stereochemistry and explanation.

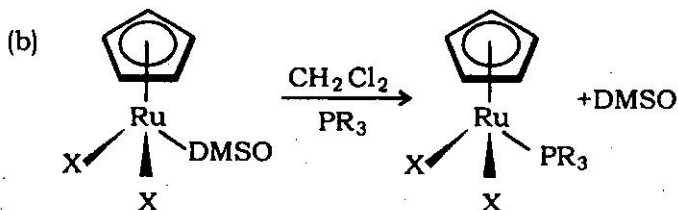


(Inorganic Special)

Answer any *four* questions.

1. (a) Derive rate law for the dissociative mechanism for R-X complex where five-coordinated intermediate has an appreciable lifetime. Consider Y as an attacking molecule.

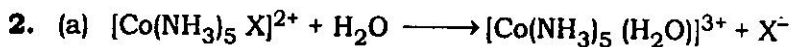
If $K_2 [Y]$ is very large or very small what will be the effect on rate law. 3+2



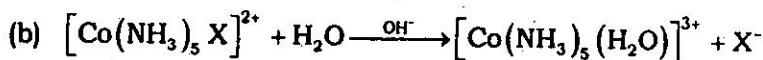
The above reaction shows following observations

- (i) With excess PR_3 & DMSO a first order reaction is followed in both PR_3 and Ru .
- (ii) K_0 vs PR_3 gives saturation kinetics.
- (iii) Addition of excess DMSO slow down the reaction.

Comment on these observations with proper explanation. 5



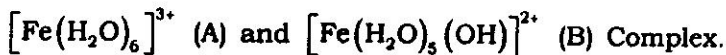
In the above reaction, rate of aquation varies as $\text{X} = \text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$ but when the complex is changed as $[\text{Co}(\text{CN})_5 \text{X}]^{3-}$ the rate of the aquation is reversed i.e. $\text{X} = \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$. Explain this observation. 4



Propose a base catalyzed mechanism of this reaction. 3

(c) What do you mean by acid catalyzed Pseudo substitution? Explain with suitable Example. 3

3. (a) The variation of rate of octahedral ligand substitution in



(B) With other ligands (Y_n) are given below :

Y^n	$K(\text{M}^{-1}\text{S}^{-1})$ for A	$K(\text{M}^{-1}\text{S}^{-1})$ for B
SO_4^{2-}	1.1×10^5	2.3×10^3
Cl^-	5.5×10^3	4.8
Br^-	2.6×10^3	1.6
NCS^-	5.1×10^3	90

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

- (b) Rate constant for acid aquation reaction of $[\text{Co}(\text{NH}_3)_5\text{X}]^{n+}$ and anation by Y^- of $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ are given below as table - 1 and 2 respectively

Table - 1

Complex	$K(\text{S}^{-1})$
$[\text{Co}(\text{NH}_3)_5(\text{OP}(\text{OMe}))_3]^{3+}$	2.5×10^{-4}
$[\text{Co}(\text{NH}_3)_5(\text{NO}_3)]^{2+}$	2.4×10^{-5}
$[\text{Co}(\text{NH}_3)_5\text{I}]^{2+}$	8.3×10^{-6}

Table - 2

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

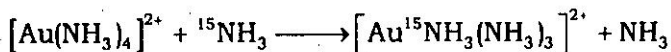
Comment on the variation of the rate constant in these two cases for aquation and anation. Also propose which of the above mechanisms is favourable. 4

(c) What are the requirements for labile and inert systems ?

2

4. (a) Exchange of $^{15}\text{NH}_3$ in $[\text{Au}(\text{NH}_3)_4]^{2+}$ studied in aqueous solution having $0.050 < [^{15}\text{NH}_3] < 0.50$. The rate law was found to be, $\text{rate} = (k_1 + k_2 [^{15}\text{NH}_3])[\text{Au}(\text{NH}_3)_4]^{2+}$.

$$k_1 = 3 \times 10^{-6} \text{S}^{-1} \text{ and } k_2 = 1.69 \times 10^{-1} \text{M}^{-1} \text{S}^{-1}.$$



(i) What do the data suggest about the exchange mechanism ?

(ii) Calculate the half-life for ammonia exchange in 1.0M $^{15}\text{NH}_3$. 2+2

(b) Write down an inner and outer sphere mechanism for Cr^{2+} reduction of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$. 3

(c) Some volume activation for base hydrolysis is given below. Rationalize the trends observed. 3

Complex	ΔV^* (cm ³ / mol)
$[\text{Co}(\text{NH}_3)_5\text{O}=\text{C}(\text{NMe}_2)\text{H}]^{3+}$	+43.2
$[\text{Co}(\text{NH}_2\text{Me})_5\text{Cl}]^{2+}$	+32.7
$[\text{Co}(\text{NH}_2\text{Et})_5\text{Cl}]^{2+}$	+31.1
trans - $[\text{Co}(\text{en})_2\text{Cl}_2]^+$	+24.8
Cis - $[\text{Co}(\text{en})_2\text{Cl}_2]^+$	+27.9

5. (a) Write short notes on :
- (i) Half wave potential
- (ii) Polarographic maxima 2+2
- (b) Why is oxygen to be expelled from the polarographic cell before the experiment ? 3
- (c) State the application of polarographic method for analysis. 3
6. (a) What is cyclic voltammetry ? Why it is called so ? 1+1
- (b) Write down the cyclic voltammogram of the insecticides parathion. 4
- (c) State and explain the application of cyclic voltammetry. 4

7. Give schematic diagram alongwith its working principle of

(a) TGA instrument.

(b) DSC instrument.

5+5
