2019

M.Sc.

4th Semester Examination

CHEMISTRY

Paper - CEM 402

(Special Paper)

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.

PHYSICAL SPECIAL

Group A

Answer any *four* from the following questions : 2×4=8

1. Why number Average Molecular wieght $(\bar{M}_n)$ is determined by measuring the colligative property osmotic pressure ? 2

2. What is 'atomic scattering factor' of an atom ? 2

3. Why Zimm plot is more accurate than Debye plot for the determination of mass average molecular weight of a polymer ? 2

4. Define the term 'Chemical Affinity'. 2

5. Why F-enter is more stable than F'-center ? 2

6. Write down the relations which relate an osmotic effect to a streaming effect ? 2

7. The intrinsic viscosity of myosin is 217 cm^3g^{-1}. Calculate the approximate concentration of myosin in water which would have as relative viscosity of 1.5. 2

8. Define weight average molecular weight $\left(\bar{M}_w\right)$ of a macromolecule. 2

Group B

Answer any *four* from the following qeustions: 4×4=16

9. Define intrinsic viscosity. How does the molar mass of a polymer is determined by viscosity method ? 1+3

10. What is meant by phenomenological co-efficients ? Discuss the significance of the cross co-efficients. 2+2

11. Why a structured band is observed when *KBr* crystal is heated with excess bromine gas ? 4

12. Given the density of *KBr* is 2.75g/cc. and that the length of an edge of a cubic unit cell is 654 pm, determine how many formula units of *KBr* there are in a unit cell ? Does the unit cell have a *NaCl* or *CsCl* structure ? 3+1

13. Discuss the working principle of a diode (n-p junction). 4

14. Equal numbers of molecules with $M_1 = 10,000$, $M_2 = 50,000$ and $M_3 = 1,00,000$ are mixed. Calculate the polydispersity index (PDI) of the polymer sample and comment on your result. 3+1

15. Obtain the expression for entropy production for flow of matter. 4

16. Define Hall-effect. What is Hall mobility and Hall potential ? 2+1+1

Group C

Answer any *two* from the following questions: 8×2=16

17. Obtain the expression for the rate of entropy production for the transfer of material when an applied electric field causes a pressure difference at equilibrium and hence obtain an expression for streaming potential in terms of appropriate phenomenological co-efficients. 6+2

18. Define 'Frenkel defect' in a crystal and hence derive the expression for the number of Frenkel defect in a lattice. 2+6

19. Obtain the suitable expression used for the determination of the weight average molecular weight of a polymer by light scattering method. 8

20. (a) Discuss the sedimentation Velocity method for the determination of molar mass of a polymeric molecule.

    (b) At 20°C, the diffusion co-efficent, the molar mass and specific volume of haemoglobin are $6.9\times10^{-11}m^2s^{-1}$, 64,500 g mol^{-1} and $0.75cm^3g^{-1}$, respectively. Calculate its frictional ratio and comment on your result. The

co-efficient of viscosity of water at the given temperature is 1.005 cP. 5+3

INORGANIC SPECIAL

Group A

Answer any *four* questions from the following : 2×4=8

1. (a) What are the requirements for labile and inert system ? 2

   (b) Write the basic principle of cyclic voltammetry ? 2

   (c) What do you mean by diffusion current ? 2

   (d) Define migration current ? 2

   (e) Why the conjugate base is active in the base catalyzed reaction ? 2

   (f) Acid catalyzed aquation of Nickle (II) complex of phenanthroline is slower than that of the bipyridine complex. Explain. 2

(g) Generally $\left[Fe(CN)_6\right]^{3-}$ complexes are inert, but in presence of Hg^{2+} it readily get hydrolyzed. Explain. 2

(h) What do you mean by η_{pt}-scale ? 2

Group B

Answer any *four* questions from the following : 4×4=16

2. (a) Write short notes on : 2+2

(i) Half wave potential

(ii) Polarografic Maxima.

(b) Why is oxygen to be expelled from the polarographic cell before the experiment ? 4

(c) State and explain the application of cyclic voltammetry. 4

(d) Give a instrumental set up for modern DSC instruments. 4

(e) Write down the working principal of a TGA instrument along with the flow diagram of the instrument. 4

(f) What do you mean by acid catalyzed pseudo substitution reaction ? Explain with a sutitable example. 4

(g) Activation parameters for some reduction by V^{2+} are follows :

complex	$\Delta H^{\neq}$ (kJ / mol)	$\Delta S^{\neq}$ (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 outer or inner-sphere mechanism for each of these reactions. 4

[Turn Over]

(h) Rate constant for some redox reaction at 25°C are given below.

Reaction	Product	$k\left(M^{-1}s^{-1}\right)$
$CoNCS(NH_3)_5]^{2+} + Cr^{2+}$	$CrSCN^{2}$	19
$CoN_3(NH_3)_5]^{2+} + Cr^{2+}$	CrN_3^{2+}	$3x10^5$
$CoSCN(NH_3)_5]^{2+} + Cr^{2+}$	$71\%CrNCS^{2+} + 29\%CrSCN^{2+}$	$1.9x \times 10^5$

What can you conclude about the inner or outer sphere nature of the reactions ? 4

Group C

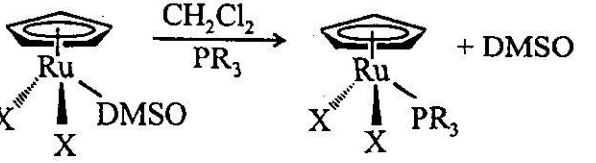
Answer any *two* questions from the following : 8×2=16

3. (a) Consider the following reaction scheme. 4

$$MX_6 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MX_5 + X$$

$$MX_5 + Y \xrightarrow{k_2} MX_5Y$$

where MX_5 has appreciable life time. Derive the rate law for the above reaction scheme if $K_2[Y]$ is very large or very small.

(b) 

The above reaction shows the following observations

(i) In presence of excess PR_3, a first order reaction is seen.

(ii) k_0 vs $[PR_3]$ gives saturation kinetics

(iii) Addition of excess DMSO reduces the rate of the reaction.

Comment on these observation with proper explanations.

4. (a) $\left[Co(NH_3)_5X\right]^{2+} + H_2O \rightarrow$

$$\left[Co(NH_3)_5(H_2O)\right]^{3+} + X^-$$

In the above reaction the rate of aquation varies as $X = I^- > Br^- > Cl^- > F^-$ but when the complex is $\left[Co(CN)_5X\right]^{3-}$, the rate of the aquation is reversed i.e.

$X = F^- > Cl^- > Br^- > I^-$. Explain. 4

(b) $\left[Co(NH_3)_5X\right]^{2+} + H_2O \xrightarrow{OH^-}$

$\left[Co(NH_3)_5(H_2O)\right]^{3+} + X^-$

Propose a mechanism for the reaction. 4

5. (a) Consider the following table : 4

ligand	$k\left(M^{-1}s^{-1}\right)$ for $[Fe(H_2O)_6]^{3+}$	$k\left(M^{-1}s^{-1}\right)$ for $\left[Fe(H_2O)_5(OH)\right]^{2+}$
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 $\left[Fe(H_2O)_6\right]^{3+}$ and $\left[Fe(H_2O)_5(OH)\right]^{2+}$, based on the electronic charge with proper explanation.

(b) Rate constants for acid catalysed aquation of $\left[Co(NH_3)_5X\right]^{n+}$ are given below. 4

Complex	$k(s^{-1})$
$\left[Co(NH_3)_5(OP(OMe)_3)\right]^{3+}$	2.5×10^{-4}
$\left[Co(NH_3)_5(NO_3)\right]^{2+}$	2.4×10^{-5}
$\left[Co(NH_3)_5I\right]^{2+}$	8.3×10^{-6}
$\left[Co(NH_3)_5(H_2O)\right]^{3+}$	5.8×10^{-6}

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

Y	$K(s^{-1})$
H_2O	100×10^{-6}
SO_4^{2-}	24×10^{-6}
Cl^-	21×10^{-6}
NCS^-	16×10^{-6}

Comment on the variation of rate constants in aquation and anation reactions. By which mechanism reactions proceed ?

[Turn Over]

6. (a) Exchange of $^{15}NH_3$ in $\left[Pt(NH_3)_4\right]^{2+}$ studied in aqueous solutions having

$0.050 < \left[^{15}NH_3\right] > 0.50$ the rate law was found to be, rate =

$$\left(k_1 + k_2\left[^{15}NH_3\right]\right)\left[Pt(NH_3)_4\right]^{2+}.$$

$k_1 = 3.9 \times 10^{-6} s^{-1}$ and

$k_2 = 9.5 \times 10^{-1} M^{-1} s^{-1}$.

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

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

(ii) Calculate the half-life for ammonia exchange in $1.0M\ NH_3$. 4

(b) Volumes of activation for base hydrolysis of Co III complexes is given below. Rationalize the trend.

Complex	$\Delta V^{\neq}(cm3/mol)$
$\left[Co(NH_3)_5(O=C(NMe_2)H)\right]^{3+}$	+43.2
$\left[Co(NH_2Me)_5Cl\right]^{2+}$	+32.7
$\left[Co(NH_2Et)_5Cl\right]^{2+}$	+31.1
$trans-\left[Co(en)_2Cl_2\right]^{+}$	+24.8
$Cis-\left[Co(en)_2Cl_2\right]^{+}$	+27.9

4

ORGANIC SPECIAL

1. Answer any *four* questions from the following : 2×4=8

(a) Draw the 3d structures for the following conformers and show in them different steric interactions and comment on their optical properties.

(i) *cis-transoid-cis* perhydroanthracene

(ii) *trans-cisoid-cis* perhydrophenanthrene

(iii) 9,10-dimethyl *cis* decalin

(iv) *trans-transoid-trans* perhydrophenanthrene

(b) Write in brief with one example in each case :

(i) Allylic 1,2-strain

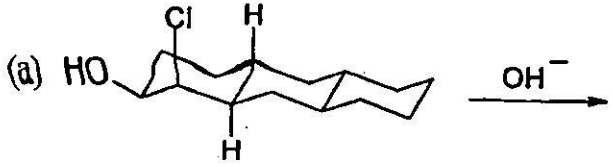
(ii) 2-alkylketone effect

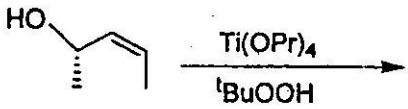
(iii) 3-alkylketone effect

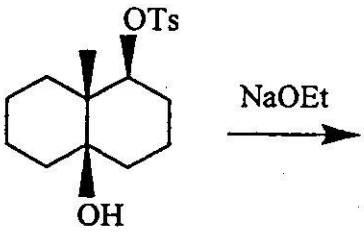
(iv) Allylic 1,3-strain

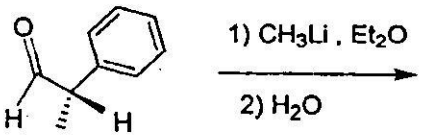
2. Answer any *four* questions from the following : 4×4=16

2 (a-d) 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.

(a) 

(b) 

(c) 

(d) 

(e) How CD curves can be used to determine the configuration of a compound. Illustrate your answer with an example.

(f) Discuss the usefulness of plain curves.

(g) Write briefly about variation of sign of *CE* with ring size.

(h) Explain "M" and "P" type chirality as per helicity rule with one example.

[Turn Over]

3. Answer any *two* questions from the following : 8×2=16

(a) Write in brief about the following : 2×4

(i) Drude equation

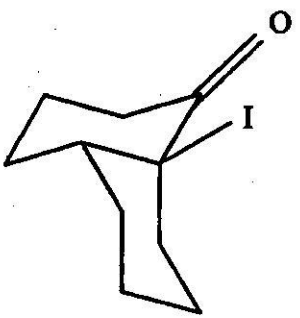
(ii) Circular birefringence

(iii) Cotton Effect (CE)

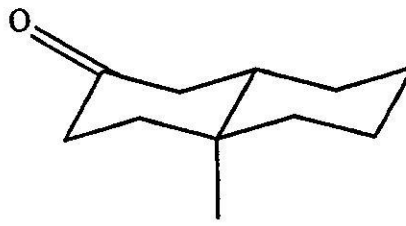
(iv) Sector rule

(b) Explain the followings : 2×4

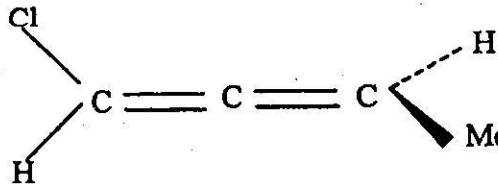
(i) Predict the Cotton Effect (CE) of the following compound as per haloketone rule with reasoning.



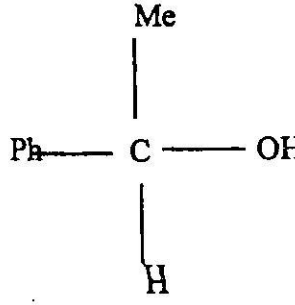
(ii) Applying the Octant Rule predict the CE of the following compound.



(iii) Using Lowe's rule predict the appropriate configuration of the following compound.



(iv)



[Turn Over]

(c) State and derive Winstein-Holness and Eliel equations. What are the drawbacks of these equations ? 8

(d) (i) *cis*-2-decalone enolise towards C-1 whereas *trans*-2-decalone enolises at C-3 Explain.

(ii) Discuss axial halokenone rule with an example.
