2021

CHEMISTRY

PAPER-II

Time Allowed — 3 Hours *Full Marks — 200*

If the questions attempted are in excess of the prescribed number, only the questions attempted first up to the prescribed number shall be valued and the remaining ones ignored.

Answer may be written either in ***English*** *or in* ***Bengali*** *but all answers must be in one and the same language.*

Section-I

This Section comprises 15 questions in three Groups. Answer *any ten* questions taking *at least three* questions from each Group.

Group-A

1. Which among the following bidentate ligands would you expect to give innermetallic hexa-coordinated complexes with transition metals M^{3+} ions? $H_2N–CH_2–COOH$, HOOC–COOH, $H_3C–CO–CH_2–CO–CH_3$. Justify your answer. 4

2. Explain the phenomenon due to which $Ni(CO)_4$ has got stability despite zero valent state of Nickel. 4

3. The enthalpy of hydration of the Fe^{2+} ion is 11·4 kcal/mol higher than would be expected if there were no crystal field stabilisaton energy. Assuming the aqua complex to be high spin, estimate the magnitude of Δ_0 for $Fe(H_2O)_6^{2+}$. 4

4. The aqueous solution of $\left[Ti(OH_2)_6\right]^{3+}$ show a maximum absorption around 20,300 cm^{-1} in its electronic spectrum. Express the band position in nm. Has the complex ion visible in colour? 4

5. Evaluate the ground state term for a free metal ion with $3d^7$ configuration. 4

Group-B

6. Define partial molar volume. Can it be negative? Justify your answer. 4

7. Draw a potential energy profile for an exothermic reaction clearly identifying the activation energy and transition state. In the same diagram indicate the effect of addition of catalyst to the system. 4

8. Write Arrhenius equation for the temperature dependence of the rate constant identifying all the parameters. What will be the dimension of the pre-exponential factor for a second order reaction? 4

9. Define number and weight-average molecular weights of polymers. Name one experimental technique each to determine them. 4

10. State the selection rules for rotational transition of a symmetric rotor. 4

Group-C

11. Write a conformational structures for all of the stereoisomers of 1,3-diethylcyclohexane. Label pairs of enantiomers and meso compounds if they exist. 4

12. Predict the stereochemistry of the thermal electrocyclic ring closure of (2E,4Z,6E)–2,4,6-octatriene to 5,6-dimethyl-1,3-cyclohexadiene. 4

13. An enantiomerically pure sample of (*S*)–(+)–2-butanol shows a specific rotation of +13·52°. The mixture of 2-butanol enantiomers shows a specific rotation of +6·76°. What is the percent enantiomeric excess of this sample? 4

14. *trans*-1,2-dimethylcyclopropane is more stable than that of its *cis* isomer. Use Newman projection to explain this observation. 4

15. Draw three dimensional representation(s) of 1-chloro-3-methyl-1,2-pentadiene. Is this compound chiral? Justify your choice. 4

Section-II

This Section comprises *six* questions in three Groups. Answer *any four* questions taking *at least one* question from each Group.

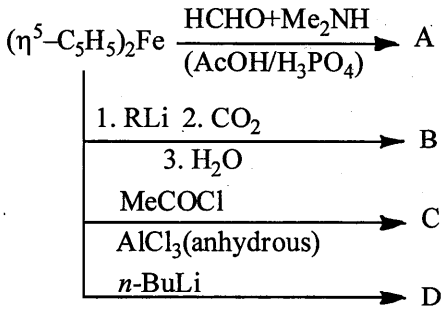
Group-A

1. (a) One red coloured co-ordination compound (A) slowly transforms into another coordination compound (B), that is yellow in colour. Elemental analysis of both A and B give the same composition $Co:NH_3:Cl:NO_2 = 1:5:2:1$. One millimole of each of A and B on treatment with an excess of $AgNO_3$ solution in dilute HNO_3 medium give two millimole of AgCl.

   Write the possible co-ordination formula of A and B, give their IUPAC names and rationalize the transformation A→B. 8

   (b) Explain the biological functions of haemoglobin and myoglobin stating the role of the metal ion(s) present at their active sites. 4+4=8

(c) Identify the compounds A, B, C and D in the following reaction sequence: 8



(d) Using 18-electron rule as guide, find the number (x) of CO ligands in the following compounds: 3+3=6

(i) $\left[Co(\eta^5\text{-}C_5H_5)(CO)_x\right]$

(ii) $Fe(CO)_x(NO)_2$

(e) Explain the following terms with an example in each: 4+3+3=10

(i) Insertion reaction (ii) Oxidative addition reaction (iii) Reductive elimination reaction

2. (a) Construct the orgel diagram for $[CrF_6]^{3-}$ and assign the three electronic transition bands found at 14900 cm^{-1}, 22400 cm^{-1} and 34800 cm^{-1}. Find out the value of 'Dq' amount. 8+2=10

(b) What is *trans* effect? Outline a synthetic route for the synthesis of *cis* and *trans* $[Pt(NH_3)(NO_2)Cl_2]^-$.

(Given: The *trans* directing influence is $NH_3 < Cl^- < NO_2^-$) 4+3+3=10

(c) Chromium (II) fluoride and manganese (II) fluoride both have a central metal ion surrounded by six fluoride ligands. The Mn–F bond lengths are equidistant but four of the Cr–F distances are long and other two are short. Provide an explanation. 4

(d) The complexes $[Mn(H_2O)_6]^{2+}$, $[Fe(H_2O)_6]^{3+}$, $[MnCl_4]^{2-}$ and $[FeCl_4]^-$ all have magnetic moments of nearly 5·92 B.M. What does this tell you about the geometric and electronic structures of these complexes? Why is the spin-only formula so precise in these cases? 6

(e) Draw the molecular structure of the following complexes: 1·5×4=6

(i) *cis*-dichlorotetracyanochromate (III)

(ii) *mér*-triamminetrichlorocobalt (III)

(iii) *trans*-dichlorobis (trimethylphosphine) palladium (II)

(iv) *fac*–triaquatrinitro cobalt (III)

(f) Explain the term 'Chelate effect'. Why is it called entropy effect? 4

Group-B

3. (a) Consider the expression:

$$F = C - P + 2$$

What is F? How is C defined? For a NaCl soution what will be C? Justify your answer. 6

(b) What is half-life of a reaction? Obtain the expression of half-life for a second order reaction. 4

(c) For the reaction

$$A + B \rightleftharpoons I \rightarrow P$$

obtain an expression for $d[P]/dt$ using a steady state approximation. 6

(d) Draw Jablonski diagram. Describe the mechanism of fluorescence. In what respects is a fluorescence spectrum not the exact mirror image of the corresponding absorption spectrum? 12

(e) For a stepwise polymerization reaction obtain an expression for degree of polymerization as a function of reacted monomers.

Consider a polymer formed by a stepwise process with a rate constant $1{\cdot}00\ dm^3\ mol^{-1}s^{-1}$ and an initial monomer concentration of $[A]_0 = 4{\cdot}00\times10^{-3}\ mol.dm^{-3}$. Calculate the degree of polymerization at time $t = 1{\cdot}5\times10^4 s$. 12

4. (a) What is Lambert-Beer law? Define molar extinction coefficient and obtain its units in SI system.

A radiation of wavelength 280 nm was passed through 1·0 mm of an aqueous solution containing a chromophore at a concentration of 0·50 m mol. dm^{-3}. The light intensity is reduced to 54% of its initial value. Calculate the molar extinction coefficient of the chromophore. What would be the transmittance through a cell of thickness 2·0 mm? 12

(b) Collision theory depends on knowing the fraction of molecular collision having at least the kinetic energy E_a along the line of flight. What is this fraction when E_a = 100 kJ/mol at 300 K? Calculate the percentage increase in fractions when the temperature is raised by 10 K. 5

(c) Derive the rate law for the decomposition of Ozone in the reaction $2O_3(g) \rightleftharpoons 3O_2(g)$ on the basis of the following mechanism: 6

$$O_3 \rightarrow O_2 + O \quad K_a$$

$$O_2 + O \rightarrow O_3 \quad K'_a$$

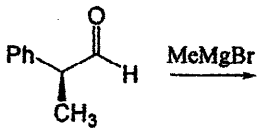
$$O + O_3 \rightarrow O_2 + O_2 \quad K_b$$

(d) What is chemical potential of a pure substance? What happens to it when (i) temperature is raised, (ii) pressure is raised? Justify your answer. The standard molar entropy of liquid water at 100°C is $86 Jk^{-1}mol^{-1}$ and that of water vapour at the same temperature is $196\ Jk^{-1}\ mol^{-1}$. What is the effect of increasing the temperature by 1·0 K? Comment on the spontaneity of the vapourization process. 10

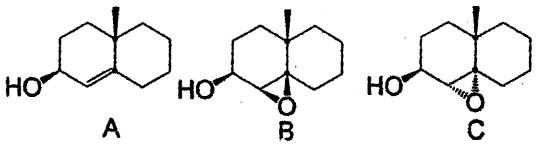
(e) What is physisorption? Define fractional coverage. For a spontaneous absorption process the enthalpy of absorption is negative. — Justify or criticize this statement. 7

Group-C

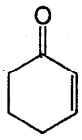
5. (a) Draw the stereochemistry of the major organic product formed in the following reaction. Justify your choice. 5

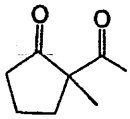


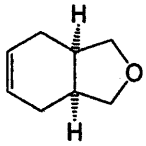
(b) Show how would you convert the allylic alcohol A into compounds B and C. 6



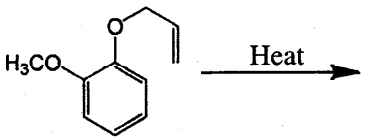
(c) Show giving reasonable mechanism how the following compounds might be synthesized: 15

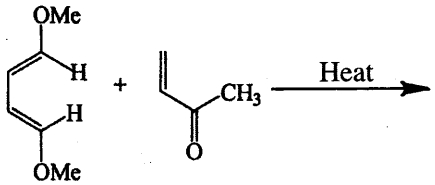
(i)  from C_6H_5OMe

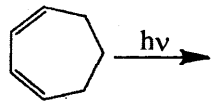
(ii)  OC_2H_5 from diethyl hexanedioate

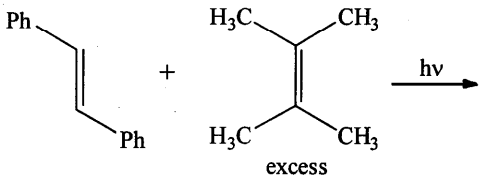
(iii)  from butadiene

(d) Predict the product formed in each of the following reaction. Explain their formation. 14

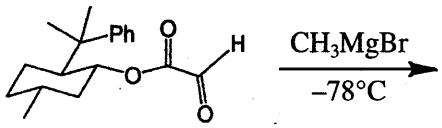
(i) 

(ii) 

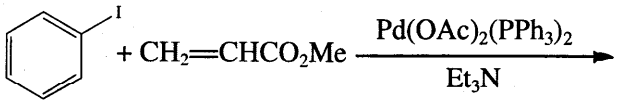
(iii) 

(iv) 

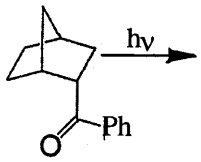
6. (a) Draw the stereochemistry of the major organic product formed in the following reaction. Justify your choice using Prelog's rule. 5

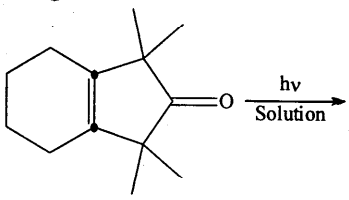


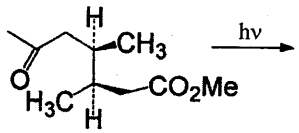
(b) Predict the structure of the product(s) formed in the following reaction and give a mechanism. 5

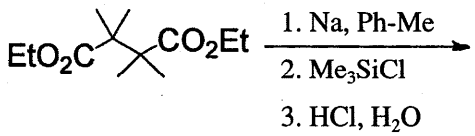


(c) Write the product(s) in the following reactions. Explain their formation. 20

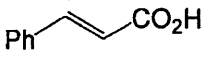
(i) 

(ii) 

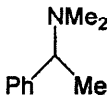
(iii) 

(iv) 

(d) Outline a synthetic route for each of the following compounds. Propose plausible mechanism. 10

(i) 

using PhCHO & Ac_2O

(ii) 

from PhCOMe
