HCS (Ex.) 2003

7

Code—04

CHEMISTRY

Time Allowed : 3 Hours *Maximum Marks :* 150

Note : Attempt any *Five* questions. All questions carry equal marks. Q. No. **1** is compulsory. Answer *two* questions from Part I and *two* questions from Part II. The parts of the same question must be answered together and must not be interposed between answers to other questions.

1. Write critical notes on any *four* of the following : **(4×7½=30)**

(a) Explain bonding in $Ni(CO)_4$, $[Fe(CN)_6]^{4-}$ and $[Co(NH_3)_6]^{3+}$ using valence bond approach.

(b) Imperfections in crystals.

(c) Application of second law of thermodynamics in relation to the entropy changes in an ideal gas.

P.T.O.

(d) Mechanism of Reimer-Tiemann reaction.

(e) Factors which stabilise carbanions and the methods of generation of carbanions.

(f) Chemical shift and coupling constant.

Part I

2. (a) Write the electronic configuration of O^{2-} and molecular orbital representation of He_2^+.

(b) Draw the *d*-orbital splitting pattern for a transition metal ion in a tetrahedral complex.

(c) Write the reduction of $KMnO_4$ in acidic, neutral and alkaline media and also determine the ratio of changes in the oxidation state of Mn in these three media. **(30)**

3. (a) Half-life period of a chemical reaction is 50 minutes. The half-life period of the reaction is doubled on doubling the concentration of the reactant. Calculate the order of the reaction.

(b) Calculate the molecular translational partition function for 1 mole of nitrogen gas at 27°C and 1 atm assuming the gas to behave ideally (given, $h = 6{\cdot}625 \times 10^{-27}$ erg sec and $k = 1{\cdot}38 \times 10^{-16}$ erg deg^{-1}).

(c) (i) Derive the following expression for the change in entropy of an ideal gas :

$$\Delta S = C_V \log \frac{T_2}{T_1} + R \log \frac{V_2}{V_1}.$$

(ii) Explain reasons for high and low quantum yield reactions. (30)

4. (a) EMF of the following cell at 25°C is 0·56V.

Pt; Fe^{2+} (0·5 M), Fe^{3+} (0·75 M) ||

$Cr_2O_7^{2-}$ (2·0 M), Cr^{3+} (4·0 M), H^+ (XM), Pt.

Calculate the value of X if :

$E^o_{(Fe^{3+}/Fe^{2+})} = 0{\cdot}77V$ and

$E^o_{(Cr_2O_7^{2-}/Cr^{3+})} = 1{\cdot}33V$.

(b) How will you calculate bond order in CO molecule with the help of molecular orbital theory ? Explain also negligible dipole moment of the molecule with this theory.

(c) (i) Give the resonance structures of NO_3^- and CO_3^{2-}.

(ii) Explain the term 'Chemical Potential' ? Obtain an expression for the variation of chemical potential with temperature. (30)

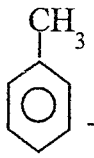
Part II

5. (a) Explain kinetic and thermodynamic control of products in elimination reactions with suitable examples.

(b) Write the stereoelectronic requirements of Beckmann rearrangement. Discuss the mechanism of this reaction with suitable example and describe its synthetic importance.

(c) Draw an orbital picture to account for the Claisen arrangement. (30)

6. (a) Complete the following reactions by writing the intermediates and final products :

(i)  $\xrightarrow{CrO_2Cl_2}$ (A)

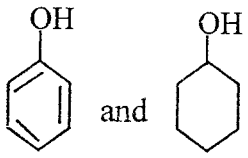
$\xrightarrow{\text{Aq.Conc.KOH}}$ (B) + (C)

(ii) $CH \equiv CH \xrightarrow[Hg^{2+}]{H_2SO_4\ (dil)}$ (A) $\xrightarrow{O}$ (B)

$\xrightarrow{SOCl_2}$ (C) +  $\longrightarrow$

$\xrightarrow{\text{Anhydrous}\,AlCl_3}$ (D)

(b) How do the IR spectra of the following compounds differ ?

(i)  and

(ii) C_6H_5CHO and

$C_6H_5 - CO - CH_2 - CO - CH_3$

(c) Explain number and weight average molecular weight of polymers. Describe viscosity measurement method to determine molecular weight of polymer. (30)

7. (a) Describe preparations and properties of polystyrene and teflon.

(b) Explain the following :

(i) Singlet and triplet states in electronic spectra.

(ii) Woodward-Fieser Rules

(iii) Isotope effect and its appliations

(c) Describe the principles of NMR and discuss the applications of HNMR to simple organic molecules. (30)