

This question paper contains 8 printed pages]

**CODE : FRO-2017**

**CHEMISTRY**

*Roll. No. ....*

*Time : 3 Hours*

*Maximum Marks : 200*

*Note :—* (1) Question paper consists of two parts viz. Part I and Part II. Each part contains *four* questions. The paper as a whole carries eight questions. Question Nos. 1 and 5 are compulsory. The candidates are required to attempt *three* more questions out of the remaining six questions taking at least *one* question from each part i.e. this is in addition to the compulsory question of each part. Attempt *five* questions in all. *All* questions carry equal marks. The parts of a question are to be attempted at one place in continuation. Answers should be brief and to the point.

(2) Parts of same question must be attempted together and not to be attempted in between the answers to other questions.

P.T.O.

## Part I

1.
  - (i) Write down the Schrödinger wave equation for single-electron Coulomb systems in spherical coordinates. 8
  - (ii) According to molecular orbital electronic configuration of the  $O_2$  molecule, show that this molecule will be strongly paramagnetic. 8
  - (iii) Describe how Werner proved that six coordinated complexes possess octahedral stereochemistry. 8
  - (iv) What is the difference between photochemical reactions and thermochemical reactions ? 8
  - (v) How do you measure the surface area of samples with the help of Langmuir's isotherm. 8
2.
  - (i) From the molecular orbital picture, show that the  $He_2$  molecule does not exist, but  $He_2^+$  molecule ion can exist. 6
  - (ii) Discuss the formation of sigma-bond and a pi-bond with suitable illustrations. Explain why a pi-bond is less stable than a sigma-bond. Show that a triple bond is made up of one sigma and two pi-bonds. Why two s-orbitals do not form a pi-bond ? 16
  - (iii) Name and explain the *three* mechanistic steps in free-radical chain reactions. 6

- (iv) Explain heterogenous catalysis. Give *two* examples. 6
- (v) How does a fuel cell differ from traditional methods of energy generation (like batteries) ? 6
3. (i) Explain the hydrolysis of sodium acetate in the light of Bronsted-Lowry concepts of acids and bases. What are its limitations ? 16
- (ii) Using the Debye-Hückel theory to calculate the activity coefficients of the  $\text{Na}^+(\text{aq.})$  in 0.010 M aqueous solution of NaCl. 6
- (iii) The reaction is : 6
- $$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \quad E^\circ = 1.229 \text{ V}$$
- $$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni} \quad E^\circ = -0.257 \text{ V}$$
- Construct a galvanic cell using these reactions.  
Find :
- (a) Write and balance the total cell redox reaction.
- (b) Calculate  $E^\circ_{\text{cell}}$  of the galvanic cell.
- (iv) A Carnot engine converts one-fifth of the heat input into work. If the sink temperature is reduced by  $80^\circ\text{C}$ , the efficiency gets doubled. Find the source and the sink temperature. 6
- (v) Elucidate the operation and control of polymer electrolyte membrane (PEM) fuel cells. 6

4. (i) In a particular enzyme-catalysed reactions :

$$V_{\max} = 0.2 \text{ mol/sec and } k_m = 5 \text{ mH}$$

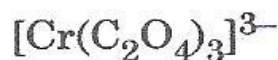
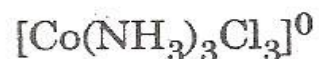
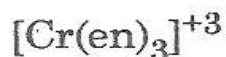
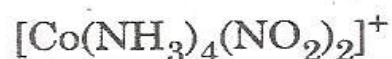
What is the rate of reaction when  $[S] = 10 \text{ mH}$  ?

(Assume the enzyme shows standard Michaelis-Menten kinetics) 6

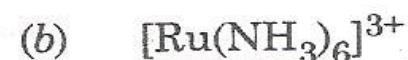
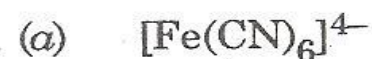
- (ii) Write IUPAC names of the following co-ordination compounds : 6



- (iii) Give the structure of the possible isomers of the following and write their IUPAC names under each structure : 16



- (iv) Predict the no. of unpaired electrons, the spin-only magnetic moments at  $25^\circ\text{C}$  for each of the following : 6



- (v) What is the most common oxidation states of lanthanides ? Why do lanthanide ions show paramagnetic behaviour ? 6

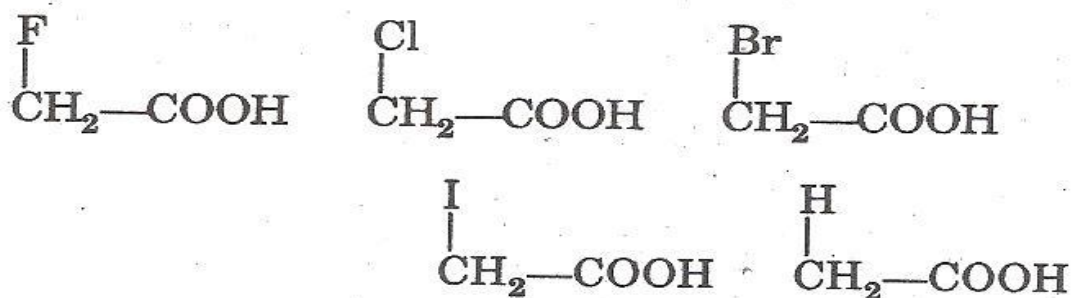
### Part II

5. (i) For each of the following draw reasonable resonance structures : 8  
 $O_3$ ,  $CH_3CNO$ ,  $CH_3SCN$ .
- (ii) Explain the mechanism of Beckmann rearrangement. 8
- (iii) Explain the mechanism of mutarotation of glucose. 8
- (iv) Draw and labelled Jablonski energy level diagrams in photochemistry. 8
- (v) Give some examples of intermetallic compounds and alloys. What is the difference between the two ? 8
6. (i) Explain the comparative stability of primary, secondary and tertiary carbocations using inductive effect. 6

- (ii) The addition of HBr to propene could afford two different products A and B : 16



- (a) Write mechanisms (show electron movements and all intermediates that shows how both products could be formed. Which step is rate determining ? Circle the most stable of the two intermediates.
- (b) Show the reaction diagram (i.e. reaction coordinates Vs. activation energy). Label the products by putting an A or B.
- (iii) Explain why conjugate effect is stronger than (-I) effect. 6
- (iv) Why is the boiling point of aldehyde and ketone greater than that of an alkene with comparable molecular weight ?
- (v) (a) Arrange increasing order of acidity : 6



- (b) Why is phenol more acidic than methanol ? 6

7. (i) Give some examples about the synthetic uses of the following : 6

(a) Acetoacetic and malonic esters

(b) Carbene and diazomethane.

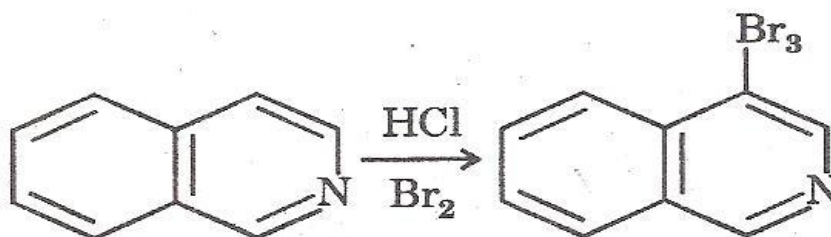
(ii) Give the products of reduction of nitrobenzene : 16

(a) Nitrobenzene  $\xrightarrow[\text{Acidic Medium (Sn/Conc. HCl)}]{\text{Strongly}}$

(b) Nitrobenzene  $\xrightarrow{\text{Alkaline medium}}$

(c) Nitrobenzene  $\xrightarrow[\text{Zn dust}]{\text{Neutral medium}}$

(iii) Give the mechanism of : 6



(iv) Give *two* examples of nucleophilic substitution reactions in pyridine. 6

(v) State the most stable conformation of ethane and the most stable form of butane. Draw the Newmann projection of butane. 6

8. (i) State some uses starch and cellulose in pharmaceutical. Why do we need it ? 5
- (ii) What is denaturation and renaturation of proteins ? Why do plants produce alkaloids when these compounds are not absolutely necessary for growth and reproduction ? 10
- (iii) State the reason of high and low quantum yield ? 5
- (iv) Consider a polymer sample comprising of 5 moles of polymer molecules having molecular weight of 40,000 g/mol and 15 moles of polymer molecules having molecular weight of 30,000 g/mol. Calculate their number average and weight average of molecular weights. 10
- (v) Discuss dynamic light scattering of polymer solutions. 10