Total No. of Questions—12]   [Total No. of Printed Pages—8

S.E. (Chem.) (First Semester) EXAMINATION, 2010

CHEMISTRY–I

(2008 COURSE)

Time : Three Hours   **Maximum Marks : 100**

N.B. :— (*i*) Answers to the two Sections should be written in separate answer-books.

   (*ii*) Neat diagrams must be drawn wherever necessary.

   (*iii*) Figures to the right indicate full marks.

   (*iv*) Use of logarithmic tables, slide rule, Mollier charts, electronic pocket calculator and steam tables is allowed.
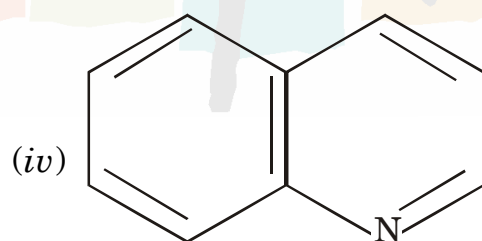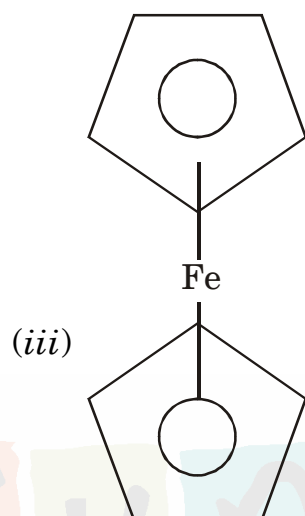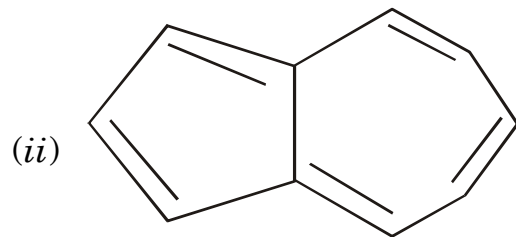
   (*v*) Assume suitable data, if necessary.

SECTION I

1. (*a*) What are the postulates of molecular orbital theory ? Explain the paramagnetic behaviour of O_2 molecule. [6]

   (*b*) Sketch the shapes of the M.O's formed by the overlap of atomic orbitals. [6]

   (*c*) Classify the following compounds as aromatic and non-aromatic : [4]

   (*i*)

(ii)

(iii)

(iv)
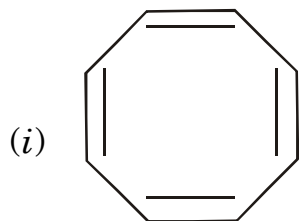
<center>Or</center>

2. (*a*) What are the conditions necessary for delocalization ? Explain the delocalization in benzene. [6]

(*b*) Give reasons :

(*i*) Guanidine is a strong base

(*ii*) Phenol is acidic in nature

(*iii*) Oxalic acid is stronger than formic acid. [6]

(c)   Draw the orbital picture and show the relative order of stability of free radicals and carbanions.   [4]

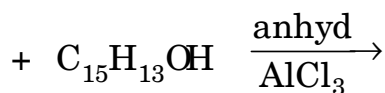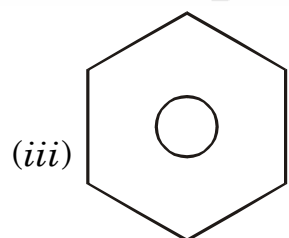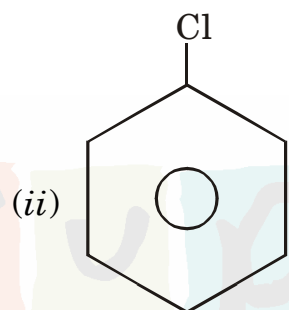**3.**   (a)   Give an comparative account for S_N1 and S_N2 reactions.   [6]

(b)   Explain why $-NO_2$ group is deactivating and *m*-directing.   [4]

(c)   Predict the product :   [6]

(i) $CH_3Br + CH_3NH_2 \rightarrow$

(ii)

Cl on benzene ring, $\xrightarrow[\text{Heat}]{\text{Fuming } H_2SO_4}$

(iii)   benzene $+ C_{15}H_{13}OH \xrightarrow[\text{AlCl}_3]{\text{anhyd}}$

(iv) $CH_3COCl \xrightarrow{\text{NaNH}_2}$

(v) $CH_3CH = CH_2 + HI \rightarrow$

(vi) $(CH_3)_3CCl \xrightarrow[\text{Polar Solvent}]{\text{Base}}$
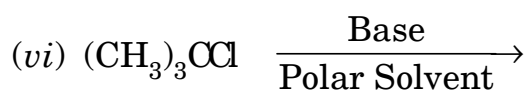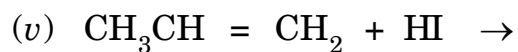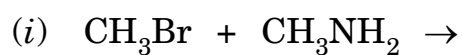
Or

4. (*a*) Discuss the mechanism of Beckmann's rearrangement.   [4]

(*b*) What is sulphonation ? Give the mechanism for sulphonation of benzene.   [6]

(*c*) Identify A and B in the following reactions :

(*i*) $6CH_3-CH=CH_2 + B_2H_6 \rightarrow A \xrightarrow{6H_2O_2} B$

(*ii*)

$\rightarrow$ A

(*iii*) $CH_3OCH_2CH_3 \qquad\qquad A + B$

(*iv*) $C_6H_5CHO + Br-CH_2-COOC_2H_5 \xrightarrow[\text{(ii) H}^+,\ H_2O]{\text{(i) Zn, ether}} A$

(*v*)

$+ CH_3COCl \xrightarrow[\text{AlCl}_3]{\text{anhyd}} A + B$

(vi)

$$\underset{\text{(toluene with } CH_3)}{\bigcirc} \xrightarrow{\text{Fe, } Cl_2} \quad A \ + \ B. \qquad [6]$$
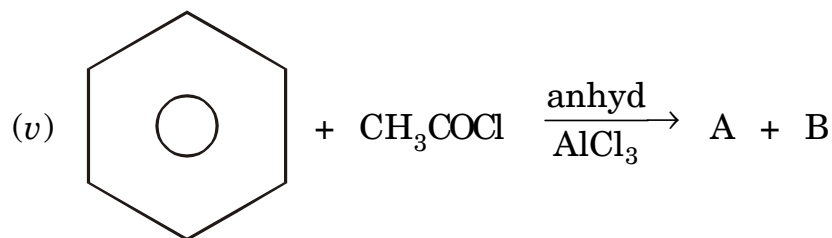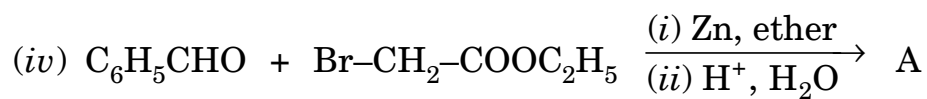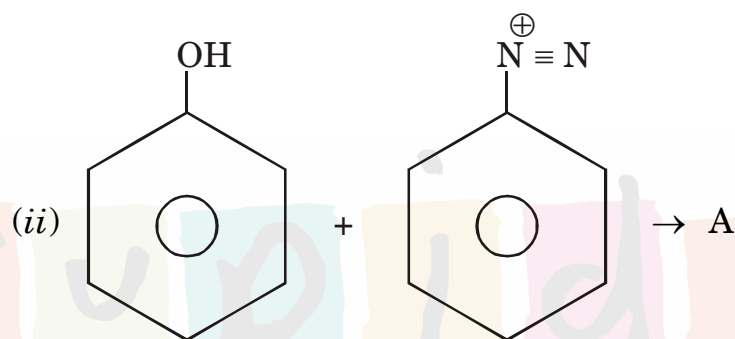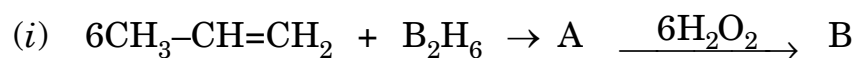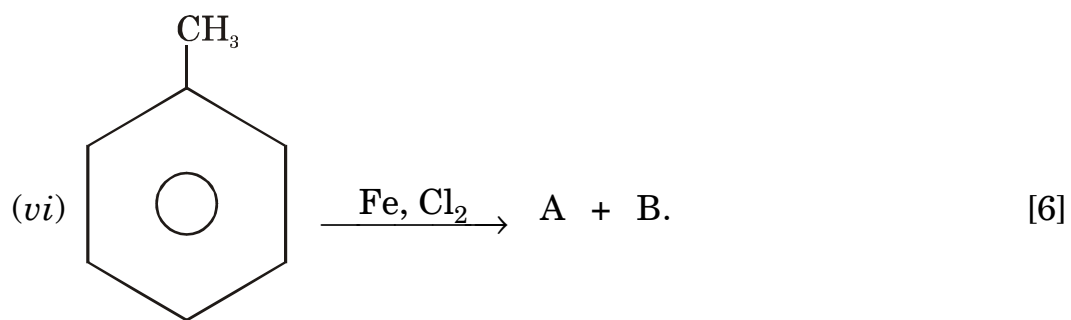
5. (a) What are conductometric titrations ? Describe briefly the different types of conductometric titrations. [6]

(b) Discuss the interferences and limitations in flame photometry. [4]

(c) Give reasons :

(i) The equivalent conductance of an aqueous solution of a weak electrolyte increases on dilution but the specific conductance decreases.

(ii) The equivalent conductance of a strong electrolyte changes with its concentration. [6]

(d) Electrolytic specific conductance of 0.25 mol L^{-1} solution of KCl at 25°C is 2.56×10^{-2} ohm^{-1} cm^{-1}. Calculate its molar conductance. [2]

Or

6. (a) What are ion-selective electrodes ? Describe the working and construction of a glass electrode as a solid-state membrane electrode. [4]

(b) State and explain Kohlrausch's law. The ionic conductance $\lambda^0_{H^+}$ and $\lambda^0_{Cl^-}$ are 349.8 and 196.7 cm^2 ohm^{-1} $equiu^{-1}$ respectively. At 25°C κ of water = 5.7 × 10^{-8} ohm^{-1} cm^{-1}. Calculate the ionic product of water. Given $\quad_0 = \Lambda$. [6]

(c) What is the principle of flame photometry ? Describe the premix or laminar flow burner. [4]

(d) Calculate the electrode potential of titration mixture when 90 ml of Ce^{+4} is added during titration of 100 ml of 0.1 N Fe^{+2} ion solution taken in flask against 0.1 N Ce^{+4} ion solution added from burette. [4]

(Given : E^0_1 = 0.785 volt, E^0_2 = 1.45 volt)

$Fe^{+2} \qquad Fe^{+3} + e^-$ $(E^0_1 = 0.785$ volt)

$Ce^{+4} + e^- \qquad Ce^{+3}$ $(E^0_2 = 1.45$ volt)
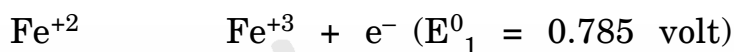
SECTION II

7. (a) Obtain rate equation for first order kinetics and give its characteristics. [6]

(b) Define the rate of chemical reaction. Explain the experimental techniques for the rate determination. [6]

(c) For the decomposition of acetone dicarboxylic acid rate constant is 2.46 × 10^{-5} at 273 K and 1.63 × 10^{-3} at 303 K. Calculate the energy of activation of the reaction. [4]

Or

8. (a) What is steady state approximation ? How is it useful in deriving rate law for a photochemical reaction ? [6]

(b) Show that in first order reaction, time required for 75% completion is double the time required for 50% reaction completion. [6]

(c) The reaction $2HBr \rightarrow H_2 + Br_2$ is second order with rate constant 1.2×10^{-5} liter per mole per sec. at 600 K. How long will it take to decompose 40% if HBr is kept at 50 kPa at 500 K in closed vessel. [4]

9. (a) Explain the principle, technique and applications of column chromatography. [6]

(b) What is fuel cell ? Explain construction and working of polymer electrolyte membrane fuel cell. [6]

(c) Define :

(i) Charge-discharge cycles

(ii) Energy density

(iii) Specific energy

(iv) Power density. [4]

Or

10. (a) Write a note on lithium batteries with various compositions. [6]

(b) What is gas chromatography ? Give its instrumentation. [6]

(c) State the applications of HPLC. [4]

11. (a) Give any *one* synthetic method and uses of the following dyes :

(i) Phenolphthalein

(ii) Crystal violet. [6]

(b) Discuss the aromatic character of pyrrole by giving its orbital and resonance structure. [6]

(c) Write the chemical reactions for the following :

(i) Reduction of quinoline with platinum catalyst in the presence of CH_3COOH.

(ii) Action of sodamide on pyridine.

(iii) Catalytic reduction of furan in presence of Nickel. [6]

Or

12. (a) How are dyes classified according to their chemical constitution ? Give specific example of each. [6]

(b) Write a note on Skraup synthesis of quinoline. [6]

(c) Complete the reaction : [6]

(i) $+ \ (CH_3CO)_2O \ \xrightarrow{\ BF_3/0°C\ }$

(ii)

[quinoline structure] $+ \ CH_3I \longrightarrow$

(iii)

[pyrrole structure with N–H] $+ \ CHCl_3 \ + \ KOH \longrightarrow$