

This question paper contains 8 printed pages]

Your Roll No.....

657

A

**B.Sc. (Physical Sciences/Life Sciences (Semester II)**

**CHEMISTRY—Paper CHPT-202**

**(Physical Chemistry/Organic Chemistry)**

**(Admissions of 2010 and Onwards)**

*Time : 3 Hours*

*Maximum Marks : 75*

*(Write your Roll No. on the top immediately on receipt of this question paper.)*

Use separate answer-sheets for Section A and Section B.

**Section A**

Attempt any *three* questions.

*All* questions carry equal marks.

1. (a) Calculate the entropy change when 1 mole of ethanol is evaporated at 351°K. The molar heat of vaporization of ethanol is 39.84 kJ mol<sup>-1</sup>. 5
- (b) At a certain temperature, degree of dissociation of pure water is  $1.81 \times 10^{-9}$ . Calculate the ionic product of water at this temperature. 5
- (c) Write explanatory note on factors influencing the equilibrium of a chemical reaction. 2½

P.T.O.

2. (a) Derive the Clausius-Clayperon equation and show that :

$$\log_{10} \frac{P_2}{P_1} = \frac{\Delta H}{2.303} \left( \frac{1}{T_1} - \frac{1}{T_2} \right). \quad 5$$

- (b) What is meant by the terms 'degree of hydrolysis' and 'hydrolysis Constant' ? Describe the relationship between hydrolysis constant and the dissociation constant of the base for the hydrolysis of a salt of strong acid and a weak base. 5
- (c) Explain common ion effect with one example. 2½
3. (a) Derive the concept of entropy from the second law of thermodynamics. Show that entropy is a state function. 5
- (b) State Le-Chatelier principle and discuss its application to the following reactions :
- (i)  $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2 + \text{Heat}$
- (ii)  $3\text{H}_2 + \text{N}_2 \rightleftharpoons 2\text{NH}_3 - \text{Heat}$  5
- (c) Calculate the pH of  $10^{-8}$  N HCl. 2½

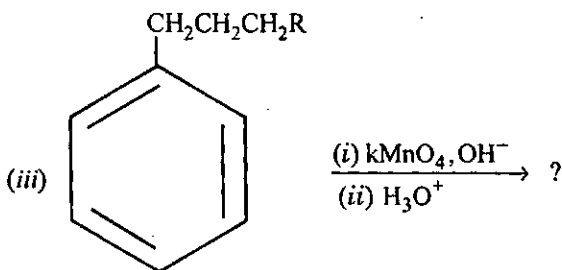
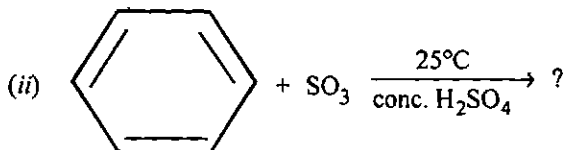
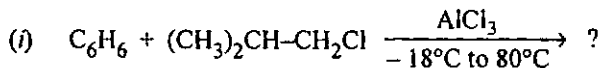
4. (a) Find  $\Delta E$ ,  $q$  and  $w$  for an ideal gas when 2 moles of it at 3 atm pressure expand isothermally at  $50^\circ\text{C}$  and reversibly to a pressure of 1 atm. 5
- (b) Two moles of HI were heated in a sealed bulb at  $444^\circ\text{C}$  till equilibrium state was reached and it was found to be 22% dissociation at that time. Calculate the equilibrium constant for the dissociation and synthesis reaction. 5
- (c) Explain the criteria of spontaneity.  $2\frac{1}{2}$

### Section B

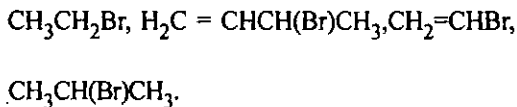
Attempt any *three* questions.

1. (a) Give the mechanism of Friedel-Crafts acylation. Why is the acylium ion more stable than ordinary carbocations ?

(b) Complete the following reactions :



(c) Rank the following substances in order of their expected  $S_N1$  reactivity :



(d) Draw the contributing resonance structures for the arenium ion, produced when nitronium ion (generated by mixture of  $HNO_3 + H_2SO_4$ ) reacts with benzene.

2. (a) How would you prepare the following compounds using a Williamson synthesis ?

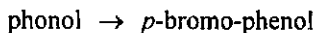
(i) Methyl propyl ether

(ii) *tert*-Butyl methyl ether

(b) With the help of a suitable example, write down elimination-addition (benzyne) mechanism for nucleophilic aromatic substitution.

(c) (i) Write down key differences between the  $S_N2$  and  $S_N1$  mechanisms followed by alkyl halides.

(ii) Convert :

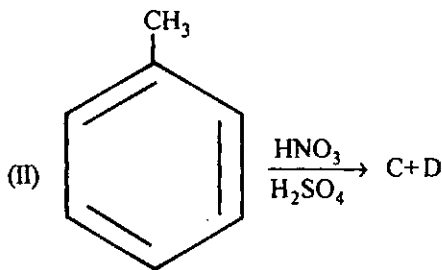
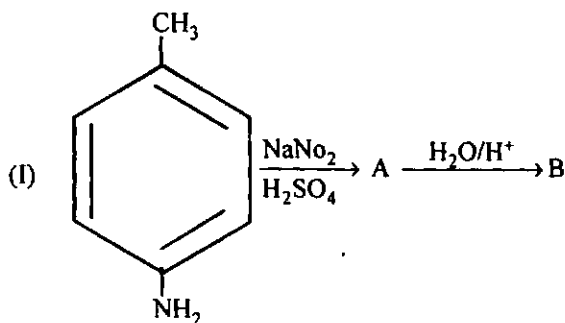


(d) Give steps involved in the formation of phenol from benzene by cumene hydroperoxide method. 3,3,4,2½

P.T.O.

3. (a) (i) A carboxylic ester is hydrolysed to a carboxylic acid and an alcohol when heated with aq. base. Why is this reaction essentially irreversible ?

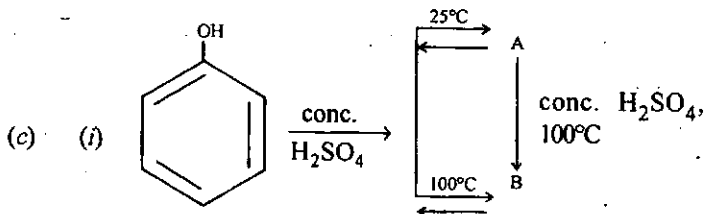
(ii) Write down the structures of A, B, C and D :



(b) Write notes on any two of the following :

- (i) Benzoin condensation;
- (ii) Wittig reaction;
- (iii) Reimer-Tiemann reaction.

- (c) Describe Lucas test to distinguish between a primary, secondary and tertiary alcohol.
- (d) Simple aryl halides are relatively unreactive toward nucleophilic substitution. Explain giving reasons. 4,4,2,2½
4. (a) Explain Houben-Hoesch condensation by taking a suitable example.
- (b) With the help of a suitable example write down  $S_N1$  mechanism.



Identify A and B. Which is more stable and why ?

- (ii) Convert a secondary alcohol to ketone by Oppenauer oxidation.

- (d) What products are likely to be obtained when a primary alcohol is oxidized with PCC and alk.  $\text{KMnO}_4$  respectively ? Explain with the help of an example.

2½,3,4,3