2014

M.Sc. Part–II Examination

CHEMISTRY

PAPER—VI

Full Marks : 75

Time : 3 Hours

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Illustrate the answers wherever necessary.

(Physical Special)

Answer any *five* questions taking at least *two* from each group.

Group—A

1. (a) Obtain the expression for the rotational contribution to its molar entropy of a homonuclear diatomic molecule.   8

   (b) Calculate the molecular translational partition function, for hydrogen molecules in a contain of

volume $100 \ cm^3$ at $27°C$.

Given, $k = 1.38 \times 10^{-23} JK^{-1}$ and $h = 6.626 \times 10^{-34} JS$.

7

2. (a) Define grand partition function Z and obtain the expression for ln Z for bosons.

   (b) Obtain the relationship between Pressure of a gas and Z.

   (c) State and explain the Ergodic hypothesis.

   $(3+4)+4+4$

3. (a) Establish the Prigogene principle of minimum entropy production.

   (b) Explain what is meant by phenomenological coefficients. $10+5$

4. Derive the expression for the rate of entropy production for a flow in a system when a pressure difference is observed as a result of an electrical potential. Obtain the expressions for any two electrokinetic effects. $9+6$

Group—B

5. (a) Give a description of the instrumentation of Mossbauer spectrometer.

   (b) What are the characteristics of Mossbauer nuclides ?

   (c) What is Doppler shift ? Calculate the Doppler shift of Fe nucleus (57), where the velocity of source is $10^2 ms^{-1}$, frequency $= 34.886 \times 10^{-17} Hz$ and velocity of light $= 3 \times 10^8 ms^{-1}$.

   $6+4+(2+3)$

6. (a) Give quantilative treatment of transition state theory using partition function.   10

   (b) Show that the standard equilibrium constant at 400K for the reaction $H_2 + D_2 \rightleftharpoons 2HD$ is equal to 3.54 .

   Given that :   5

|	$I \times 10^{46} kgm^2$	$\theta_{v/k}$	$D_0/KJmol^{-1}$
H_2	4.60	5986	431.8
D_2	9.20	4308	439.2
HD	6.13	5226	435.2

4

7. (a) For reaction between ions, explain Double sphere activated complex model theory. **7**

(b) Give an interpretation of the pre-exponential factors of ionic reactions from the double sphere activated complex model. **4**

(c) How rate constant of an ionic reaction is influenced by ionic strength of the solution? Explain with graphical representation. **4**

8. (a) Derive expressions for rate constant of both acid catalyzed and uncatalyzed step polymerisation. **6**

(b) Explain the following items : **1×4**

  (i) Relative viscosity ;

  (ii) Reduced viscosity ;

  (iii) Intrinsic viscosity ;

  (iv) Inherent viscosity ;

In connection with a polymer solution.

(c) About how long will it take for a boundary of a polymer sample to move 1 mm in a centrifuge operating at 50,000 rotation per minute if the initial distance of the sample boundary from the centre of the rotation is 6.0 cm ? The sedimentation co-efficient for the sample is $2 \cdot 20 \times 10^{-13}$ S at 20°C.

5

(Organic Special)

Answer any *five* questions taking at least *two* from each group.

Group—A

1. (a) What are the criteria of a good disconnection? Illustrate your answer with the disconnection of the following compound : **5**

$$PhCH_2CH_2CO_2Et$$

(b) Illustrate the use of Functional Group Inter Conversion in the retrosynthetic analysis of the following compounds (any *two*) : **5×2**

(i)

(ii)

(iii)
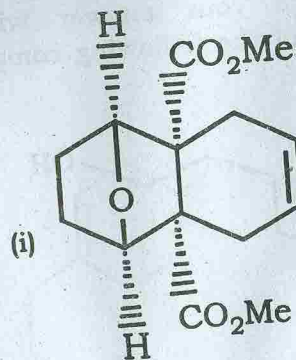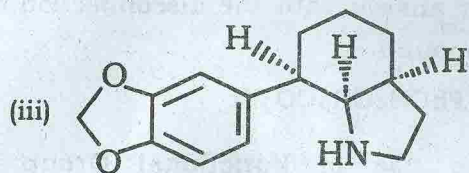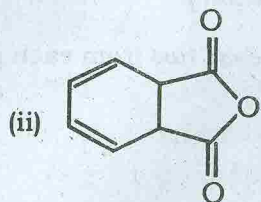
**2. (a)** Explain with illustration the statement : Disconnection of 1, 6—dicarbonyl actually involves reconnection. Illustrate your answer with the retrosynthetic analysis of the folllowing compound :
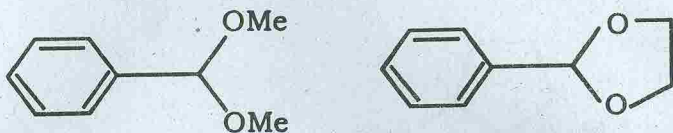
5
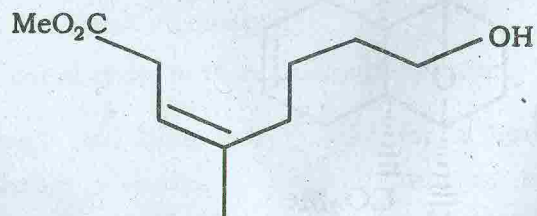
(b) Work backwards using the principle of retrosynthetic analysis to find out simple starting materials for the synthesis of any *two* of the following compounds :

5×2

(i)

(ii)

(iii)
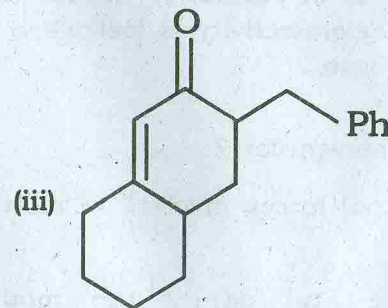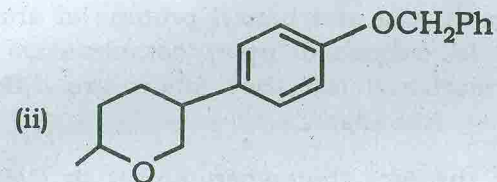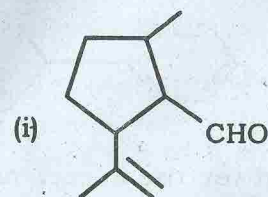
3. (a) Account for the products obtained upon treeating the chromiumtricarbonyl complexes of the following acetals with $TiCl_4$ and Me_3Al in dichloromethane at – 78°C ? **8**

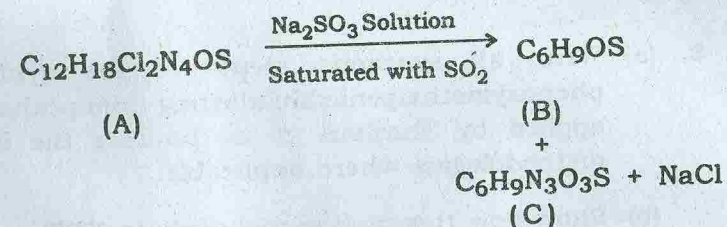How much Lewis acid would you use in each case for obtaining the best results and why ?

(b) 'Acidity of both ring and benzyl protons of aromatic compounds is enhanced upon complexation with chromiumtricarbonyl but they follow two differtent mechanism — Elucidate. **4**

(c) Account for the fact that when KoBut in DMSO is used as base in the deprotonation of chromium tricarbonyl complex of toluene, it is totally regioselective, but regioselectivity is lost when alkyl lithium is used as base. **3**

4. (a) What is molecular recognition ?

(b) What are the principal forces involved in molecular recognition ?

(c) Design, synthesize and depict the mode of complexation of an adipic acid receptor.

(d) Write the applications of crown ethers.

(e) Define hydrophobic effect.

2+2+(2+2+2)+2+3

5. (a) Define Cryptands. Give examples and elaborate on their complexation properties.

(b) How can cryptands be used for light conversion devices ?

(c) How can water act as a better solvent than common organic solvents for a simple Diels-Alder reaction ? Illustrate with examples.

(d) What is Lipoproteins ?   4+4+4+3

Group—B

6. (a) The following Vitamin(A) shows the property as :

$$C_{12}H_{18}Cl_2N_4OS \xrightarrow[\text{Saturated with } SO_2]{Na_2SO_3 \text{ Solution}} C_6H_9OS$$

(A)   (B)
+
$C_6H_9N_3O_3S$ + NaCl
(C)

Chemical and spectral evidence showed that Compound (B) is a thiazole and Compound (C) is a pyrimidine derivative.

Identify B and C. Establish the structure of A.   3+3+3

(b) Discuss the mode of the action (with mechanism) of the coenzymes derived from various vitamins (any *two*) :   3+3

(i) Coenzyme derived from niacin ;

(ii) Coenzyme derived from pantothenic acid ;

(iii) Coenzyme derived from riboflavin.

7. (a) Establish the structure of chloramphenicol (M.F. $C_{11}H_{13}Cl_2N_2O_5$) through chemical and spectroscopic evidenses.   6

(b) Write three main and important steps to the biosynthesis of benzylpenicilin and explain.   5

(c) Write the structure of Sterptomycin and Cephalosporin C and also mention their medical uses.   2+2

8. (a) Write all synthetic steps for the synthesis of phenoxymethylpenicillin starting from phthalimide as applied by Sheehan *et. al.* Indicate the important methodologies where applicable.   5+2

(b) Show how thiamine pyrophosphate (TPP) acts in the metabolism of carbohydrate. Indicate all the steps involved.   4

(c) Complete the following transformations (any *two*) :   2+2

(i)

Malate   Oxaloacetate

(ii)

Succinate   Fumarate

(iii)

Pyruvate   acetyl-CoA

9. (a) What is aromatic-aromatic (π–π) interaction ? Give an example of Host-Guest Complexation utilizing aromatic-aromatic interaction.

(b) What are Cyclodextrins ? What are the major driving forces for Cyclodextrin complexation ? Write some applications of Cyclodextrins. What is the effect of added α-CD on the following chlorination reaction :
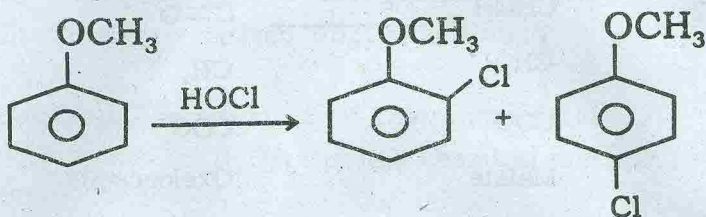
(c) What is Cofactors and Coenzymes ?

$$(2+2)+(2+2+2+2)+3$$

10. (a) Why is Nucleotide and Nucleoside ?

(b) Show hydrogen bonding interaction between DNA Base pair.

(c) What is enzymes ? Classify the different types of enzymes.

(d) How DNA fingerprinting perform by a forensic chemist ?

(e) Write down the structure and one application of Vasopressin and Oxytocin.

$$3+3+(1+3)+2+3$$