2015

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 molar rotational entropy of a heteronuclear dratomic molecule.　　8

(b) Calculate the molar translational partition function of an ideal gas in a volume of 500 cm^3 at 25°C.

[Given k = 1.38 × 10^{-23} JK^{-1},

h = 6.62 × 10^{-34} JS]   7

2. Define the grand canonical partition function Z, obtain the expression for In Z for fermions and derive the Fermi-Dirac distribution law.   2+4+9

3. (a) What do you mean by phenomenological coefficients ? Express the expression for the rate of entropy production in term of forces and fluxes.   2+3

(b) Consider that these is a pressure difference causing a difference in electrical potential. Derive the appropriate expression for the rate of entropy production for such a process and identify the force and the flux. Define streaming potential and derive the expression for this quantity in terms of phenomenological coefficient.   10

4. (a) Obtain the relationship between Pressure of a gas and the grand cononical partition function.   6

(b) Establish the Prigagene principle of minimum entropy production.   9

Group—B

5. (a) What is Ziegler-Natta Catalysis ?   3

(b) Indicate the differences between isotactic, syndiotactic and atactic polymers.   3

(c) Obtain the rate expression for condensation polymerization reaction.   6

(d) A protein sample consists of an equimolecular mixture of hemoglobin (M_m = 15.5 kg mol^{-1}), ribonuclease (M_m = 13.7 kg mol^{-1}) and myoglobin (M_m = 17.2 kg mol^{-1}). Calculate the number average and mass average molecular weight. Which is greater ?   3

6. (a) What is Mossbauer nuclides ? Give its important characteristics.   1+2

(b) Discuss some applications of Mossbauer spectroscopy.   6

(c) Write notes on — (i) Recoillers emission and (ii) Chemical shift.   3+3

7. (a) Explain what is meant by partition function.   3

(b) For a bimolecular reaction of this type

$$A + B \xrightarrow{k} Product$$
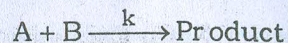
Derive an expression for pre-exponantial factor using partition function. 8

(c) Show that the standard equilibrium constant at 400 K for the reaction :

$$H_2 + D_2 \rightleftharpoons 2HD$$
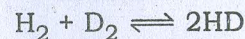
is equal to 3.54. Given that 4

	1×10^{46} kgm^2	$\theta v/k$	Do/kJ mol^{-1}
H_2	4.60	5986	431.8
D_2	9.20	4308	439.2
HD	6.13	5226	435.2

8. (a) What is solvent binding effect ? 2

(b) Using double sphere activated complex model for ionic reaction show that the value of pre-exponantial factor decreases and increases by the unit of 10^2 for each unit of $Z_A Z_B$ for equal and opposite sign of charge of ionic species respectively.

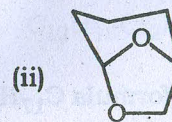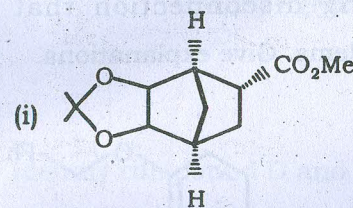(c) How does ionic strength influence the rate constant ? Illustrate your answer with examples. 3
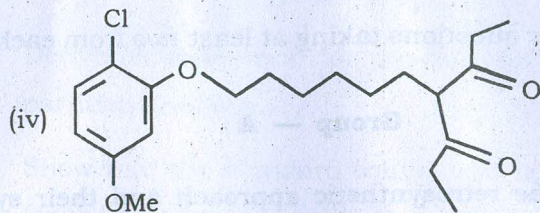
_____

(Organic Special)

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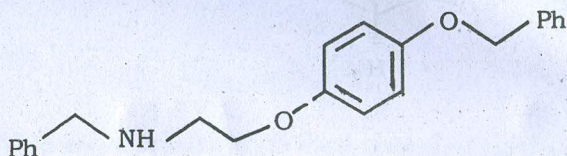
Group — A

1. (a) Give the retrosynthetic approach and their synthetic strategies of the following compounds (any *three*) :
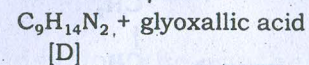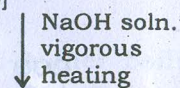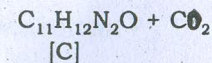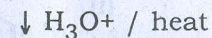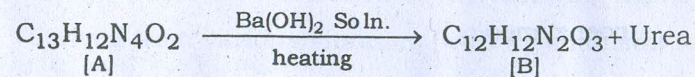
3×4

(i)

(ii)

(iii)

(iv)
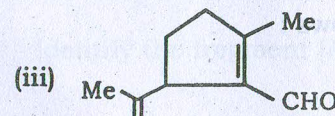
(b) How would you design the synthesis of the following compound avoiding disconnection that causes chemoselective problems. Give explanations. 3
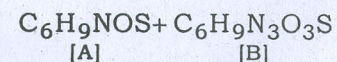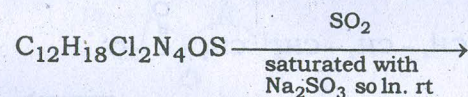

2. (a) A compound (Vit B$_2$) with molecular formula $C_{17}H_{20}N_4O_6$ yields $C_{13}H_{12}N_4O_2$ (A) on exposure to sunlight in dil NaOH solution. Compound A on following transformation yields as follows :

$$C_{13}H_{12}N_4O_2 \xrightarrow[\text{heating}]{\text{Ba(OH)}_2 \text{ Soln.}} C_{12}H_{12}N_2O_3 + \text{Urea}$$
[A]   [B]

$\downarrow$ H$_3$O+ / heat

$C_{11}H_{12}N_2O$ + CO$_2$
[C]

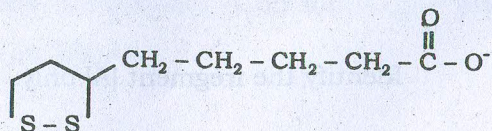$\downarrow$ NaOH soln. vigorous heating

$C_9H_{14}N_2$ + glyoxallic acid
[D]

Identify compound D and deduce the structure A. 9

(b) Vitamin B$_1$ is cleared through following treatment : 6

$$C_{12}H_{18}Cl_2N_4OS \xrightarrow[\substack{\text{saturated with} \\ \text{Na}_2\text{SO}_3 \text{ so ln. rt}}]{\text{SO}_2}$$

$C_6H_9NOS + C_6H_9N_3O_3S$
[A]   [B]

Identify the fregment [A] only.

3. (a) Carry out the following transformations using enzymes / coenzymes : 3×2

(i)

$$\text{(fumarate with COO}^-\text{ groups)} \longrightarrow {}^{\ominus}OOC - \overset{\overset{\displaystyle O}{\|}}{C} - CH_2COO^-$$

(ii)

$$\begin{array}{c} COO^- \\ | \\ CH_2 \\ | \\ CHCOO^- \\ | \\ CHOH \\ | \\ COO^- \end{array} \longrightarrow \begin{array}{c} COO^- \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ C=O \\ | \\ COO^- \end{array}$$

(iii)

$$\begin{array}{c} CH_2 - CH_2 - CH_2 - CH_2 - \overset{\overset{\displaystyle O}{\|}}{C} - O^- \\ | \qquad\qquad | \\ SH \qquad SH \end{array} \longrightarrow$$

$$\begin{array}{c} CH_2 - CH_2 - CH_2 - CH_2 - \overset{\overset{\displaystyle O}{\|}}{C} - O^- \\ | \qquad | \\ S - S \end{array}$$
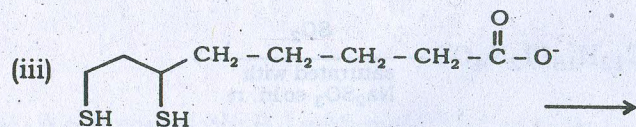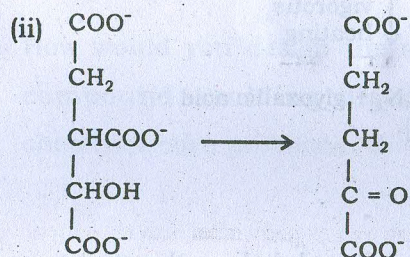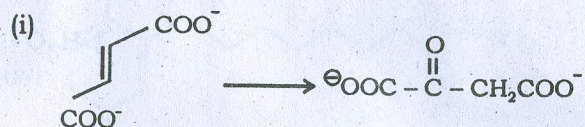
(b) Discuss the mode of action of the following coenzymes derived from various vitamins (with mechanism) :

(i) Coenzyme derived from Niacin

(ii) Coenzymes derived from Pantothenic acid

4+4

(c) What is catabolism ? 1
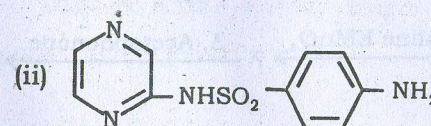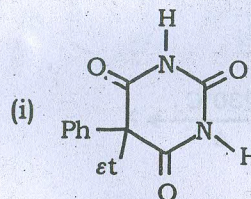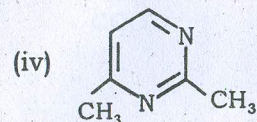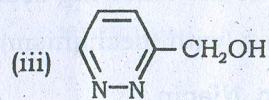
4. (a) Pyridazine has higher boiling point than the other diazines — Why ? Explain. 1

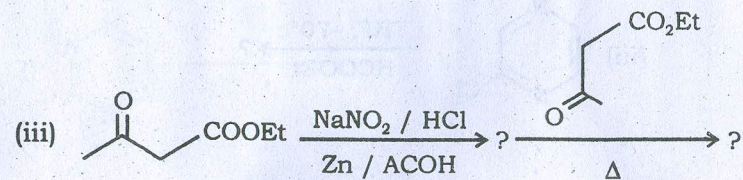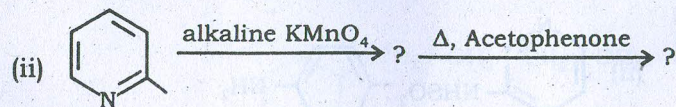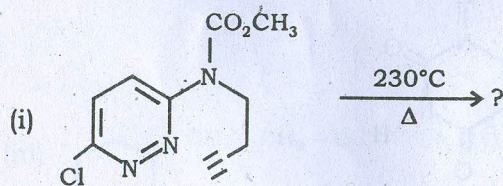(b) Logically develop the synthesis of the following compounds (attempt any *three*) : 3×2

(i)

Ph, et substituted barbituric acid structure

(ii)

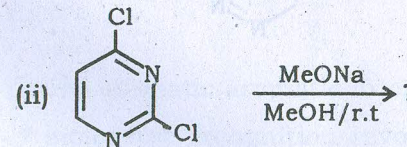pyrazine — NHSO$_2$ — C$_6$H$_4$ — NH$_2$

(iii)

(iv)
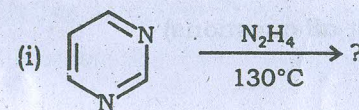
(c) Predict the product(s) in each case of the following reaction and suggest mechanism :

$$2+(2\times1\tfrac{1}{2})+(2\times1\tfrac{1}{2})$$
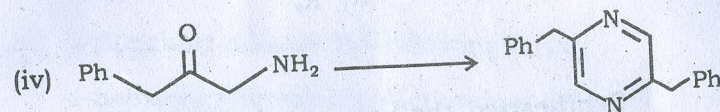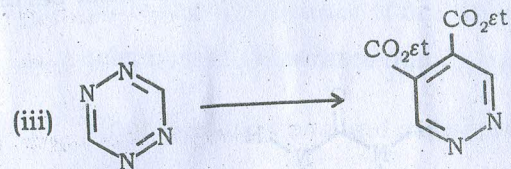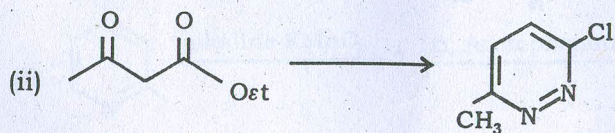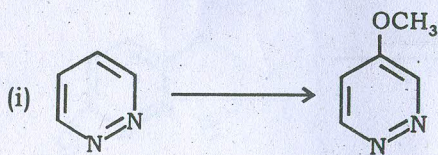
(i)

(ii)

(iii)

5. (a) 'Diazines are much weaker bases than pyridine' — Explain.   1

(b) Predict the product(s) of the following reaction with mechanism. (attempt any *three*)   3×2

(i)

(ii)

(iii)

$$\text{(pyrazine with Cl)} \xrightarrow[\text{HCOOEt}]{\substack{\text{LiTMP} \\ \text{THF, }-70^\circ c}} ?$$

(iv)

$$\text{(pyrazine N-oxide)} \xrightarrow{POCl_3} ?$$
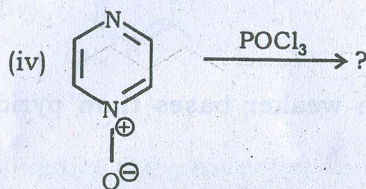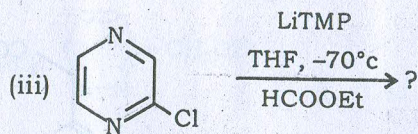
(c) Carry out the following transformations with proper mechanism. (attempt *all* questions) 2×4

(i)

$$\text{(pyridazine)} \longrightarrow \text{(4-methoxy pyridazine, OCH}_3)$$

(ii)

$$\text{(ethyl acetoacetate, } O\varepsilon t) \longrightarrow \text{(3-chloro-6-methyl pyridazine, Cl, CH}_3)$$

(iii)

$$\text{(tetrazine)} \longrightarrow \text{(pyridazine with } CO_2\varepsilon t, CO_2\varepsilon t)$$

(iv)

$$Ph \text{-CH}_2\text{-CO-CH}_2\text{-}NH_2 \longrightarrow \text{(pyrazine with Ph-CH}_2 \text{ and Ph)}$$

Group — B

6. (a) Define template effect. During crown ether synthesis, illustrate the role of metal ions.

(b) What are cryptands ? How do you justify that cryptands form more selective and stronger complexes than crown-ethers.

(c) Define aromatic-aromatic interaction. Give an example of molecular recognition involving aromatic-aromatic interaction.

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

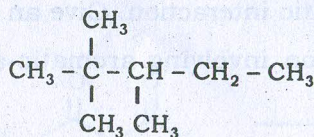7. (a) Design a receptor for the complexation of barbital :
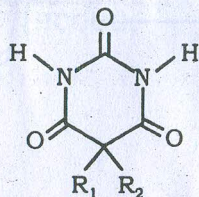
Synthesized the compound. Show complexation with barbital. Give evidence for complexation.

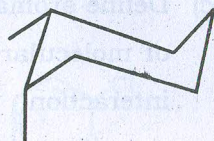(b) Define Hydrophobic effect. How hydrophobic effect enhance the rate of reaction ?

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

8. (a) What is cyclodextrins ? Give application of cyclodextrins.

(b) Calculate the heat of formation of the following compound :

S.E = 0   S.E = 10.1 k.cal/mole

(c) Write the significance of multiple recognition sites in the selection of substrates during host-guest complexation.

(d) What is coenzymes and cofactors ?

$$(2+2)+(2+2)+4+(1\tfrac{1}{2}+1\tfrac{1}{2})$$

9. (a) Write short note on the following term :

α-helix, Vanderwall interaction and RNA.

(b) What is Rotaxane ? Give it's application.

(c) Give some application of proteins.

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

10. (a) Starting from pthalimide carryout the synthesis of phenoxymethyl penicillin. How penicillin was biologically synthesized in the culture medium of the fungus penicillium chrysogenum ? Write all the steps as outlined by Annstein and Morris.   3+2

(b) Discuss the antibacterial pathway of penicillin against a gram positive bacteria.   3

(c) Outline the synthesis of benzyl penicillin as described by sheehan et.al. Describe the synthetic methodologies applied during the course of synthesis.   2+2

(d) Classify antibiotics in terms of the type of functional group present and give example of each type.   3