C/19/DDE/MSc/Part-2/CEM/6

2018

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*)

New Syllabus

F.M. – 100   Time : 4 Hrs.

Answer any *five* questions
taking at least *two* from each group (A and B) and
answer *five* questions from group C.

Old Syllabus

F.M. – 75   Time : 3 Hrs.

Answer any *five* questions
taking at least *two* from each group (A and B).

Group—A

1. (a) Assuming, without derivation, the appropriate expression for the translational partition function. Obtain the Sackur-Tetrode equation for the absolute molar entropy of a monatomic gas. 10

   (b) Calculate the characteristic rotational temprature for H_2 gas.

   (Given, moment of inertia of H_2 gas = 4.60×10^{-48} kg m^2 and $k = 1.38 \times 10^{-23}$ JK^{-1}) 5

2. Define grand canonical partition function Z, obtain the expression for ln Z for bosons and derive the Bose-Einstein distribution law in terms of β and μ. 2+5+8

3. (a) What are meant by 'forces' and 'fluxes' in irreversible processes ? 2+2

   (b) State and explain the Onsager reciprocity relations. 1+2

   (c) Obtain the expression for the entropy production due to flow of metter. 8

4. Consider an irreversible process where a pressure difference develops due to an electrical potential difference. Derive the expression for the rate of entropy production and obtain the expression for electroosmosis in terms of phenomenological coefficients. 10+5

Group—B

5. (a) What is Mossbauer spectroscopy ? Describe some of its important applications. 3+4

   (b) How is Mossbauer effect related with resonance fluoresence ? 4

   (c) What is recoilness emission ? 4

6. (a) For ionic reaction using double sphere activated complex model derive the expression for rate constant. 9

   (b) Show that the rate constant for the fully diffusion-controlled reaction does not depend on the size of reactant molecule. 6

7. (a) What is Degree of Polymarization (DP) ? 2

   (b) Using kinetics of chain polymarization

   prove that $DP = \dfrac{[M]}{[I]^{\frac{1}{2}}} . K''$

   where $K'' = \dfrac{k_P}{\left(2f\, k_d\, k_t\right)^{\frac{1}{2}}}$

   where the symbols indicate usual meaning. 5

   (c) Derive Flory-Huggins solution theory for polymer solution. 8

8. (a) For a bimolecular reaction, prove that

$$k = \left(\frac{RT}{h}\right) \cdot e^{-\Delta_r U_r / RT} \left\{ \frac{q_{\neq}/v}{(q_A/v)(q_B/v)} \right\}$$

   where the symbols indicate usual meaning.   6

   (b) Applying Activated Complex Theory in viscosity process prove that

$$\eta = \left(\frac{hN}{v}\right)\left(e^{-\Delta S^* / R}\right) \cdot e^{\Delta H^* / RT}$$

   where the symbols indicate usual meaning.   9

Group—C

9. Answer any *five* questions :   5×5

   (a) What are streoregular polymer ? Indicate the difference between isotactic, synbio tactic and atactic polymers.

   2+3

   (b) Compare flash photolysis with relaxation method.

   (c) For ionic reaction prove that pre-exponantial factor will increase by a factor 10^2 for each unit of $Z_A Z_B$.

   (d) What is Mössbauer Effect ?

   (e) Consider two microcanonical ensembles to define the Lagrangian particle multipliers α and energy multiplier energy multiplier β and establish their relationship.

   (f) Define the ensemble average and time average of a statistical parameter and state the Ergodic hypothesis.

   (g) Show that the molecular partition function can be factorised into translational, rotational, vibrational and electronic partition functions.

   (h) Show that the entropy production is an irreversible process is given by

$$\Delta S = \sum_i J_i X_i$$

   where the terms have usual meaning.

   _____

(Organic Special)

New Syllabus

F.M. – 100   Time : 4 Hrs.

Answer any *five* questions
taking at least *two* from each group (A and B) and
answer *five* questions from group C.

**Old Syllabus**

F.M. – 75   Time : 3 Hrs.

Answer any *five* questions
taking at least *two* from each group (A and B).

Group — A

1. (a) What is cyclodextrine ? Provide the name of different compounds which form complex with cyclodextrine. Mention the major driving forces for the complexation between cyclodextrine and guest molecules.   2+2+2

   (b) Give applications of cyclodextrins. How do cyclodextrins act as a regioselective reagent ?   2+2

   (c) What is molecular mechanics calculation ?   2

   (d) Calculate the heat of formation of the following compounds
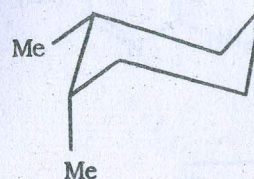
S.E = 10.1 KCal/mole   S.E = 6.3 KCal/mole

S.E. = Steric Energy $1\frac{1}{2} + 1\frac{1}{2}$

2. (a) What is gel ? What is gel transition temperature (t_g) ? What are the techniques uses for studying the gel morphologies ?   2+2+2

   (b) Define Hydrophobic effect. How Hydrophobic effect enhance the rate of reaction ?   2+3

   (c) Write short note on the following term :
       α-helix and RNA.   2+2

3. (a) Pyridine is much stranger base than diazines — Explain.   2

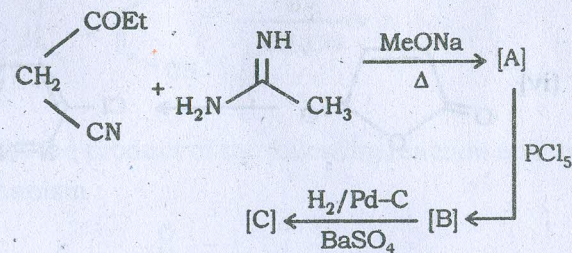   (b) Predict the product(s) in each case of the following reactions. Indicate the mechanism. (attempt any *two*)

(i)

$$\xrightarrow[40°C]{Cl_2/CCl_4} \ ?$$

(ii)

$$\xrightarrow[130°C]{N_2H_4} \ ?$$

(iii)

$$\xrightarrow[MeOH, RT]{MeONa} \ ?$$
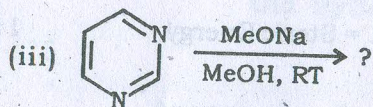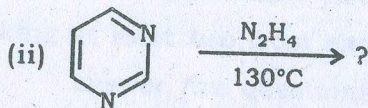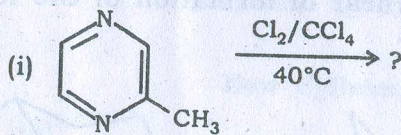
2+2

(c) Logically develop the synthesis of the following compounds : (attempt any *three*)

(i)

(ii)

(iii)

(iv) Ph

(v)
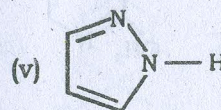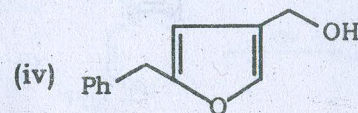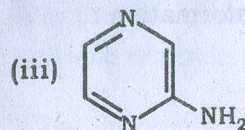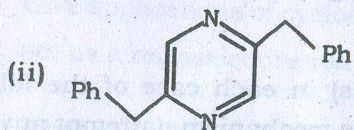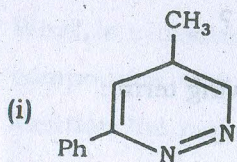
3×3

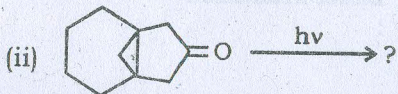4. (a) The following is the transformation :

Identity A, B and C.

3

(b) Carry out the following transformation : 4×3
    (attempt any *four*)

(i)

(ii)

(iii)

(iv)

(v)

5. (a) What is Di-π-methane rearrangement ? Explain it with suitable example. Cite the proper mechanism. 4

(b) What happens when the following compounds are photolysed : (attempt any *three*)

(i)

(ii)

(iii)

(iv) 2×3

(c) Predict the product of the following reaction and suggest mechanism :

 5

Group — B

6. (a) What are the difference between Norrish type-I and type-II reactions. Explain with example in each case.

2+2

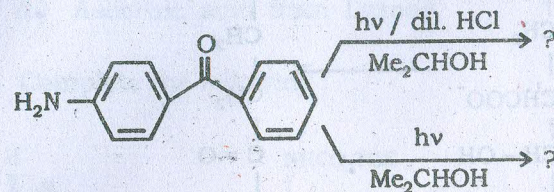(b) Predict the products of the following reactions with mechanism : (attempt any *four*)

(i) $\xrightarrow{h\nu}$?

(ii) $\xrightarrow{h\nu}$?

(iii) $\xrightarrow{h\nu}$?

(iv) $\xrightarrow[H_2O]{h\nu}$?

(v) $\xrightarrow[\text{Photosensitizer}]{h\nu /}$?

4×2

(c) Predict the product of the following reactions with mechanism :

 $\xrightarrow[Me_2CHOH]{h\nu \,/\, dil.\ HCl}$?

$\xrightarrow[Me_2CHOH]{h\nu}$?
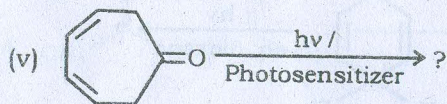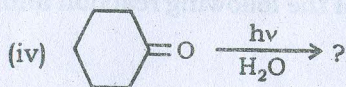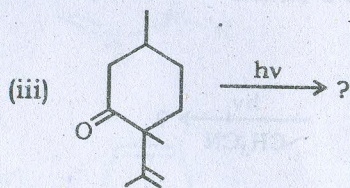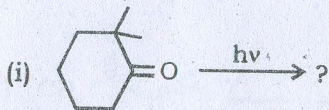
$1\frac{1}{2} \times 2$
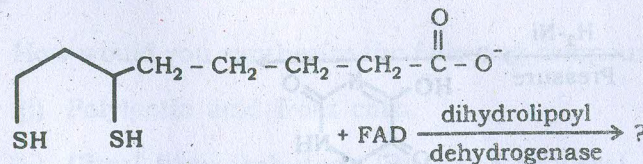
7. (a) Define co-enzymes and holoenzymes with examples.

2

(b) Discuss the mode of action of the following coenzymes derived from vitamins (with mechanism).
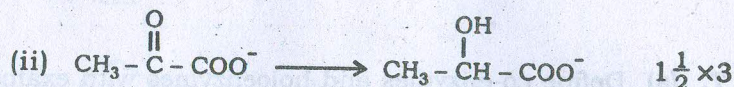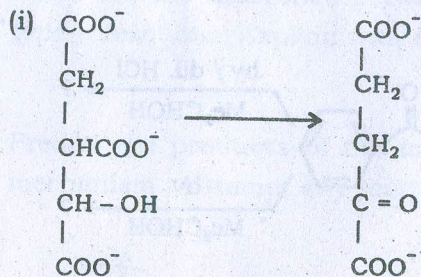
Coenzyme derived from Thiamine 4
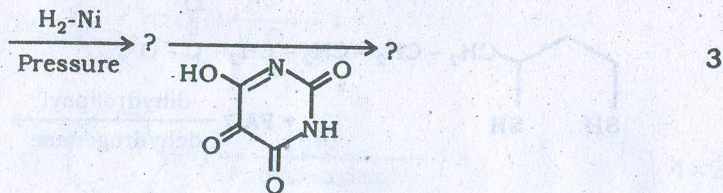
(c) Write the structure of the product with mechanism.
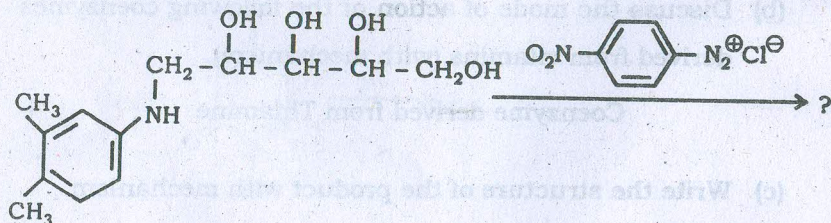
 $\xrightarrow[\text{dehydrogenase}]{\text{dihydrolipoyl}}$?

$+$ FAD

3

(d) Carry out the following transformation using enzymes/coenzymes :

(i)
$$
\begin{array}{c}
COO^- \\
| \\
CH_2 \\
| \\
CHCOO^- \\
| \\
CH-OH \\
| \\
COO^-
\end{array}
\longrightarrow
\begin{array}{c}
COO^- \\
| \\
CH_2 \\
| \\
CH_2 \\
| \\
C=O \\
| \\
COO^-
\end{array}
$$

(ii) $CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - COO^- \longrightarrow CH_3 - \overset{\overset{\displaystyle OH}{|}}{CH} - COO^-$ $1\frac{1}{2} \times 3$

(e) Complete the following :

$$
\begin{array}{c}
\underset{\overset{|}{\underset{\overset{|}{NH}}{\qquad}}}{} \\
CH_2 - \overset{\overset{\displaystyle OH}{|}}{CH} - \overset{\overset{\displaystyle OH}{|}}{CH} - \overset{\overset{\displaystyle OH}{|}}{CH} - CH_2OH
\end{array}
+ \; O_2N-\!\!\!\bigcirc\!\!\!-N_2^{\oplus}Cl^{\ominus} \longrightarrow \; ?
$$

$\xrightarrow[\text{Pressure}]{H_2-Ni} ? \qquad \xrightarrow{\quad} ?$ 3
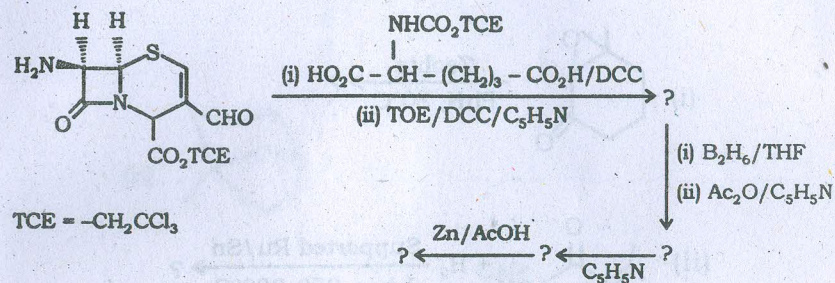
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8. (a) Write all the steps for the synthesis of the following compounds :

     (i) (+) - Penicillamine from (±) valine

     (ii) Ascorbic acid from Lyxose.   3+4

(b) Complete the following :

$$TCE = -CH_2CCl_3$$

(c) How antibiotic show their activity ? When penicillin does not show antibacterial activity ?   2+2

9. (a) What is green chemistry ? How renewable sources are related to sustainability ?   1+2

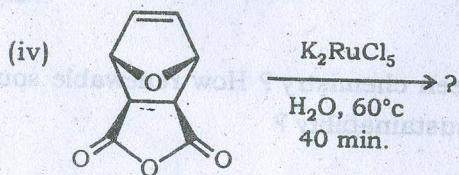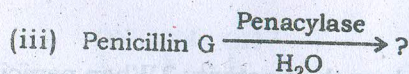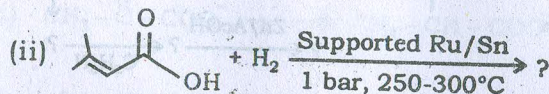(b) How would you synthesize the following compounds :
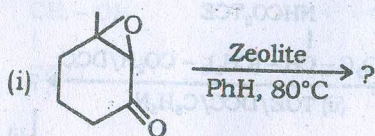
     (i) Polylactic acid from corn.

     (ii) Citral from isobutene (By BASF process).   2+3

(c) Give example (Green Synthesis) :

    (i) Diels-Alder Reaction (Aqueous solvent)

    (ii) Borono-Mannich reaction (Solvent free)

   (iii) Sonogashira reaction (using ionic liquid).

(d) Predict the product of the following reactions :

(i) $\xrightarrow[\text{PhH, 80°C}]{\text{Zeolite}}$?

(ii) + H_2 $\xrightarrow[\text{1 bar, 250-300°C}]{\text{Supported Ru/Sn}}$?

(iii) Penicillin G $\xrightarrow[H_2O]{\text{Penacylase}}$?

(iv) $\xrightarrow[\substack{H_2O, 60°c \\ 40 \text{ min.}}]{K_2RuCl_5}$?

4

10. (a) Define the terms Disconnection and synthon. What are the criteria of a good disconnection?   3

(b) Work backwards using the principles of retrosynthetic analysis to find the suitable starting material for any four :
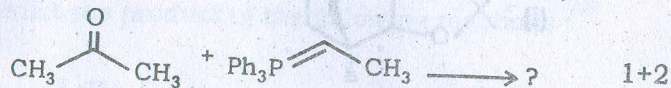
(i)

(ii)

(iii)
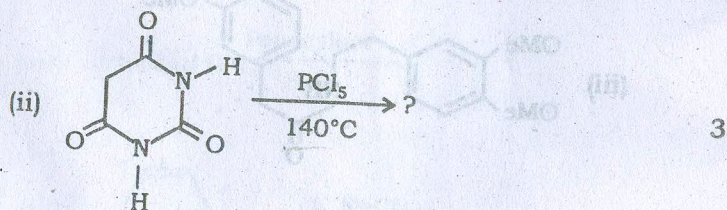
(iv)

(v)
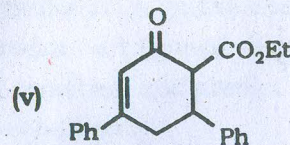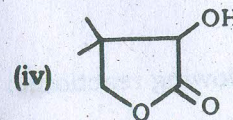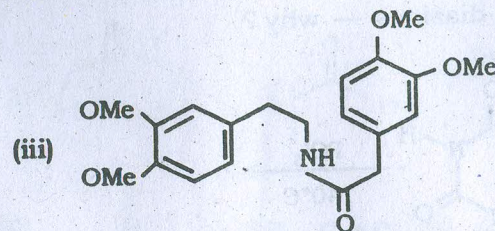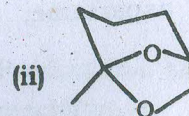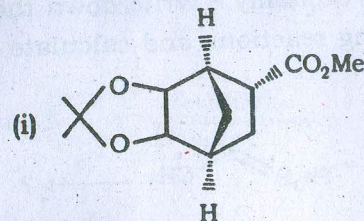
3×4

Group—C

Answer any *five* questions.

(a) (i) What is atom economy ? Write down the product of the following reactions and calculate the atom economy :
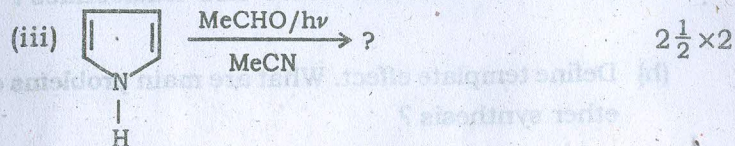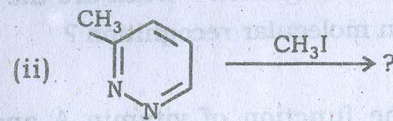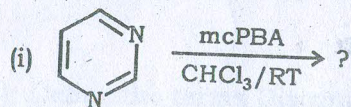
$$CH_3-CO-CH_3 + Ph_3P=CH-CH_3 \longrightarrow ?$$ 1+2

(ii) Using biocatalyst prepare aspartame, artificial sweetner. 2

(b) (i) Pyridazine has higher boiling points than the other diazines — why ? 2

(ii) [barbituric acid structure] $\xrightarrow[140°C]{PCl_5}$? 3

(c) Predic the product(s) of the following reactions : (any *two*)

(i) [pyrimidine] $\xrightarrow[CHCl_3/RT]{mcPBA}$?

(ii) [methylpyridazine] $\xrightarrow{CH_3I}$?

(iii) [pyrrole] $\xrightarrow[MeCN]{MeCHO/h\nu}$? $2\frac{1}{2} \times 2$

(d) Predict the product of the following reaction with mechanism :

(i) [norbornene] + [Ph-CO-Ph] $\xrightarrow{h\nu}$?

(ii) $Ph-CHO + CH_3-C\equiv C-CH_3 \xrightarrow[-78°C]{h\nu}$?
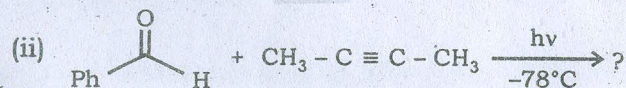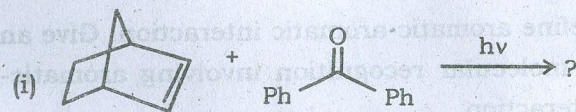
$2\frac{1}{2} \times 2$

(e) Irradiation of butadiene in presence of sensitizer three product are formed with different yield. Explain the rule of sensitizer and predict the product (A → C) with suitable mechanism. 5

(f) What is molecular recognition ? What are the principal forces involved in molecular recognition ?   2+3

(g) (i) What are the function of vitamin A and K.   2

(ii) What are nucleosides and nucleotides ?   3

(h) Define template effect. What are main problems of crown ether synthesis ?   2+3

(i) What are cryptands ? How do you justify that cryptands form more selective and stronger complexes than crown ethers.   2+3

(j) Define aromatic-aromatic interaction. Give an example of molecular recognition involving aromatic-aromatic interaction.   3+2

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