

West Bengal State University

B.A./B.Sc./B.Com. (Honours, Major, General) Examinations, 2013

Part - III

CHEMISTRY — HONOURS

Paper-V (GR. - A + B)

Duration : 4 Hours

[Maximum Marks : 100

*The figures in the margin indicate full marks.***Answers to different Groups must be made in separate answer-scripts.**

GROUP - A

(50 Marks)

Answer any *three* questions, taking *one* from each Unit.

UNIT - I

1. a) What is thermodynamic probability ? Arrive at the Boltzmann distribution formula for an ensemble of non-degenerate system. 1 + 5
- b) Explain qualitatively the reason as to why the vapour pressure of the solution of a non-volatile solute is lower than that of the pure solvent.
- At 27°C an aqueous solution of a carbohydrate containing 18 gms per 100 ml of the solution is found to be isotonic with another aqueous solution 100 ml of which contain 2.923 gms of sodium chloride. Find the molecular weight of the carbohydrate. 2 + 2
- c) Two metals which are completely soluble in the liquid state but show no solid-solid solubility form an eutectic. Apply the phase rule to find whether the eutectic point is invariant or not. How can it be verified that the eutectic mixture is not a compound ? 2 + 2
- d) State Konoualoff's rule. 2
2. a) Write a note on Nernst heat theorem. 2
- b) Express internal energy (U) and Gibbs free energy (G) of a system in terms of partition function. 2 + 2

- c) Derive thermodynamically using chemical potentials a relation between the depression of freezing point of a dilute solution and the molal concentration of the solute. 4
- d) 10 gm of a substance was dissolved in 250 ml of water and osmotic pressure of the solution was found to be 600 mm of mercury at 15°C. Find the molecular weight of the substance. 2
- e) Deduce the phase rule from thermodynamic stand point. 4

UNIT - II

3. a) A metal crystallises with the most compact form among the three cubic crystals. Atomic weight of the metal is 27 and its density is 2.69 gm/cc. Find the closest approach of the atoms in the crystal. 3
- b) Show that Einstein equation of heat capacity of solids reduces to Dulong-Petit's law at very high temperature. 2
- c) Which factors are responsible for the stability of lyophobic and lyophilic colloids? State Schultz-Hardy rule. 3 + 2
- d) What is surface excess? Plot γ vs. $\log C$ of SDS solutions in water and denote the CMC point. $1\frac{1}{2} + 1\frac{1}{2}$
- e) Differentiate between number average and weight average molecular weights of polymer. 3
4. a) The first order reflection of a beam of X-rays from 100 planes of NaCl occurs at an angle of $6^\circ 30'$. Calculate the wavelength of the X-rays.
($\rho_{\text{NaCl}} = 2.165 \text{ gm/c.c.}$) 3
- b) NaCl and KCl show different crystal structures in respect of X-ray crystal study. Explain. 2
- c) Define molar refraction. What is its unit? The refractive index of CCl_4 for the sodium D-line at 20°C is 1.457 and its density is 1.595 gm/c.c. Calculate molar refraction. 1 + 1 + 2
- d) Write a note on 'emulsion'. 2
- e) What is meant by degree of polymerisation? 2
- f) Show graphically the variation of molar polarisation with temperature for (i) a polar substance, (ii) a non-polar substance. Explain the difference. 2 + 1

UNIT - III

5. a) State Lambert-Beer's law of photochemistry. Is there any deviation observed from these laws ? 2 + 1
- b) Absorption of each calorie gives 1.44×10^{-5} gm of hydrogen in the photodissociation of HI vapour using radiation of wavelength 2070 Å. Calculate the quantum yield. 4
- c) Show that the rotational spectral lines of a rigid diatomic molecule are equispaced. 2
- d) The wave number of vibration of HCl^{35} molecule is 2991 cm^{-1} . Calculate the force constant of the HCl bond. 3
- e) What do you mean by Stokes and anti-Stokes lines in Raman spectra ? Compare their intensities. 3
- f) Give a comparative statement on fluorescence and phosphorescence. 3
6. a) Define the following terms : 3
- i) Optical density
- ii) Einstein
- iii) Molar extinction coefficient.
- b) Describe the kinetic features of photochemical reaction of hydrogen and bromine. 3
- c) What is photosensitized reaction ? Explain with two examples. 3
- d) State Stark-Einstein law of photochemical equivalence. 2
- e) Give examples of model systems where the energy gap between successive levels —
- i) remains same
- ii) decreases. 2
- f) Vibrational spectra are band spectra. Explain. 2
- g) The rotational spectrum of FBr ($F = 19$, $\text{Br} = 79$) shows a series of equidistant lines spaced 0.7 cm^{-1} apart. Calculate the rotational constant and bond length. 3

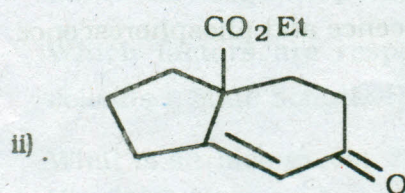
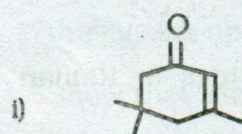
GROUP - B

(50 Marks)

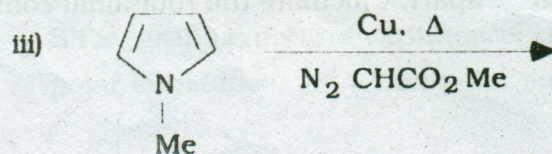
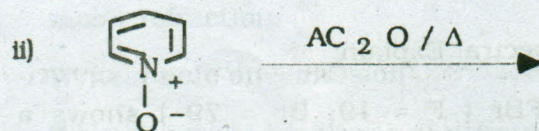
Answer any *three* questions, taking one from each Unit.

UNIT - I

7. a) What do you mean by synthon and synthetic equivalent ? Explain with examples. 2
- b) Carry out the synthesis of any *two* of the following compounds showing the retrosynthetic pathway : 2 × 3 = 6

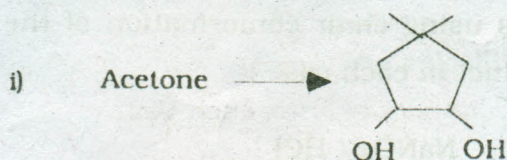


- c) Write down the Feist-Benary synthesis of furan derivative. 2
- d) Write down the structure of phenobarbitol and mention its medicinal use. 2
- e) Outline the synthesis of methyl orange. 2
- f) Predict the product(s) with mechanism (any *two*) : 2 × 2 = 4



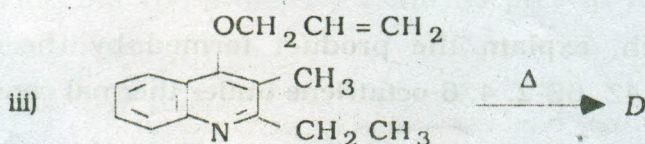
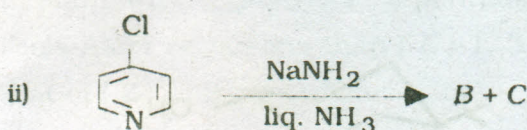
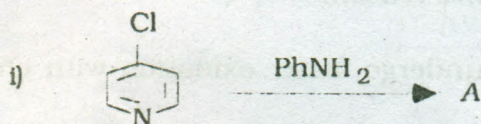
8. a) Carry out the following transformations (any two) :

$$2 \times 2 \frac{1}{2} = 5$$



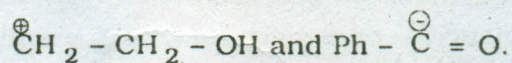
b) Identify A to D with proper explanation :

$$4 \times 1 \frac{1}{2} = 6$$



c) Write down the steps involved in sulphadiazine synthesis. 2

d) Suggest one synthetic equivalent for each of the following : 2



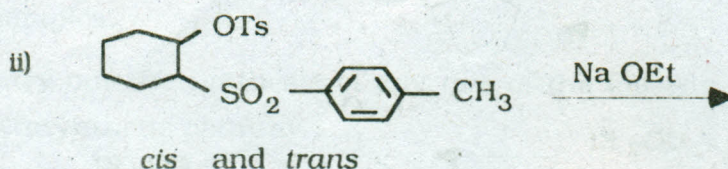
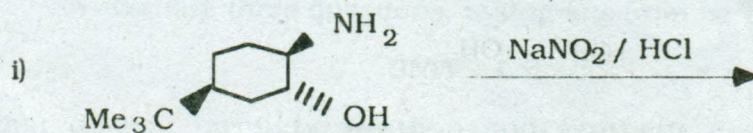
e) Suggest a reason why pyridine is miscible with water, whereas pyrrole has little water solubility. 2

f) Indicate the product of the following reaction (mechanism not required). 1



UNIT - II

9. a) Explain the following reactions using chair conformation of the cyclohexane ring and predict the major product in each case :



2 + 3

- b) Draw the preferred conformations of *trans*-1, 3-di-*tert*-butyl cyclohexane and 1-methyl-1-phenylcyclohexane. Give reason.

 $1\frac{1}{2} + 1\frac{1}{2} = 3$

- c) Which one of the following will undergo faster oxidation with chromic acid ? Give reason.

3



- d) Using FMO approach, explain the product formed by the electrocyclic transformation of 2*E*, 4*Z*, 6*E*-2, 4, 6-octatriene under thermal condition.

3

- e) Give the diene and dienophile that would react in a Diels-Alder reaction to give each of the following product :

2



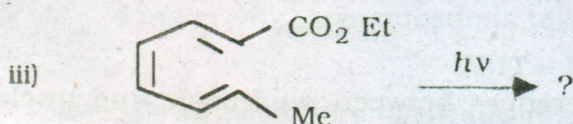
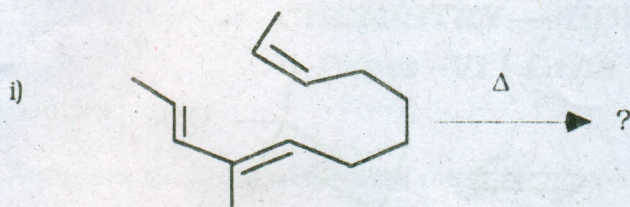
10. a) Explain the following observations (any two) :

 $2 \times 2 = 4$

- i) *Trans*-isomer of 4-*tert*-butyl cyclohexane carboxylic acid is stronger acid than its *cis*-isomer.

- ii) *Cis*-1, 2-dimethyl cyclohexane is optically inactive at room temperature even though the molecule lacks any element of symmetry.

- b) Comment on the strain factors to discuss the relative stabilities of chair and boat forms of cyclohexane. 2
- c) Predict the product(s) of the following reactions with proper stereochemistry : 2 + 2 + 2

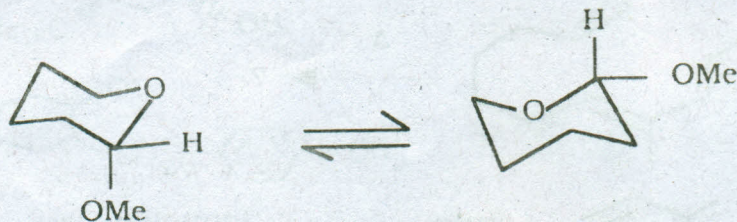


- d) Explain why 4-methyl-1, 3-pentadiene is much less reactive as a diene in Diels-Alder reactions than (E)-1, 3-pentadiene, but its reactivity is similar to that of (Z)-1, 3-pentadiene. 3
- e) Find out the symmetry elements present in the twist boat conformation of cyclohexane. 1

UNIT-III

11. a) Synthesize the tripeptide 'Ala-gly-phe' using Merrifield's method. 3
- b) When aqueous solution of S-alanine is treated with ninhydrin, a purple colour is produced. Show the sequence of reactions with mechanism involved. 3
- c) Write down the different bases present in DNA and RNA. $1\frac{1}{2} + 1\frac{1}{2} = 3$
- d) How would you convert the following ? $2 + 2 = 4$
- i) D-glucose \rightarrow 3-deoxyglucose
- ii) D-mannose \rightarrow D-arabinose.
- e) Bromine-water oxidises β -D-glucose faster than α -D-glucose. Explain with mechanism. 3

12. a) Write down the structure of *L* (+) - arabinose. Why does it exhibit abnormal mutarotation? 1 + 2 = 3
- b) Write down the azalactone synthesis of phenylalanine. 3
- c) Explain why the position of the equilibrium shown below is solvent dependent? 3



In CCl_4 : 83%

17%

In H_2O : 52%

48%

- d) Indicate the structural differences between nucleoside and nucleotide with example. 3
- e) Write short notes on any two of the following : 2 × 2 = 4
- i) Secondary structure of protein
 - ii) Isoelectric point
 - iii) Strecker synthesis.