West Bengal State University

B.A./B.Sc./B.Com. (Honours, Major, General) Examinations, 2012

PART-III

CHEMISTRY - Honours

Paper– V

Duration : 4 Hours | Full Marks : 100

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

The figures in the margin indicate full marks.

GROUP – A

(Full Marks - 50)

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

UNIT - I

1. a) (i) A system consists of three energy states — a ground state ($E_0 = 0$), a first excited state ($E_1 = 2kT$) and a second excited state ($E_2 = 6kT$). The degeneracies of the energy states are respectively 1, 3 and 2. Find out the molecular partition function.

(ii) Show that the relation connecting entropy S of a system with the partition function Q is given by : $S = Nk_B \ln Q + \frac{E}{T}$

E = internal energy of system

k_B = Boltzmann constant

N = Number of molecules in the system

T = Temperature of the system. 2 + 4

b) Mention the assumptions and approximations involved in studying colligative properties of a dilute solution. Derive thermodynamically, using chemical potentials, a relation between the elevation of boiling point of a dilute solution and the molal concentration of the solute. 2 + 4

c) Write notes on any *two* of the following : 2 × 2

(i) Critical solution temperature

(ii) Adiabatic demagnetization

(iii) Abnormal colligative properties

(iv) Eutectic mixtures.

2. a) (i) Derive the expressions for Pressure (P) and Enthalpy (H) in terms of partition function. 2 + 2

(ii) Entropy is a function of thermodynamic probability. How can one conclude that the function is logarithmic ? 2

b) Derive Duhem – Margules equation stating clearly the assumptions. Show that if Raoult's law is applicable to one of the constituents of a binary liquid mixture, at all compositions, it must be equally applicable to the other constituent. 4 + 2

c) (i) Find out the osmotic pressure of a 0·001 M aqueous K_2SO_4 solution at 27° C.

(ii) Boiling point of acetone is 56·5° C and its latent heat of vaporization is 6920 cal/mole. Hence, calculate the molal boiling point elevation constant of acetone. 2 + 2

UNIT - II

3. a) Solid '*A*' has a face centered cubic lattice with the length of the unit cube a = 2·62 Å. Another solid '*B*' has a body centered cubic lattice with a = 2·90 Å. Calculate the ratio of the densities of the two solids. 4

b) Explain the stability of colloid in the context of zeta potential. What do you mean by 'Gold number' and 'Tyndall effect' ? 2 + 1 + 1

c) (i) Explain the action of surface active material from thermodynamic stand point.

(ii) Describe the viscometric method of determination of molecular mass of a polymer. 2 + 2

d) For SO_2(g) at 0° C and 1 atm pressure the dielectric constant is 1·00993. This gas has a permanent dipole moment of 1·63 debye. Assuming that SO_2 behaves as an ideal gas, calculate per mole the orientation and the induced polarization. 2 + 2

4. a) State the assumptions involved in Einstein's theory of heat capacities of a solid. Demonstrate the limitations of the theory through a plot of C_v *vs* T. Mention its probable reasons and suggest the scope of modification. 5

b) A polymer sample contains equal masses of particles with molecular weights 10,000 and 20,000 respectively. Calculate the 'number average' and 'mass average' molecular weight of the polymer. 3

c) What is meant by polarizability of a molecule ? How does molar polarization of polar molecules vary with temperature ? 4

d) (i) Lyophobic colloids are more sensitive to electrolytes than lyophilic colloids. Explain.

(ii) What is salting out ? How is it different from coagulation ? 2 + 2

Unit - III

5. a) What do you understand by rotational constant of a diatomic molecule ? How can it be determined ? 1 + 2

b) (i) What is the essential condition for a molecule to be Raman active ? 1

(ii) Which of the vibrational modes of CO_2 are infrared active and which of them are Raman active ? Why ? 2 + 2

c) State Franck-Condon principle and illustrate with a suitable diagram. 3

d) Use a suitable example to explain the photostationary state. 3

e) In the photochemical combination of H_2 (g) and Cl_2(g) a quantum efficiency of 1×10^6 has been obtained with a wavelength of 4800 Å. How many moles of HCl would be produced under these conditions per calorie of radiant energy absorbed ? 4

6. a) Existence of zero-point energy in a vibrating molecule does not violate Heisenberg's uncertainty principle. Comment. 3

b) What is the difference between overtones and hot bands in the IR spectra ? 2

c) Write down the principle involved in determining the A — A bond distance in a homonuclear molecule (A_2) by spectroscopic method. 4

d) A solution of a coloured compound of concentration $1{\cdot}0 \times 10^{-4}$ M has 20% transmission in a cell of pathlength 1·0 cm at 450 nåm wavelength. Calculate the molar absorption coefficient (ε) of the substance. If the pathlength and the concentration are both halved calculate the percentage transmission. Will the value of 'ε' change if light of wavelength 550 nm is used ? 5

e) Calculate the number of photons of wavelength (i) 350 nm, (ii) 70 nm that have the same energy content of 1 K Cal. 4

GROUP – B

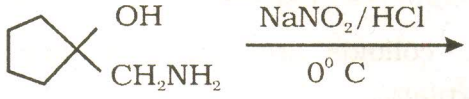
(Full Marks - 50)

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

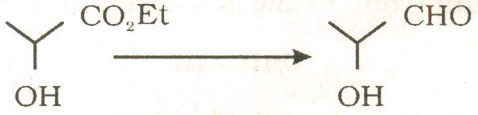
UNIT - I

7. a) What is illogical electrophile ? Explain with an example 2

b) Explain the course of the following reaction and identify the products : 2

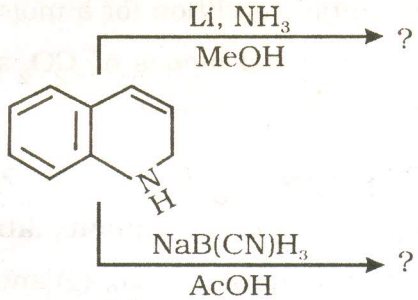


c) Using protection-deprotection technique carry out the following transformation.

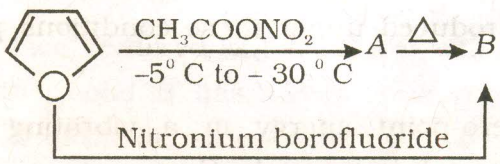


2

d) Predict the products with suitable mechanistic explanation. 3



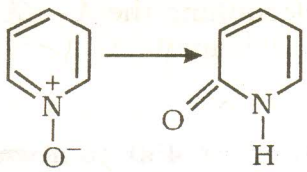
e) Identify *A* and *B* and explain all the steps. 3



f) Carry out the following transformations giving mechanism of the reactions :

2 × 2

(i)



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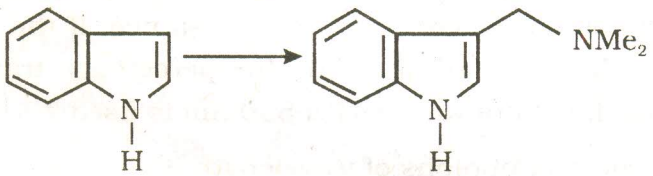
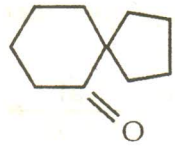
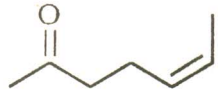
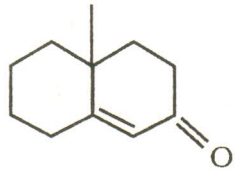


g) Outline the synthesis of fluorescein and write one of its uses. 2

8. a) Show the retrosynthesis of the following compounds by disconnection approach (any *two*) : 2 × 3

(i) 

(ii) 

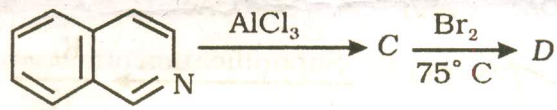
(iii) 

b) Illustrate the use of acyloin reaction for the synthesis of large rings. Does the method require the high dilution technique ? Comment. $2\frac{1}{2}$

c) Write down the Skraup quinoline synthesis mentioning the role of different constituents. 3

d) Compare the basicity of pyrrole and pyridine. 2

e) Predict the products with mechanism : 2

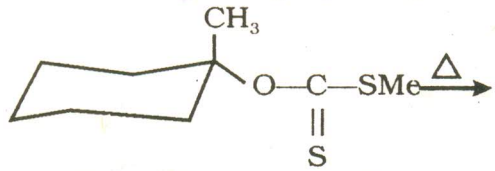


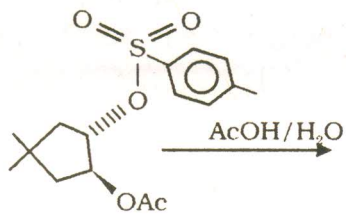
f) Outline the synthesis of phenobarbitol and give one use of it. $1\frac{1}{2}$

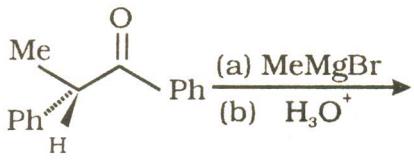
g) Write down the structure of Alizarin. 1

UNIT - II

9. a) Complete the following with proper explanation (any *two*) : 2 × 2

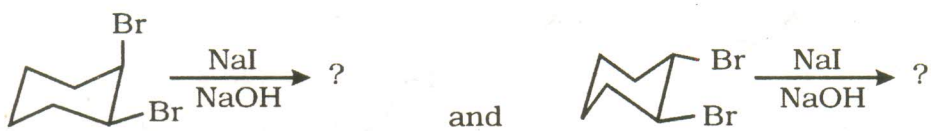
(i) 

(ii) 

(iii) 

b) What is sigmatropic reaction ? What type of [1, 3] H shift do you expect when a reaction is carried out thermally ? Explain considering FMO theory. 1 + 1 + 1

c) Identify the product(s) in the following reactions with proper mechanism : 3



d) Comment on the optical activity of *cis* 1, 2 –di-methylcyclohexane. 2

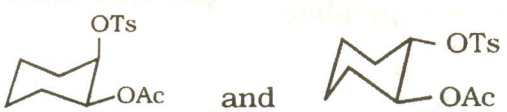
e) Give an example of $\Pi^2s + \Pi^2s$ cycloaddition reaction with proper justification. 2

f) Draw all the conformations of 1-methyl-1-phenylcyclohexane. Which one is more stable and why ? 2

10. a) Explain the following observations (any *two*) : 3 × 2

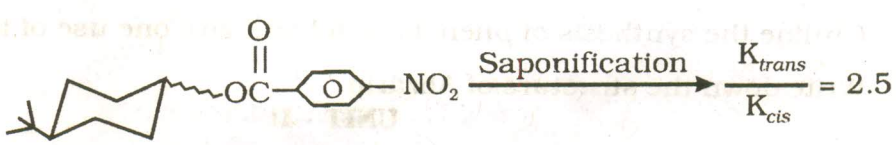
(i) Cyclohexane *cis*-1, 2-diol is cleaved by lead tetra-acetate about 22 times faster than its *trans*-isomer despite the fact that the dihedral angle between the C-OH bonds is same in both the isomers.

(ii) Acetolysis of both *cis*-and *trans*-tosylates shown below give the same *trans*-diacetate.



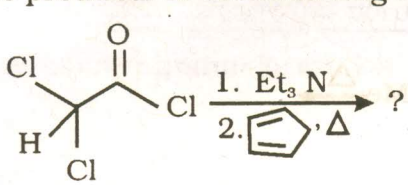
(iii)

but

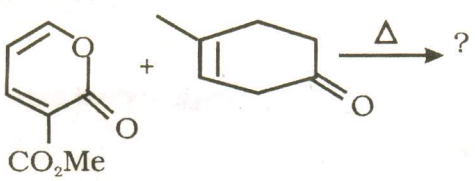


b) Predict the products in the following reactions (any *two*) : 2 × 2

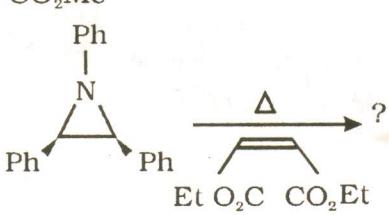
(i)



(ii)



(iii)



c) What happens when the diastereomers of 2-aminocyclohexanol are separately treated with $NaNO_2$ / HCl ? 3

d) Draw the preferred conformation of *cis*-and *trans*-1, 3-dimethylcyclohexane. Comment on their optical activity. 2

e) Write down the symmetry elements present in the boat form of cyclohexane. 1

UNIT - III

11. a) Explain the following (any *two*) : $2 \times 2\frac{1}{2}$

(i) α-D-Glucose exhibits mutarotation when dissolved in water, but methyl α-D-Glucoside does not.

(ii) Sucrose is non-reducting sugar

(iii) α-D-Galactose readily forms diacetonide with acetone/ H^+, but α-D-Glucose does only after isomerisation to the furanose form.

b) How would you convert the following (any *two*) ? 2×2

(i) D-glucose ⟶ D-fructose

(ii) Adenosine triphosphate ⟶ Adenosine

(iii) D-xylose ⟶ D-glucose.

c) Illustrate an application of 2, 4 –dinitrofluorobenzene for the determination of N-terminal amino acid residue of polypeptide. How would you justify its choice over the much less expensive 2, 4 –dinitrochlorobenzene ? 4

d) Propose Strecker synthesis of methionine starting from 2-propenal. Show the appropriate reagents and reaction conditions. 3

12. a) Compare with proper justification the relative proportions of α-D-Glucose and β-D-Glucose (i) in water and (ii) in anhydrous methanol. 3

b) Write down azalactone synthesis of phenylalanine. 2

c) What is co-enzyme ? Give one example. 2

d) When aq. solution of an (S)-alanine is treated with ninhydrin, a purple colour is produced. Show the sequence of reactions with mechanism involved. 4

e) Indicate the structural differences between nucleoside and nucleotide giving suitable example. 3

f) D-glucose exhibits mutarotation in the presence of 2-hydroxypyridine. Explain. 2