

West Bengal State University

B.A./B.Sc./B.Com. (Honours, Major, General) Examinations, 2010

PART - I (Honours)

CHEMISTRY

Paper - I

Duration : 4 Hours]

[Maximum 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

(Marks : 50)

Answer any *three* questions taking one question from each of the *three* Units.

Unit - 1

1. (a) (i) Write down Maxwell's expression for the distribution of molecular speeds in three dimensions and obtain an expression for the distribution of translational kinetic energy. 2 + 4
- (ii) Derive an expression for the number of molecules with translational kinetic energy greater than ϵ' assuming $\epsilon' \gg kT$, k = Boltzmann constant. 2 + 4
- (b) If compressibility factor, Z , for a van der Waals gas be 1.000056 at 0°C and 1 atmosphere and the Boyle temperature be 107 K, calculate neglecting higher terms of P , the values of the van der Waals constants a and b . 4
- (c) Draw the one dimensional velocity distribution curve of the molecules of an ideal gas at two different temperatures and comment on the area under each curve. 3
- (d) Apply the equipartition principle to calculate the average energy per molecule of CO_2 gas at T K. 3

2. (a) A gas obeys equation $P (V - b) = RT$.
- (i) Is it possible to liquefy the gas ? Justify your answer. 2
 - (ii) Show that the gas does not have the Boyle temperature. 2
- (b) Define mean free path of a gas molecule. Derive a relation between mean free path and collision diameter of gas molecules. 1 + 3
- (c) Obtain expressions for the van der Waals constants in terms of critical constants. 6
- (d) Give a schematic plot of Z vs P to show the effect of temperature on deviation of a real gas from ideal behaviour. 2

Unit - 2

3. (a) One mole of an ideal monatomic gas at 298K expands to double its volume at constant pressure. Calculate the heat absorbed by the gas. 2
- (b) Show that $(\partial U / \partial V)_T = 0$ for a gas obeying $P (V - nb) = nRT$ [Derivation of Maxwell relation is not necessary]. Evaluate $(\partial U / \partial V)_T$ for an ideal gas. 2 + 2
- (c) Calculate the change in entropy when 10 g of tin is heated from 293 K to 573 K. The melting point of tin is 505 K. The latent heat of fusion of tin is 14 cal g^{-1} and specific heats of solid and liquid tin are 0.055 cal g^{-1} and 0.064 cal g^{-1} respectively. 4
- (d) One mole of an ideal gas is expanded adiabatically but irreversibly from V_1 to V_2 and no work is done.
- (i) Does the temperature of the gas change ?
 - (ii) What is ΔS for the gas and the surroundings ? 4
- (e) If a reversible Carnot cycle working between two temperatures T_1 and T_2 ($T_2 > T_1$) is plotted on a $T - S$ diagram, show that the area enclosed is equal to the work done in the reversible cycle. Indicate the efficiency of the process as a ratio of two areas in the properly drawn diagram. 4

4. (a) What is meant by Clausius inequality ? 2
- (b) Show that $C_p - C_v = \frac{\alpha^2 TV}{\beta}$
 where, α = coefficient of thermal expansion and
 β = coefficient of compression of gas. 4
- (c) Prove that $\left[\frac{\partial (G/T)}{\partial (1/T)} \right]_P = H$ 4
- (d) For a certain reaction, the change in the Gibbs free energy is ΔG (in lit-mole^{-1}) = $14000 + 7.0 T \ln T - 72.0 T$. Compute ΔS and ΔH of the reaction at 27°C . 6
- (e) For an adiabatic process find the $P - V$ relationship for a van der Waals gas. 2

Unit - 3

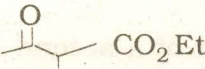
5. (a) Obtain the expression for the rate constant of a second order reaction with different initial concentrations of the reactants. 4
- (b) "Unimolecular reactions are not always first order." Justify the statement using Lindemann's mechanism. 4
- (c) In the gas phase reaction $k = 2.05 \times 10^{13} \exp (-24.65 \text{ k cal mole}^{-1} / RT) \text{ sec}^{-1}$.
 (i) Give the values of A and E_a
 (ii) Find k and $t_{1/2}$ at 0°C . 2 + 2
- (d) Consider the following parallel first order reactions :
 $A \xrightarrow{k_1} B, \quad A \xrightarrow{k_2} C$
 Show that (i) $[B]/[C] = k_1/k_2$ (ii) for the set of initial condition $[B] = [C] = 0$ and $k_1/k_2 = 2$, give a schematic plot of $[A]$, $[B]$ & $[C]$ as a function of time on the same graph. 4
6. (a) Discuss the physicochemical principle of the measurement of energy of activation of a reaction. 4
- (b) Show that the ratio of $t_{1/2}/t_{1/4}$ of any n th order reaction ($n \neq 1$) with identical initial concentration of the reactants, can be written as a function of n alone. 2
- (c) Draw the concentration-time diagram of A , B and C for the following consecutive reactions :
 $A \xrightarrow{k_1} B \text{ and } B \xrightarrow{k_2} C$
 Justify your answer with suitable mathematical forms for concentration. 4
- (d) Discuss the activated complex theory of bimolecular reactions and explain how this helps in evaluating the standard entropy of activation. 4
- (e) Discuss the effect of pH on the enzyme-catalysed reaction. 2

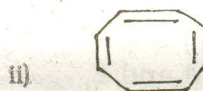
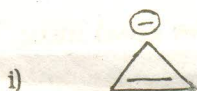
GROUP - B

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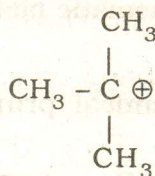
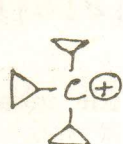
Answer any *three* questions taking one question from each of the *three* Units.

Unit - 1

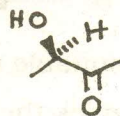
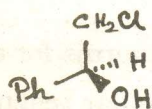
1. (a) Draw the π - MO pictures of the following : 2
- (i) 1,3-butadiene (HOMO in the excited state)
- (ii) Allyl anion (HOMO in the ground state).
- (b) Write the IUPAC names of the following compounds : 2
- (i) $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{C} \equiv \text{CH}$
- (ii)  CO_2Et
- (c) Indicate, with reasons, whether the following compounds are aromatic, non-aromatic or anti-aromatic : 3



- (d) The dipole moment of *p*-nitroaniline is greater than the sum of the dipole moments of aniline and nitrobenzene. Explain. 2
- (e) Which of the following species is more stable and why ? 2

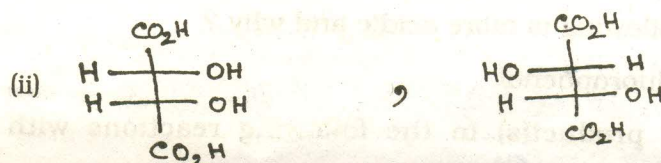
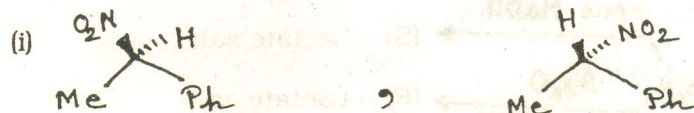


- (f) (i) Draw the potential energy diagram of 1, 2-dichloroethane for rotation around carbon-carbon bond and indicate the most stable conformer. 3
- (ii) Assign R/S descriptors to the stereogenic centres of the following compounds. 3

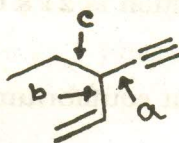


- (iii) Calculate the double bond equivalent of a compound having molecular formula $\text{C}_7\text{H}_9\text{N}$. 1

2. (a) Define the following terms with suitable example :
- Chirotopicity 3
 - Alternating axis of symmetry (S_n). 3
- (b) Write the Fischer projection formula of (2S, 3R)-3-bromo-2-butanol and represent it also in Sawhorse projection formula. 2
- (c) Indicate the relationship (homomer, enantiomer, diastereomer) of the following compounds in each pair. 2



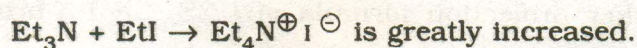
- (d) Arrange the following compounds in order of their increasing heat of hydrogenation values. Explain the order. 2
1-hexene, cis-3-hexene, trans-3-hexene.
- (e) Show that the enol form of ethyl acetoacetate ($\text{CH}_3\text{COCH}_2\text{CO}_2\text{Et}$) may exist as different diastereomers. Indicate, with reason, the more stable diastereomer. 2
- (f) (i) KMnO_4 is insoluble in benzene, but it undergoes dissolution in the presence of 18-crown-6. Explain. 2
- (ii) Compare the boiling point of the following isomeric alcohols :
n-butyl alcohol, sec-butyl alcohol, isobutyl alcohol. 2
- (g) (i) Arrange the indicated bonds of the following compound in order of increasing length. Justify your answer. 2



- (ii) Indicate the most stable conformation of ethylene glycol in Newman projection formula. 1

Unit - II

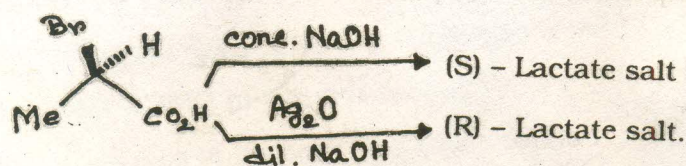
3. (a) When the solvent polarity is increased the rate of the S_N^2 reaction $HO^- + CH_3OSO_2Ph \rightarrow CH_3OH + PhSO_3^-$ is slightly reduced but that of the S_N^2 reaction



Explain.

3

- (b) Explain the following observations :



4

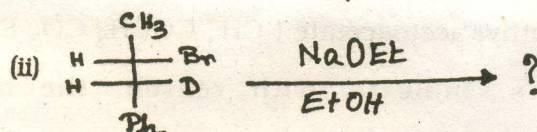
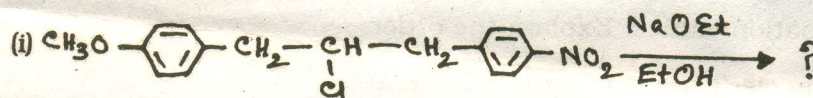
- (c) Which one of the following is more acidic and why ?

p-chlorophenol, *p*-fluorophenol.

2

- (d) Predict the major product(s) in the following reactions with appropriate mechanistic rationalisation.

2 + 2

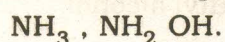


- (e) Predict the product(s) obtained in the reaction of (Z)-2-butene with carbene generated from diazomethane in the absence and in the presence of an inert gas. Give mechanism.

3

4. (a) Compare the nucleophilicity of the following and explain :

2



- (b) Draw explanatory energy profile diagram of the following :

A reaction is endothermic by 16 k cal/mole. The activation energy for the reverse process of that reaction is 21 k cal/mole. Indicate the activation energy of the forward reaction.

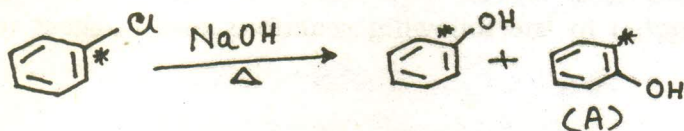
3

- (c) Compare the enol content at equilibrium of the given compounds :

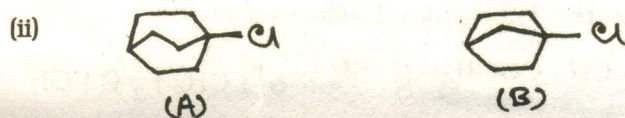
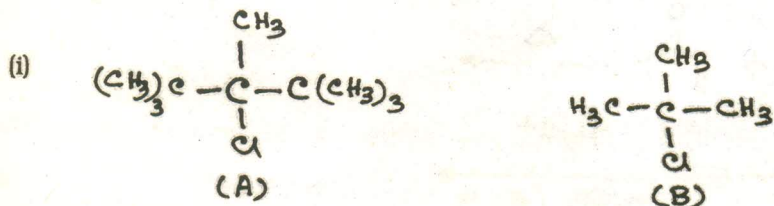
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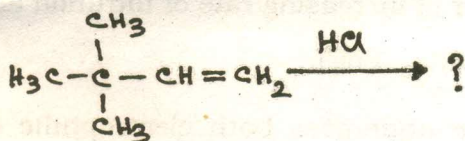
- (d) How would you explain the formation of compound 'A' in the following reaction? 2



- (e) Which of two alkyl chlorides in each set will undergo faster hydrolysis in an S_N1 process? 3



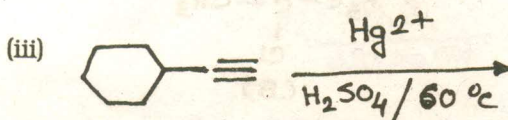
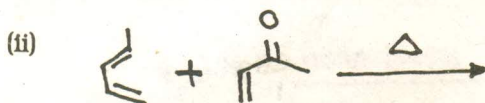
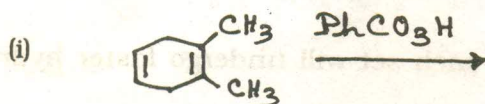
- (f) Indicate the product(s) with mechanism. 4



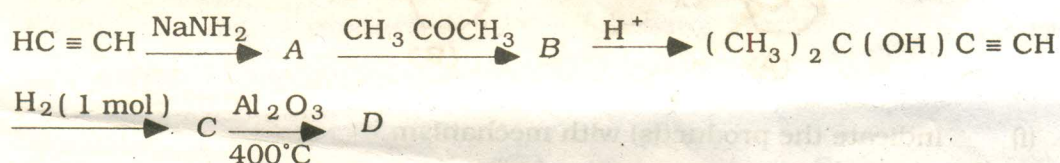
Unit - III

5. (a) Explain the following observations :
- (i) Treatment of benzene with isobutyl chloride in the presence of anhyd. AlCl_3 gives mainly tert-butyl benzene. 2
 - (ii) Bromine adds to E-2-butene with ~ 100% anti-stereoselectivity whereas addition of bromine to 1-phenyl propene takes place with ~ 70% anti-stereoselectivity. 3
 - (iii) Acidic hydration of propene yields 2-propanol while the hydroboration-oxidation gives 1-propanol. 3

- (b) Acetanilide decolourises bromine when treated with Br_2/CCl_4 solution, though it does not contain olefinic unsaturation. Explain. 2
- (c) Predict the product(s) in the following reactions and suggest mechanism in each case. 3×2



6. (a) Identify A, B, C and D in the following transformation : 2



- (b) Arrange the following in order of increasing rate of nitration and give reason : 3
PhH, PhMe, C_6D_6 , PhNO_2 , PhCl.
- (c) Explain why 1, 3-butadiene undergoes both electrophilic and nucleophilic addition reactions. 2
- (d) How can you carry out the following transformations ? 3×3
- (i) 2-butyne \rightarrow Meso - 2, 3-butanediol
- (ii) Acetylene \rightarrow Phenyl acetylene
- (iii) Z-2-butene \rightarrow E-2-butene.