WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 1st Semester Examination, 2022-23

CEMACOR01T-CHEMISTRY (CC1)

ORGANIC CHEMISTRY

Time Allotted: 2 Hours | Full Marks: 40

The figures in the margin indicate full marks.
Candidates should answer in their own words and adhere to the word limit as practicable.
All symbols are of usual significance.

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

UNIT-1

1. (a) Which of the following resonance structures of diazomethane is more stable and why? 2

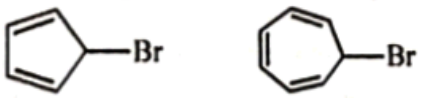
$$CH_2 = \overset{\oplus}{N} = \overset{\ominus}{N} \longleftrightarrow \overset{\ominus}{C}H_2 - \overset{\oplus}{N} \equiv N$$

(b) Can you compare the stabilities of but-1-ene, *cis* and *trans* but-2-ene and 2-methyl-propene by measuring their heat of hydrogenation? If not, why not? What method could you use? 4

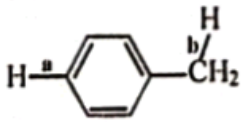
(c) Draw the HOMO of 1,3-butadiene (ground state configuration) and LUMO of 1,3,5-hexatriene (excited state). 3

(d) Compare the dipole moment of *o*-nitroaniline and *p*-nitroaniline. 2

(e) Which of the following bromo compound when treated with $AgNO_3$ solution, is expected to give precipitate of AgBr? Give reason for your choice. 3



(f) Compare the bond dissociation energies of the labelled C-H (**a** & **b**) bonds in toluene. 2



2. (a) Which has the higher dipole moment— (i) allyl bromide or (ii) vinyl bromide? Explain. 3

(b) Assign the following compounds as aromatic, antiaromatic or nonaromatic. Justify. 3

(i) 

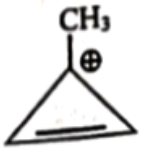
(ii) 

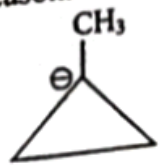
(iii) 

(c) Mention the state of hybridization of each atom except hydrogen in $CH_3-CH=C=O$. Draw the orbital picture of this molecule. 4

(d) Arrange the following ions in order of increasing stability. Give reason. 2

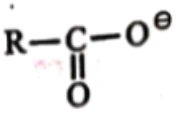
(i) $(CH_3)_2\overset{\oplus}{C}H$

(ii) 

(iii) 

(e) Compare the C=O bond distances in 2

(i) 

(ii) 

(iii) $Me_2C{=}O$

(f) Compare the H–C–H angles in methyl cation and methyl anion. 2

UNIT-2

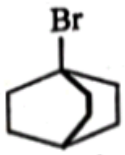
3. (a) Arrange the following ions in the increasing order of nucleophilicity in (i) DMSO and (ii) ethanol and explain the fact. 3

F^-, Cl^-, Br^- and I^-

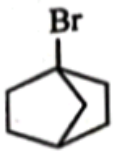
(b) What do you mean by ambident nucleophile? Explain with suitable example. 2

(c) Explain the relative rates of solvolysis (in 80% aqueous ethanol) for the following compounds. 3

Relative rates: 1



10^{-6}



10^{-14}

4. (a) Despite of 1°-nature of the halide in neopentyl halide, it undergoes very slow S_N2 reaction. — Explain. 2

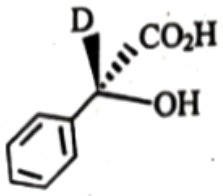
(b) Draw the orbital pictures of singlet and triplet Carbenes. Which state has higher energy and why? 3

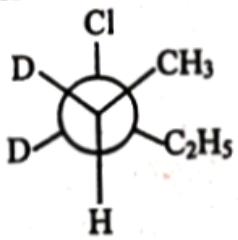
(c) What are carbonium and carbenium ions? Give examples. 3

UNIT-3

5. (a) Indicate symmetry elements present in (i) *trans*-2-butene (ii) acetylene. 2+2

(b) Assign R/S-descriptors for the chiral centres in the following molecules. 3





(c) What happens when *R*-1-phenylethyl acetate is treated with acid? Discuss the mechanism of the reaction indicating stereochemical implications. 3

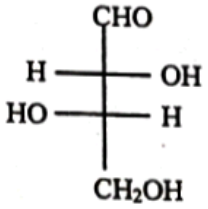
(d) Give an example of an optically active compound possessing a C_2-axis. Indicate the axis. 2

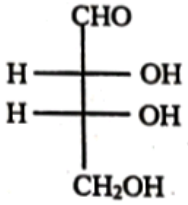
(e) Draw only the achiral stereoisomers of $\underset{\displaystyle CH_3}{\underset{|}{CH}}{=}CH-CHCl-CH{=}\underset{\displaystyle CH_3}{\underset{|}{CH}}$ and assign them with appropriate configurational descriptors (R/S; E/Z). 4

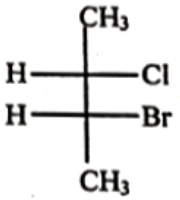
6. (a) Does the presence of chiral centre sufficient for a molecule to be optically active? Explain with suitable example. 2

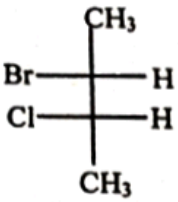
(b) Outline the method for resolution of (±)-lactic acid mixture. 3

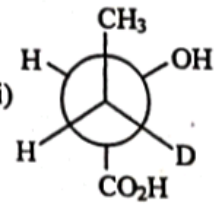
(c) Consider the following pairs of structures and designate each pair as homomer, enantiomer and diastereomer. (any *two*) 2×2=4

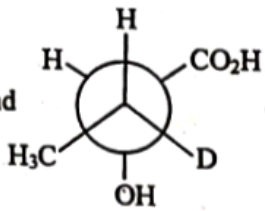
(i) 

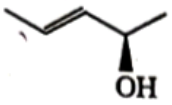
and


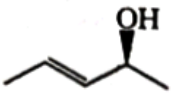
(ii) 

and


(iii) 

and


(iv) 

and


(d) Calculate the optical purity of a sample of 2-butanol which has specific rotation +3.4°. What is the enantiomeric composition of the above mixture? (Optically pure sample of (R)-2-butanol is 13.6) 3

(e) Ph CH(Cl)—CH_3 undergoes racemization when treated with $SbCl_5$. Offer an explanation. 2

(f) Distinguish between racemic modification and racemization with suitable example. 2

——×——

WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 1st Semester Examination, 2022-23

CEMACOR02T-CHEMISTRY (CC2)

PHYSICAL CHEMISTRY-I

Time Allotted: 2 Hours | Full Marks: 40

The figures in the margin indicate full marks.
Candidates should answer in their own words and adhere to the word limit as practicable
All symbols are of usual significance.

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

UNIT-I

1. (a) Plot the Maxwell speed distribution profile of He(g) at, temperature T K. How will the plot change if the temperature is changed to 2T K. Give reasons for your answer. 2

(b) Find an expression for the most probable speed from the Maxwell speed distribution formula clearly stating the conditions involved. 3

(c) Show that the fraction of molecules of an ideal gas with speeds in the range c_{mp} to 1.0001 c_{mp} is constant for a given gas at a given temperature (c_{mp} is the most probable speed). 2

(d) Is it possible to liquefy a gas obeying the equation of state $p\bar{V} = RT(1 + b/\bar{V})$? Justify your answer, where b is van der Waals constant. 2

(e) (i) Find $\left(\frac{\partial U}{\partial V}\right)_{T,n}$ for a van der Waals gas and hence deduce a physical significance of the associated van der Waals constant. 3+1

(ii) What value do you expect for the quantity $\left(\frac{\partial U}{\partial V}\right)_{T,n}$ for an ideal gas (no derivation)? Justify.

2. (a) Molecular speed distribution of gas at a temperature T is given as 1+3

$$f(c) = \frac{1}{n}\frac{dn}{dc} = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} c^x e^{-mc^2/2k_B T}.$$

(i) What does the quantity $f(c)$ signify?

(ii) Find x using only dimensional argument.

(b) Distinguish between Maxwell speed and velocity distributions of a gas at a given temperature. 2

(c) Calculate the ratio of number of molecules having speed in the range $2c_a$ and $(2c_a + dc)$ to the number of molecules having speed in the range c_a and $(c_a + dc)$ (c_a is the average speed). 3

(d) Two gases have compressibility factor values as 1.02 and 0.98. Which one is easier to liquefy? Justify your answer. 2

(e) Van der Waals equation in the virial form at a pressure p is given as 2

$$Z = 1 + \frac{1}{RT}\left(b - \frac{a}{RT}\right)p + \frac{a}{(RT)^3}\left(2b - \frac{a}{RT}\right)p^2 + \cdots\cdots$$

Deduce the condition when the behavior of the gas approaches ideality.

Find an expression for the initial slope of Z vs. p curve and comment on the relative magnitudes of the slope when, the gas behaves nearly ideal.

UNIT-II

3. (a) An ideal gas is isothermally expanded from an initial volume V_i to a final volume V_f in the following two cases: 2+2

Case-I: expansion from V_i to V_f in one step

Case-II: expansion from V_i to V_1 to V_2 to V_f where $V_i < V_1 < V_2 < V_f$.

(i) Indicate the process on separate p vs. V diagrams, and compare the net work done in the two cases.

(ii) What change in the 'net work done' do you expect if the total number of steps of the expansion process is very largely increased?

(b) Show that $C_p - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_{T,n} + p\right]\left(\frac{\partial V}{\partial T}\right)_{p,n}$ and hence show that $C_p - C_V = nR$ for an ideal gas. 4+1

(c) Represent the Carnot cycle on a T-S diagram with appropriate justification, and express the efficiency of the cycle in terms of the ratio of the areas under the curves. 3

(d) A Carnot engine converts $1/6^{th}$ of the supplied heat to work. The efficiency of the engine gets doubled when the temperature of the sink is reduced by 10 °C. Find the temperatures of the source and sink. 2

(e) Consider the following two cases for the formation of $SO_3(g)$ from sulfur: 2

Case-I: $S + O_2 \rightarrow SO_2$ enthalpy change $= \Delta H_I$

$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$ enthalpy change $= \Delta H_{II}$

Case-II: $S + \frac{3}{2}O_2 \rightarrow SO_3$ enthalpy change $= \Delta H_{III}$

How do you expect ΔH_{III} to be connected with ΔH_I and ΔH_{II}? Explain the underlying reason.

6. (a) Both the order and molecularity of a reaction can be fraction. Justify or contradict. 2

(b) (i) Explain the physical significance of the terms present in the Arrhenius equation (showing the variation of rate constant of a reaction with temperature). 2+1

(ii) Based on your answer justify the expected rate of a reaction in the limit $T \to \infty$.

(c) The rate constant of a second-order reaction $(2A \to P)$ is expressed as 4

$$\log(K/L\,\text{mol}^{-1}\text{s}^{-1}) = 10.88 - \frac{3223}{T/K}$$

Find E_a and $t_{1/2}$ at 25 °C if the initial reactant concentration is 4×10^{-3} M (time is monitored in minute).

(d) Distinguish between thermodynamic and kinetic control of product. 2

——×——