2021

CHEMISTRY — HONOURS

Paper : CC-2

Full Marks : 50

The figures in the margin indicate full marks.

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

Write the answers to ***Physical Chemistry-1*** **(Group-A)** and ***Organic Chemistry*** **(Group-B)** questions in separate answer-book.

Group - A

(Physical Chemistry – 1)

Answer ***question no.*** **1** (Compulsory) and ***any five*** questions from the rest (***question nos.*** **2 to 9**)

1. Answer the following questions : 1×8

(a) Justify that the condition $\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$ serve to give the critical constants of a van der Waals gas.

(b) For a reaction A → Product, the plot of $\frac{1}{[A]}$ vs. time is a straight line with a positive intercept. What is the order of the reaction?

(c) Mention which of the intermolecular forces (interactions) are instrumental for the deviation from ideal behaviour in ammonia and argon gas.

(d) What do you mean by a Newtonian fluid and a non-Newtonian fluid?

(e) Calculate the number of Wall-molecule collisions per cm^2 per second in O_2 at 25ºC and 1.0 atm pressure.

(f) What should be the value of the Michaelis-Menten constant K_m in terms of the substrate concentration for which the rate of an enzyme catalysed reaction following Michaelis-Menten Kinetics will be one-fourth of the maximal rate?

(g) In the flow of a liquid through a viscometer, if the radius of the capillary tube is doubled, by what factor will the flow time increase or decrease?

(h) State the law of corresponding states.

2. (a) Draw schematically the one-dimension velocity distribution plots of an ideal gas at two different temperature. What specific type of distribution is it? Calculate the average value of the component velocity of the gas molecules from the one-dimension distribution function.

(b) Show that the ratio of $t_{1/2}/t_{3/4}$ of any nth order reaction ($n \neq 1$), with identical initial reactant concentration, can be written as a function of 'n' alone. 3+2

3. (a) For the mechanism :

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C$$

$$C \xrightarrow{k_3} D$$

(i) Derive the rate law using the steady state approximation to eliminate the concentration of C.

(ii) Assuming that $k_3 <<< k_2$, express the overall activation energy E for the formation of D in terms of the activation energies E_1, E_2, E_3 for the three steps.

(b) At high temperature, the observed $\frac{C_p}{C_v}$ ratio for a non-linear polyatomic ideal gas is $^7/_6$. Determine the atomicity of the gas. 3+2

4. (a) Discuss London Dispersion force. Is it operative in all gases irrespective of its polar or non-polar character?

(b) A thin square plate of area 100 cm^2 is placed on a 1.5 mm thick layer of castor oil of viscosity 9·86 poise. Calculate the force required to pull the lamina horizontally with a velocity of 3 cm sec^{-1}. 3+2

5. (a) Consider the following reversible reaction

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

where both forward and backward reactions are of first order. Derive that :

$$(k_1 + k_{-1})t = \ln\left(\frac{x_e}{x_e - x}\right)$$

where x_e is the equilibrium concentration of B.

(b) The number of collisions sufferred by a single H_2 molecule under a given set of conditions is $6.0\times10^9 S^{-1}$. Find the average molecular speed if the mean free path is 3.0×10^{-8} m. 3+2

6. (a) Hydrolysis of ester is simultaneously catalysed by both H^+ and OH^- ions. The reaction is first-order with respect to each species. Show that the rate is minimum when $[H^+] = \left(\frac{k_{OH^-}}{k_{H^+}} \cdot k_w\right)^{1/2}$.

(b) A sphere of radius 2.0 mm falls through glycerine. What is the viscosity of glycerine if the terminal speed of the ball is 6 cm sec^{-1}? Given : density of sphere = 8.0 gm cm^{-3} and density of glycerine = 1.3 gm cm^{-3}. 3+2

7. (a) Calculate the number of binary collisions occurring per cm^3 per second in a sample of He gas (behaves ideally) kept at 25ºC and 1.0 atm pressure, the collision diameter being 3.61 Å.

(b) For a second-order reaction $A \rightarrow$ products, show that the time required for three-fourths of the reactant to decay $\left(t_{3/4}\right)$ is equal to $3t_{1/2}$. 3+2

8. (a) In an equimolar mixture of Helium (M.W. = 4) and Oxygen (M.W. = 32) gas, what will be the ratio of Wall-Collision frequencies? How will this ratio change when the molar ratio is 1 : 3? (Assume ideal behaviour)

(b) Plot $\log\left(t_{1/2}\right)$ versus $\frac{1}{T}$ for a first-order reaction ($A = 10^8\ S^{-1}$) with explanation. 3+2

9. (a) Derive the expression of the coefficient of viscosity of an ideal gas in terms of the average speed of the molecules, mean free path and number of molecules per unit volume.

(b) For an ideal gas obeying the Maxwellian Distribution of molecular speeds in three dimension, find the maximum value of $\frac{1}{N}\frac{dN_C}{dC}$ for a gas of molar mass 40 g mol^{-1} kept at 127ºC. 3+2

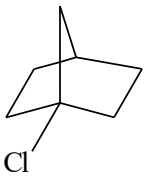
Group - B

[Organic Chemistry (1B)]

Answer ***question no.* 10** (compulsory) and ***any three*** questions from the rest (***question nos.* 11 to 15**)

10. (a) Which one of the following names : Carbonium ion or Carbenium ion, should be appropriate for $\overset{\oplus}{C}H_3$ and $\overset{\oplus}{C}H_5$? (No explanation needed).

(b) The following alkyl halide does not readily form a carbocation. Give reasons. 1+1

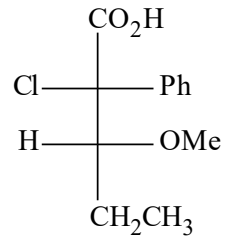


11. (a) Draw all possible stereoisomers of $CH_3CH_2CH(OCH_3)CH=CHCH_3$

Designate (*R* / *S*) and (*E* / *Z*) notations to *any one* of the isomers.

(b) Label the following pairs of molecules as homomers, enantiomers or diastereomers. Explain your answer. 3+2

(i)



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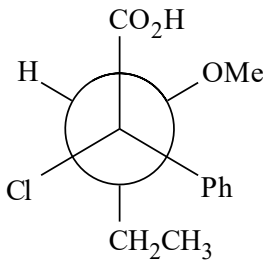
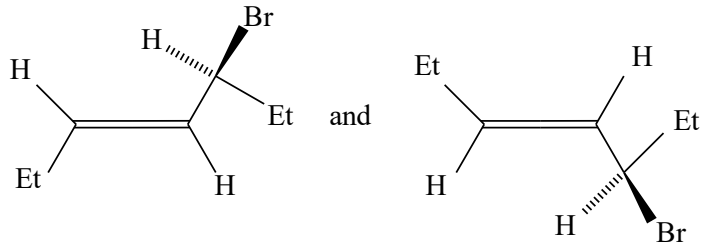


(ii) 

12. (a) Represent the following molecules in Fischer projection formula.

(i) (D) – 2 – Chloro – 2 – phenylbutane

(ii) (2*R*, 3*R*) – 2, 3 – Dibromopentane

(iii) *erythro* Butane – 2, 3 – diol.

(b) Compare the stabilities of the radicals $\dot{C}H_3$, $\dot{C}H_2F$, $\dot{C}F_3$ with proper justification. 3+2

13. (a) Diphenylcarbene is triplet in nature. Justify.

(b) Indicate the symmetry elements present in methylene bromide and acetylene. 3+2

14. (a) A 0.1(M) solution of a pure chiral compound (**A**) has an observed rotation (–)0.4° in a 1dm polarimeter tube. The molecular weight of the compound is 120. Answer the following questions :

(i) What is the $[\alpha]_D^{25°C}$ of (**A**)?

(ii) What is the observed rotation if this solution is mixed with an equal volume of a solution that is 0.1(M) in (+) enantiomer? Justify your answer.

(iii) What is the observed rotation of solution of (**A**), if the solution is diluted with an equal volume of the same solvent? Justify your answer.

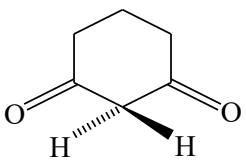
(b) (+)Ph $CH(OH)CH_3$ loses its optical activity when treated with dilute HCl. Explain. 3+2

15. (a) Give appropriate mechanism in each of the following cases. Identify the intermediate involved.

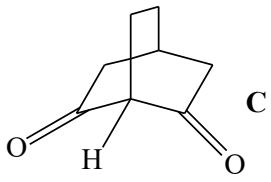
(i) Racemization of α-phenylethyl chloride in presence of antimony pentachloride.

(ii) Racemization of α-phenylethyl chloride in presence of liquid SO_2.

(b) Compound **B** is readily soluble in alkali but compound **C** is not. Explain. 3+2



B



C