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S. No. of Question Paper : **1436**

Unique Paper Code : **2171303** **F-7**

Name of the Paper : **Paper VII : (Organic + Physical Chemistry)**

Name of the Course : **B.Sc. (H) Chemistry**

Semester : **III (FYUP)**

Duration : **3 Hours** Maximum Marks : **75**

(Write your Roll No. on the top immediately on receipt of this question paper.)

This paper has two Sections.

Attempt any *three* questions from each Section.

Section A

Q. No. **1** is compulsory. Attempt any *two* from rest.

1. (*a*) An organic compound (A) C_3H_8O does not forms precipitate with 2,4–Dinitrophenyl hydrazine but gives positive haloform test. Compound (A) reacts with mild oxidizing agents to form compound (B) C_3H_6O, which on treatment with NaOH and I_2 gives yellow precipitate of C. Compounds B forms cyanohydrin with NaCN, which on treatment with dil. H_2SO_4 gives D, B on treatment with $PhMgBr/H_2O$ gives E respectively. Give the structures of compounds A, B, C, D and E. Give name and mechanism of the reaction involved from B to C.

P.T.O.

(*b*) Adipic acid on heating gives different class of compound as compared to phthalic acid.

(*c*) Why pka value of p-hydroxybenzoic acid is higher than that of pka of p-nitrobenzoic acid ? 5+2.5+3+3

2. Do any *four* from the following : 3×4

(*a*) Why CN-is highly specific base in Benzoin Condensation ?

(*b*) Give reasons and arrange the following in increasing order of reactivity towards nucleophilic reactions.

RCOOR, RCOCl, $RCONH_2$

(*c*) Give reasons why Ethyisobutyrate does not undergo Claisen condensation in presence of sodium ethoxide

(*d*) What is the effect of heat on α, β, γ-hydroxy acids ?

(*e*) Convert acetaldehyde to lactic acid.

3. Give the products in the following reactions : 4×3

(*a*) $CH_3(H_2C)_4\text{–}COOC_2H_5 \xrightarrow{\boxed{^-OC_2H_5}}$

(*b*) $C_6H_5CHO \xrightarrow[\boxed{CH_3COONa}]{\boxed{(CH_3CO)_2O}}$

(*c*) $C_6H_5CHO + CH_3CHO \xrightarrow{\boxed{OH^-}}$

(*d*) $C_6H_5COCOC_6H_5 \xrightarrow{\boxed{OH^-}}$

4. Write short notes on : 4×3

(*a*) Beckmann's rearrangement

(*b*) Benzoin condensation

(*c*) Hofmann's degradation reaction

(*d*) Hell–Volhard Zelinsky reaction.

Section B

Attempt *three* questions from Section B. Q. No. **5** is compulsory.

Use of scientific calculator is allowed

Given : $R = 8.314\ JK^{-1}\ mol^{-1}$

5. Attempt any *five* of the following :

(*a*) Chemical reactions with order greater than three are very rare. Explain.

(*b*) Order of a reaction may be positive, negative or a fractional value. Comment.

(*c*) Show by drawing a potential energy diagram that the catalyst lowers the free energy of activation of both forward and backward reaction.

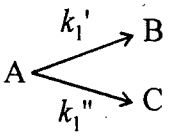
(*d*) Define steady state approximation as applicable to the reactive intermediates involved in a complex chemical reaction.

(*e*) Sketch the graph that is expected between the initial rate and the initial substrate concentration in an enzyme catalyzed reaction. Give significance of region of high initial substrate concentration in the graph.

(*f*) When the acid hydrolysis of the same quantity of ester is done separately with equal normal solutions of HCl and H_2SO_4 then the value of $[k]_{HCl}/[k]_{H_2SO_4}$ is found to be greater than one. Explain.

(*g*) Describe the activated complex theory for rate of a chemical reaction. 5×2½

6. (*a*) Show that the integrated rate expression for the concurrent elementary reaction :



Is given by :

$$\ln \frac{[A]_0}{[A]_t} = (k_1' + k_1'')t$$

Show that the ratio of concentrations of B and C is given by : 3

$$\frac{[B]}{[C]} = \frac{k_1'}{k_1''}$$

(*b*) The reaction :

$$vA \xrightarrow{k_2} \text{products}$$

is second order with respect to "A"

Write down its differential rate law and deduce integral rate law from it. What is the unit of rate constant; k_2 of the reaction ? 4½

(*c*) Thermal decomposition of an organic compound produced the following data :

$t/10^3 s$	$c/(mol/dm^3)$
	Concentration of Organic Compound
0	1.10
2	0.86
4	0.67
6	0.54
8	0.42
10	0.32
12	0.26
∞	0

Determine the order and rate constant of the reaction, using graphical method. 5

7. (*a*) Reaction between NO and O_2 follows the mechanism :

$$NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2$$

$$N_2O_2 + O_2 \xrightarrow{k_2} 2NO_2$$

Show that the rate of the reaction is given by :

$$\frac{1}{2}\frac{d[NO_2]}{dt} = k[NO]^2[O_2] \text{ where } k = k_2 K_{eq}$$

How will you account for the decrease in rate constant of reaction with increase in temperature of the reaction system ? 5

P.T.O.

(*b*) Thermal decomposition of acetaldehyde occurs via the following sequence of steps in a chain reaction :

$$CH_3CHO \xrightarrow{k_1} \cdot CH_3 + \cdot CHO$$

$$\cdot CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + \cdot CH_2CHO$$

$$\cdot CH_2CHO \xrightarrow{k_3} \cdot CH_3 + CO$$

$$\cdot CH_3 + \cdot CH_3 \xrightarrow{k_4} CH_3 - CH_3$$

Show that the differential rate law for the above reaction is given by :

$$\frac{d[CH_4]}{dt} = k\,[CH_3CHO]^{3/2}$$

where $k = k_2(k_1/2k_4)^{1/2}$. 4½

(*c*) Consider the following general reaction :

$$A + B \longrightarrow C + D$$

The rate constant value of the above reaction is 5.03×10^{-2} mol^{-1} dm^3 s^{-1} at 289 K and 6.71 mol^{-1} dm^3 s^{-1} at 333 K. Calculate the activation energy; E_a, of the reaction. 3

8. (*a*) Comparing the rate constants as given by Arrhenius equation and the collision theory, show that :

$$E_a = E_0 + \frac{RT}{2}$$

$$A = \rho N_A \frac{Z_{AB}}{N_A^* N_B^*} e^{1/2}$$

where the symbols have their usual meaning. 5½

(*b*) The bimolecular decomposition of hydrogen iodide is given by the following chemical equation :

$$2HI \longrightarrow H_2 + I_2$$

Calculate the rate of above reaction at 700 K and 1 atm pressure from the data given below :

Collision rate for collision between two identical molecules is $1.02 \times 10^{36}\ m^{-3}\ s^{-1}$. Activation energy of the reaction is 183.9 kJ mol^{-1}

The steric factor for the reaction is unity. 2½

(*c*) For the following acid catalyzed reaction :

$$S + HA \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SH^+ + A^-$$

$$SH^- + H_2O \xrightarrow{k_2} P + H_3O^-$$

Show that the differential rate of reaction is given by :

$$\frac{d[P]}{dt} = \frac{k_2 k_1 [S] [HA]}{k_{-1} [A^-] + k_2}$$

Show under what conditions the reaction may be classified as specific hydrogen ion catalysis. 4½