



1. The rate of hydrolysis of an ester, catalyzed by strong acid, is almost doubled when pH is changed from 0.80 to 0.50. Justify whether this is an example of homogeneous catalysis.

Hints: The rate of hydrolysis of ester = $K[\text{Ester}][\text{H}^+]$
Since $[\text{H}^+] = \text{constant}$ during reaction.

$$\text{Rate} = K[\text{Ester}]$$

$$\text{When pH} = 0.80; [\text{H}^+]_2 = 10^{-0.80} = 0.158$$

$$\text{When pH} = 0.50; [\text{H}^+]_1 = 10^{-0.5} = 0.316$$

$$R_1 = K_1[\text{Ester}]$$

$$R_2 = K_2[\text{Ester}]$$

R_1, R_2 , are the rate of hydrolysis at two different concentrations.

$$\frac{R_1}{R_2} = \frac{K_1}{K_2} = \frac{[\text{H}^+]_1}{[\text{H}^+]_2} = \frac{0.316}{0.158} = 2$$

\therefore The rate of hydrolysis is almost doubled when concentration of acid is almost doubles. Hence it is a case of homogeneous catalysis.

2. For the elementary reaction $A + B \xrightarrow{k} 2C$, express $d[A]/dt$ and $d[C]/dt$ in terms of:
(i) the reaction rate (r)
(ii) rate constant (k) and the molar concentrations of A and B.

Hints: (i) Rate $r = -\frac{d[A]}{dt} = \frac{1}{2} \frac{d[C]}{dt}$

(ii) $\frac{-d[A]}{dt} = K[A]^\alpha [B]^\beta$ (For elementary reaction order and molecularity must be same)

$$\text{and } \frac{1}{2} \frac{d[C]}{dt} = K[A][B] \Rightarrow \frac{d[C]}{dt} = 2K[A][B]$$

3. "Increase of temperature invariably increases the rate of reaction". Justify or criticize.



Hints: From Arrhenius equation: $\frac{d \ln K}{dT} = \frac{E_a}{RT^2}$

If $E_a = +ve$, then with increasing temperature rate constant increases.

If $E_a = 0$; then rate constant does not change with temperature.

If a reversible intermediate step is involved in reaction then, $\frac{d \ln K_{eq}}{dT} = \frac{\Delta H}{RT^2}$

And when $\Delta H = (-)ve$ i.e for exothermic reaction, with increasing temperature K_{eq} decreases and both the rate of forward and backward reaction decreases with increasing temperature. Therefore, overall rate constant decreases with increasing temperature. But for endothermic reaction ($\Delta H = positive$), rate increases with increasing temperature.

4. The initial-rate data for decomposition of N_2O_5 (g) at $55^\circ C$ are as follows :

| $[N_2O_5]/(M)$ | Initial rate / ($M \cdot s^{-1}$) |
|----------------|-------------------------------------|
| 0.02 | 3.4×10^{-5} |
| 0.05 | 8.5×10^{-5} |

Find the rate law and the rate constant for this reaction.

Hints: $-\frac{d[N_2O_5]}{dt} = k[N_2O_5]^\alpha$ $\alpha = \text{order of reaction}$

$$3.4 \times 10^{-5} \text{ Ms}^{-1} = K (0.02 \text{ M})^\alpha \quad \dots\dots(i)$$

$$8.5 \times 10^{-5} \text{ Ms}^{-1} = K (0.05 \text{ M})^\alpha \quad \dots\dots(ii)$$

$$(2) \div (1); \left(\frac{8.5}{3.4}\right) = \left(\frac{0.05}{0.02}\right)^\alpha$$

$$(2.5)^{-1} = (2.5)^\alpha$$

i.e., $\alpha = 1$ (1st order reaction)

now, From equation (i)

$$3.4 \times 10^{-5} \text{ Ms}^{-1} = K (0.02 \text{ M})^1$$

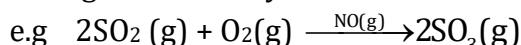
$$\therefore K = \frac{3.4 \times 10^{-5} \text{ Ms}^{-1}}{0.02 \text{ M}}$$

$$\therefore K = 1.7 \times 10^{-3} \text{ s}^{-1}$$



5. What is “homogeneous catalysis”? Give one example.

Hints: A catalyst is defined as a substance which increases the rate of reaction without undergoing any change and the phenomenon is known as catalysis. In homogeneous catalysis reactants and catalyst are in same phase



6. Sucrose is hydrolyzed to glucose and fructose in presence of H^+ as catalyst. At any initial concentration of sucrose the half-lives at $\text{pH} = 5$ and $\text{pH} = 4$ are 500 min and 50 min respectively. Find out the values of the exponents a and b in the rate law expression :

$$-d[\text{sucrose}]/dt = K[\text{sucrose}]^a[\text{H}^+]^b$$

Hints: From the given data, it is evident that the half life period of the reaction is independent of initial concentration of sucrose. Thus, the order with respect to sucrose is 1. Hence, $a = 1$.

From the given data, half life is inversely proportional to the H^+ ion concentration.

$$\frac{\left(\frac{t_1}{2}\right)_1}{\left(\frac{t_1}{2}\right)_2} = \frac{k_2[\text{H}^+]_2^b}{k_1[\text{H}^+]_1^b} = \left(\frac{[\text{H}^+]_2}{[\text{H}^+]_1}\right)^{b+1} \quad \left(\text{since, } \frac{K_2}{K_1} = \frac{[\text{H}^+]_2}{[\text{H}^+]_1}, \text{ is valid for homogeneous catalysis)}\right)$$

$$\log \frac{\left(\frac{t_1}{2}\right)_1}{\left(\frac{t_1}{2}\right)_2} = (b+1) \log \left(\frac{[\text{H}^+]_2}{[\text{H}^+]_1}\right)$$

$$\log \left(\frac{500}{50}\right) = (b+1)(\text{pH}_1 - \text{pH}_2)$$

$$1 = (b+1) \times 1$$

$$b = 0$$



C.U: 2014

7. A certain first order reaction is 20% complete in 15 minutes at 27°C, but for the same extent of reaction at 37°C, only 5 minutes are required. Calculate activation energy of the reaction.

Hints: At 27°C $K = \frac{1}{t} \ln \frac{a}{a-x}$

$$= \frac{1}{15} \ln \frac{100}{80} = 0.0148 \text{ min}^{-1}$$

$$\text{At } 37^\circ\text{C}, K = \frac{1}{5} \ln \frac{100}{80} = 0.0446 \text{ min}^{-1}$$

From Arrhenius equation,

$$\ln \frac{K_1}{K_2} = \frac{E_a}{R} \left[\frac{T_1 - T_2}{T_1 T_2} \right] \quad T_1 > T_2$$

$$\Rightarrow \ln \frac{K_{37^\circ\text{C}}}{K_{27^\circ\text{C}}} = \frac{E_a}{R} \left[\frac{310 - 300}{300 \times 310} \right]$$

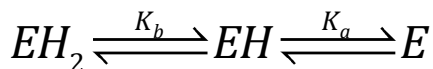
$$\Rightarrow \ln \frac{0.0446}{0.0148} = \frac{E_a}{1.987} \left[\frac{10}{93000} \right]$$

$$\Rightarrow 1.103 = E_a \times 5.41 \times 10^{-5}$$

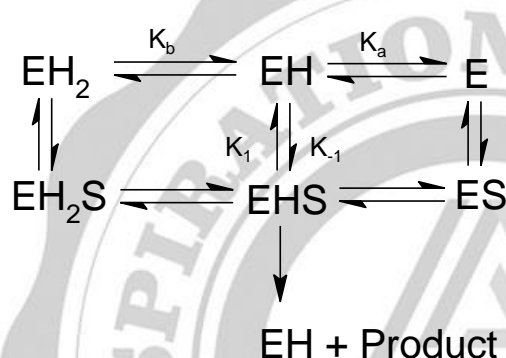
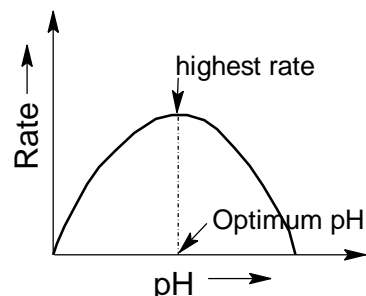
$$\therefore E_a = \frac{1.103}{5.41 \times 10^{-5}} = 20425.925 \text{ Kcal.}$$

8. With a suitable example illustrate the pH dependence of enzyme catalysed reactions.

Hints: Active centre of enzyme can exist in three states of ionization -



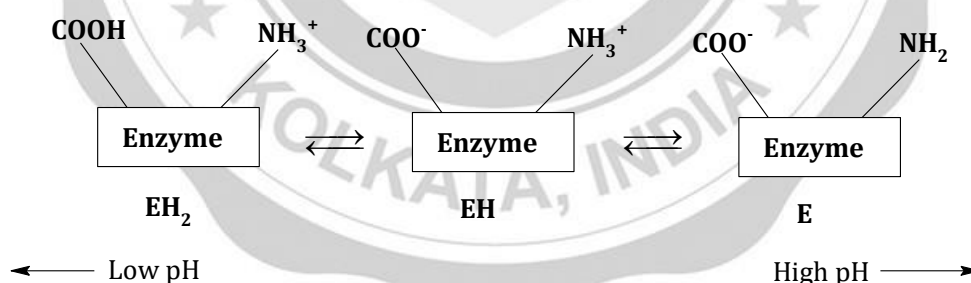
K_a , K_b are dissociation constants. Each of the three forms interacts with substrate and resulting enzyme substrate complex can also exist in three forms. It is postulated that [EHS] is only form that can give rise to product, the reaction scheme is then -



In acid solution, equilibrium all lie over to the left. The enzyme exist largely as [EH₂] and the complex as [EH₂S], since, [EHS] is the reactive form, the rate will be low. Similarly, in basic solution, the form [E] and [ES] will predominates and rate will again be low.

At some intermediate pH, the concentration of [EHS] and the rate will have their maximum value.

e.g.,



The pH behaviour can be explained by postulating that the intermediate, zwitter-ion, form is enzymically active, but that the species to the left and right are inactive. The concentration of the intermediate form goes through a maximum as the pH is varied, so the rate passes through a maximum.

9. A gas decomposes according to second order kinematics. When the initial pressure is 500 torr, 40% decomposition occurs in 30 min. Find out the



time required for 75% decomposition of the gas and the value of the rate constant.

Hints: The specific rate constant for 2nd order reaction is given by –

$$k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$$

Here 't' is the time when the amount of decomposition is 'x' and 'a' is the initial amount. By the problem,

$$k = \frac{1}{30} \cdot \frac{0.4 \times a}{a \times (a - 0.4a)}$$

$$= \frac{1}{30} \times \frac{0.4a}{a \times 0.6a}$$

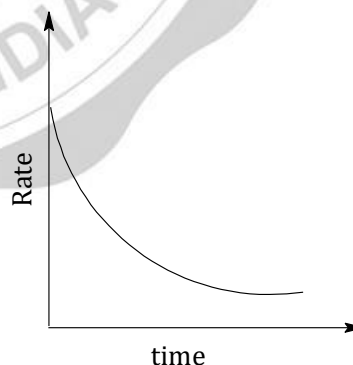
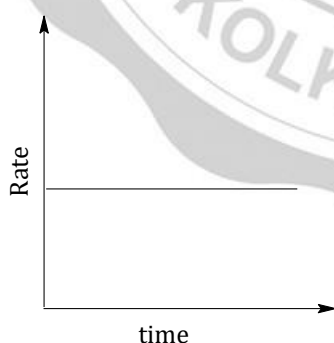
$$\therefore k = \frac{1}{30} \times \frac{0.4}{0.6 \times 500} \text{ torr}^{-1} \cdot \text{min}^{-1}$$

$$= 4.44 \times 10^{-5} \text{ torr}^{-1} \text{ min}^{-1}$$

$$\therefore t_{\frac{3}{4}} = \frac{1}{k} \cdot \frac{0.75a}{a \times 0.25a} = \frac{1}{k} \cdot \frac{3}{a} = \frac{1}{4.44 \times 10^{-5}} \times \frac{3}{500} = 135.135 \text{ min}$$

10. Draw the rate versus time profiles for (i) a zero order reaction (ii) a first order reaction.

Hints: (i) For Zero order reaction (ii) For first order reaction



11. At what value of K_M does the rate of an enzyme catalysed reaction obeying Michaelis-Menten Kinematics become one-fourth of its maximum value?



Hints:
$$r_0 = \frac{r_{0 \max} [S]_0}{1 + K_M}$$

$$\frac{r_{0 \max}}{4} = \frac{r_{0 \max} [S]_0}{[S]_0 + K_M}$$

$$[S]_0 r_{0 \max} + K_M \cdot r_{0 \max} = 4r_{0 \max} [S]_0$$

$$[S]_0 + K_M = 4[S]_0$$

$$K_M = 3[S]_0$$

K_M is 3 times of initial substrate concentration.

12. Considering the parallel reaction : $A \xrightarrow{k_1} B$ & $A \xrightarrow{k_2} C$, In an experiment, it was found that 60% decomposition of A takes places in 20 minutes and analysis of product showed that B and C are in 3 : 1 ratio. Calculate k_1 and k_2 .

Hints: By the problem, $\frac{K_1}{K_2} = 3$ $K_1 = 3K_2$

For parallel reaction: $K_1 + K_2 = \frac{1}{t} \ln \frac{a}{a-x}$

$$3k_2 + K_2 = \frac{1}{20} \ln \frac{a}{a-0.6a}$$

$$4K_2 = \frac{1}{20} \ln \frac{1}{0.4} \quad \therefore K_2 = 0.0114 \text{ min}^{-1}$$

$$K_1 = 3K_2 = 3 \times 0.0114 = 0.0342 \text{ min}^{-1}$$

C.U: 2015

13. Show that a unimolecular process behaves kinetically as second-order at low reactant concentrations.

Hints: See Lindemann's theory (NOT IN SYLLABUS NOW)

14. A sample of milk kept at 25°C is found to sour 40 times as rapidly as when it is kept at 4°C. Estimate the activation energy for the souring process.



Hints: $\frac{K_2}{K_1} = 40$; $T_2 = 298$ K; $T_1 = 277$ K, $E_a = ?$

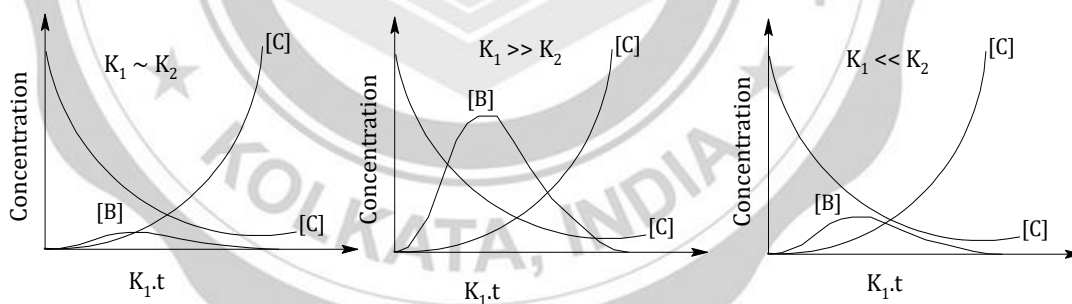
$$\ln \frac{K_2}{K_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$E_a = \frac{R \cdot \ln \left(\frac{K_2}{K_1} \right)}{\left(\frac{1}{T_1} - \frac{1}{T_2} \right)} = \frac{8.314 \ln 40}{\left(\frac{1}{277} - \frac{1}{298} \right)}$$

$$E_a = \frac{8.314 \ln 40}{2.544 \times 10^{-4}} = 12.07 \times 10^4 \text{ J mol}^{-1}$$

15. Draw the graph of concentration versus time of three species A, B, C undergoing the first-order consecutive reactions: $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ under the conditions (i) $k_1 \approx k_2$, (ii) $k_1 \gg k_2$ (iii) $k_1 \ll k_2$.

Hints:



16. In the reaction $AB_2X_2 \rightarrow AB_2 + X_2$, the rate constant is $2.28 \times 10^{-5} \text{ s}^{-1}$ at 320°C . What fraction of the sample AB_2X_2 would decompose by heating it at 320°C for 2 hours?

Hints: $t = \frac{1}{K} \ln \frac{a}{a-x}$

By the problem, $K = 2.28 \times 10^{-5} \text{ s}^{-1}$

$$t = 2 \text{ hrs} = 2 \times 60 \times 60 \text{ sec}$$



$$\therefore 2 \times 60 \times 60 = \frac{1}{2.28 \times 10^{-5}} \ln \frac{a}{a-x}$$

$$\ln \frac{a}{a-x} = 0.16416$$

$$\frac{a}{a-x} = 1.178402844$$

$$\frac{a-x}{a} = 0.848606234$$

$$1 - \frac{x}{a} = 0.8486$$

$$\frac{x}{a} = 1 - 0.8486 = 0.1514$$

So, the percentage is $0.1514 \times 100 = 15.14$

17. How does the time required for a first-order reaction to go 99% completion relate to half-life of the reaction?

Hints: For 1st order reaction $t = \frac{2.303}{K} \log \frac{a}{a-x}$

When 99% complete, then $x = 0.99a$

$$\begin{aligned} t_{0.99} &= \frac{2.303}{K} \log \frac{a}{a-0.99a} \\ &= \frac{2.303}{K} \log \frac{a}{0.01a} = \frac{2.303}{K} \log(100) \end{aligned}$$

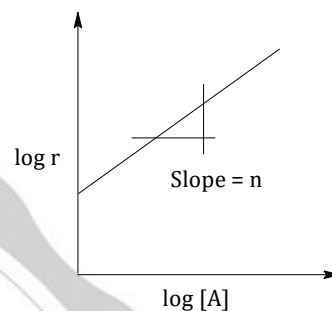
$$t_{0.99} = \frac{2.303 \times 2}{k}$$

$$\begin{aligned} \text{Again } t_{0.5} &= \frac{2.303}{K} \log \frac{a}{a-0.5a} \\ &= \frac{2.303}{K} \log 2 = \frac{2.303 \times 0.3010}{K} \end{aligned}$$



$$\frac{t_{0.99}}{t_{0.5}} = \frac{2.303 \times 2}{K} \times \frac{K}{2.303 \times 0.301} = 6.43 \approx 6.5 \text{ times.}$$

18. Draw the following plots and state the values of the slope and the intercept for each : (i) log (rate) versus log (reactant concentration) for an n-th order process, (ii) log (initial rate) versus log (substrate concentration) at low substrate concentrations for an enzyme catalysed reaction, and (iii) log (rate constant) versus pH for a specific acid catalysed process.



- Hints: (i) For nth order reaction - rate (r) = K[A]ⁿ
 $\log r = \log K + n \log [A]$

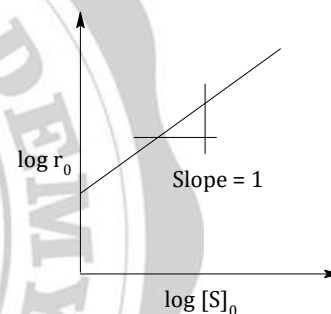
- (ii) For enzyme catalysed reaction,

$$r_0 = \frac{K[E]_0 [s]_0}{K_M + [s]_0}$$

At low substrate concentration $K_M \gg [s]_0$

$$r_0 = \frac{k[E]_0 [s]_0}{K_M} = k'[s]_0 \quad \left[k' = \frac{k[E]_0}{K_M} \right]$$

$$\log r_0 = \log K' + \log [s]_0$$



- (iii) Rate constant of specific acid catalysed process

$$K = K_{H^+} [H^+]$$

$$\log K = \log K_{H^+} + \log [H^+]$$

$$\log K = \log K_{H^+} - \text{pH}$$

