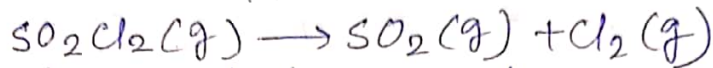


Sem - II  
Chemical Kinetics

1. The reaction



is first order and has a rate constant of  $2.24 \times 10^{-5} \text{ s}^{-1}$  at  $320^\circ\text{C}$ . Calculate the half-life of the reaction. What fraction of a sample of  $\text{SO}_2\text{Cl}_2(\text{g})$  remains after being heated for 5.00 hours at  $320^\circ\text{C}$ ? How long will a sample of  $\text{SO}_2\text{Cl}_2(\text{g})$  need to be maintained at  $320^\circ\text{C}$  to decompose 92% of the initial amount?

Ans:- We have for 1st order  $k$

$$\ln \frac{[\text{SO}_2\text{Cl}_2]}{[\text{SO}_2\text{Cl}_2]_0} = -kt$$

At  $t = t_{1/2}$ ,  $[\text{SO}_2\text{Cl}_2] = \frac{1}{2} [\text{SO}_2\text{Cl}_2]_0$ , then

$$\ln \frac{1}{2} = - (2.24 \times 10^{-5} \text{ s}^{-1}) t_{1/2}$$

$$\text{or, } t_{1/2} = 3.09 \times 10^4 \text{ s}$$

After being heated for 5 hrs. at  $320^\circ\text{C}$ , the amount of  $\text{SO}_2\text{Cl}_2$  present can be found by solving the eq<sup>n</sup>

$$\ln \frac{[\text{SO}_2\text{Cl}_2]}{[\text{SO}_2\text{Cl}_2]_0} = - (2.24 \times 10^{-5} \text{ s}^{-1}) \times 5 \text{ hr} \times 3600 \text{ s/hr}$$

$$\text{or, } [\text{SO}_2\text{Cl}_2] = 0.668 [\text{SO}_2\text{Cl}_2]_0$$

$$\text{or, } \frac{[\text{SO}_2\text{Cl}_2]}{[\text{SO}_2\text{Cl}_2]_0} = 0.668$$

$$\text{or, } [\text{SO}_2\text{Cl}_2] = 66.8\%$$

$\therefore$  66.8% of the sample will remain.

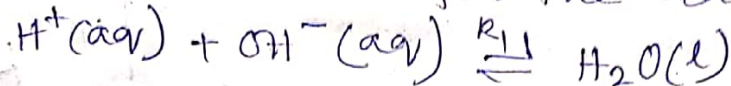
The time it takes to decompose 92% of  $\text{SO}_2\text{Cl}_2$  can be found by solving

$$\ln \frac{[SO_2Cl_2]}{[SO_2Cl_2]_0} = -(2.24 \times 10^{-5} s^{-1}) t$$

$$\text{or, } \ln (1 - 0.92) = -(2.24 \times 10^{-5} s^{-1}) t$$

$$\text{or, } t = 1.13 \times 10^5 s$$

2. The eqm. constant for the reaction



at 25°C is  $K_c = \frac{[H_2O]}{[H^+][OH^-]} = 5.49 \times 10^{15} \text{ mol}^{-1} \text{ dm}^3$

The time-dependent conductivity of the solution following a temperature jump to a final temperature of 25°C shows a relaxation time of  $\tau = 3.7 \times 10^{-5} s$ .

Determine the values of the rate constants  $K_1$  and  $K_{-1}$ .

Ans: - The conc<sup>n</sup> of water at 25°C is

$$\frac{0.997 \text{ g.cm}^{-3}}{18.015 \text{ g.mol}^{-1}} \times \left(\frac{10 \text{ cm}}{1 \text{ dm}}\right)^3 = 55.3 \text{ mol.dm}^{-3}$$

density of  $H_2O$  at 25°C is 0.997 g/cc.

Let  $x$  be the number of moles of water that dissociate per litre. Then at eqm,

$$[H_2O] = 55.3 \text{ mol.dm}^{-3} - x \quad \& \quad [H^+] = [OH^-] = x$$

$$\therefore K_c = \frac{[H_2O]}{[H^+][OH^-]} = \frac{55.3 \text{ mol.dm}^{-3} - x}{x^2}$$

$$\text{or, } 5.49 \times 10^{15} \text{ mol}^{-1} \text{ dm}^3 = \frac{55.3 \text{ mol.dm}^{-3} - x}{x^2}$$



$$x = 1.00 \times 10^{-7} \text{ dm}^{-3} \text{ mol.}$$

taking positive value of  $x$

Then  $[H^+] = [OH^-] = 1.00 \times 10^{-7} \text{ mol dm}^{-3}$ .

Again  $K_c = \frac{k_1}{k_{-1}}$

or,  $k_1 = 5.49 \times 10^{15} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$

$$k_{-1} + k_1 ([H^+] + [OH^-]) = \frac{1}{\eta}$$

or,  $\eta = \frac{1}{k_{-1} + k_1 ([H^+] + [OH^-])}$

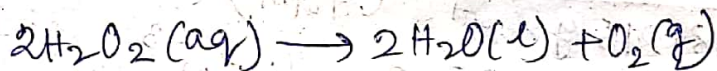
or,  $3.70 \times 10^{-5} \text{ s} = \frac{1}{k_{-1} + k_{-1} \times 5.49 \times 10^{15} (1+1) \times 10^{-7}}$

$\Rightarrow k_{-1} = 2.5 \times 10^{-5} \text{ s}^{-1}$

$k_1 = 5.49 \times 10^{15} \text{ mol}^{-1} \text{ dm}^3 \times 2.5 \times 10^{-5} \text{ s}^{-1}$

or,  $k_1 = 1.4 \times 10^{11} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$

3. ~~The gas phase~~ the protein catalase catalyzes the reaction



and has a Michaelis constant of  $K_m = 25 \times 10^{-3} \text{ mol dm}^{-3}$  and a turnover number of  $4.0 \times 10^7 \text{ s}^{-1}$ . Calculate the initial rate of this reaction if the total enzyme concentration is  $0.016 \times 10^{-6} \text{ mol dm}^{-3}$  and the initial substrate concentration is  $4.32 \times 10^{-6} \text{ mol dm}^{-3}$ . Calculate  $v_{max}$  for this enzyme. Catalase have a single active site.

Ans:- The Michaelis - Menten eq<sup>n</sup> is

$$v = \frac{k_2 [S]_0 [E]_0}{k_m + [S]_0} = \frac{v_{max} [S]_0}{k_m + [S]_0}$$

The turnover number for a single active site catalyst is

We have from Michaelis - Menten eq<sup>n</sup>

$$v_{max} = k_2 [E]_0$$

Therefore, the turnover no. for a single active site catalyst

is  $\frac{v_{max}}{[E]_0} = k_2$

$$\begin{aligned} \text{or, } v_{max} &= k_2 [E]_0 \\ &= (4.0 \times 10^7 \text{ s}^{-1}) (0.016 \times 10^{-6} \text{ mol, dm}^{-3}) \\ &= 0.64 \text{ mol, dm}^{-3} \text{ s}^{-1} \end{aligned}$$

and

$$v = \frac{(0.64 \text{ mol dm}^{-3} \text{ s}^{-1}) (4.32 \times 10^{-6} \text{ mol, dm}^{-3})}{(25 \times 10^{-3} \text{ mol dm}^{-3}) + (4.32 \times 10^{-6} \text{ mol, dm}^{-3})}$$

$$= 1.11 \times 10^{-4} \text{ mol, dm}^{-3} \text{ s}^{-1}$$

$$\left[ v = \frac{k_2 [S]_0 [E]_0}{k_m + [S]_0} = \frac{v_{max} [S]_0}{k_m + [S]_0} \right]$$

turnover number is defined as the max<sup>m</sup> rate divided by the conc<sup>n</sup> of enzyme active sites

$$v_{max} / [E]_0$$

4) The presence of  $4.8 \times 10^{-6} \text{ mol dm}^{-3}$  of a competitive inhibitor decreases the initial rate of  $(1.11 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1})$  by a factor of 3.6. Calculate  $K_I$ , the eqm. const for the binding reaction between the enzyme and the inhibitor,

Given  $v_{\text{max}} = 0.64 \text{ mol dm}^{-3} \text{ s}^{-1}$

an.  $K_m$  (Michaelis const) =  $25 \times 10^{-3} \text{ mol dm}^{-3}$

$[S]_0 = 4.32 \times 10^{-6} \text{ mol dm}^{-3}$

Ans:- The initial rate of an enzyme inhibition  $\propto K^n$ .

$$v = \frac{K_3 [E]_0 [S]_0}{K_m (1 + K_I [I]) + [S]}$$

$$= \frac{v_{\text{max}} [S]_0}{K_m (1 + K_I [I]) + [S]}$$

$$\frac{1.11 \times 10^{-4}}{3.6} = \frac{0.64 \times 4.32 \times 10^{-6}}{25 \times 10^{-3} (1 + K_I \times 4.8 \times 10^{-6}) + 4.32 \times 10^{-6}}$$

$$\Rightarrow K_I = 5.4 \times 10^5 \text{ dm}^3 \text{ mol}^{-1}$$

5) Antibiotic-resistant bacteria have an enzyme, penicillinase, that catalyzes the decomposition of the antibiotic. The molecular mass of penicillinase, that catalyses is 30,000  $\text{g mol}^{-1}$ . The turnover number of the

enzyme at  $28^{\circ}\text{C}$  is  $2000\text{ s}^{-1}$ . If  $6.4\text{ kg}$  of penicillinase catalyses the destruction of  $3.11\text{ mg}$  of amoxicillin, an antibiotic with a molecular mass of  $364\text{ g mol}^{-1}$ , in 20 seconds at  $28^{\circ}\text{C}$ , how many active sites does the enzyme have?

Ans- 
$$\frac{6.4 \times 10^{-6}\text{ g}}{30,000\text{ g mol}^{-1}} = 2.13 \times 10^{-10}\text{ mol penicillinase.}$$

$$\frac{3.11 \times 10^{-3}\text{ g}}{364\text{ g mol}^{-1}} = 8.54 \times 10^{-6}\text{ mol amoxicillin.}$$

This amount amoxicillin catalyzed in twenty seconds. Since the catalyst is not destroyed in the reaction, the same amount of penicillinase will destroy  $2.56 \times 10^{-5}\text{ mol}$  of amoxicillin in one minute, Now

$$\begin{aligned} \text{turnover no.} \times \text{active sites} \\ = \frac{2.56 \times 10^{-5}\text{ mol. min}^{-1}}{2.13 \times 10^{-10}\text{ mol}} \end{aligned}$$

$$2000\text{ s}^{-1} \times \text{active sites} = 1.20 \times 10^5\text{ min}^{-1}$$

$$\text{active sites} = \frac{2000\text{ s}^{-1}}{1.20 \times 10^5\text{ min}^{-1}}$$

$$= \frac{2000\text{ s}^{-1} \times 60}{1.20 \times 10^5\text{ min}^{-1}}$$

$$= \frac{12 \times 10^4}{12 \times 10^4} = 1$$