$$\frac{1}{300}-\frac{1}{T_2}=\frac{100-80}{100\times300}=\frac{20}{100\times300}=\frac{1}{1500}$$

$$\frac{1}{T_2}=\frac{1}{300}-\frac{1}{1500}=\frac{5-1}{1500}=\frac{4}{1500}$$

$T_2 = 375$

Change in temp = 375 – 300 = 75 Ans.

Subjective based Questions :

19. The conversion of A into B is an auto-catalytic reaction $A \rightarrow B$ where B catalyzes the reaction. The rate equation is –dx/dt = kxy where x and y are concentrations of A and B at time t. Integrate this equation for initial concentration x_0 and y_0 for A and B. Show that:

$$kt=\frac{2.303}{x_0+y_0}\log\frac{x_0-y}{x-y_0}.$$

Sol.

$$\begin{array}{ccc} A & \rightarrow & B \\ x_0 & & y_0 \\ (x_0-a) & & (y_0+a) \\ =x & & =y \end{array}$$

$\therefore x + y = x_0 - a + y_0 + a = x_0 + y_0$

$$-\frac{dx}{dt}=kx.y$$

Put $x_0 - a = x$

$$\therefore \quad -\frac{da}{dt}=\frac{dx}{dt}$$

$$\frac{da}{ddt}=K(x_0-a)(y_0+a)$$

$$= K\left[x_0y_0+ax_0-ay_0-a^2\right]$$

$$= K\left[x_0y_0+(x_0-y_0)a-a^2\right]$$

$$= K\left[(x_0y_0)-\left\{a^2-2\left(\frac{x_0-y_0}{2}\right).a-\left(\frac{x_0-y_0}{2}\right)+\left(\frac{x_0-y_0}{2}\right)^2\right\}\right]$$

$$= K\left[x_0y_0-\left(a-\frac{x_0-y_0}{2}\right)+\left(\frac{x_0-y_0}{2}\right)^2\right]$$

On integrating,

$$Kt+C=\frac{1}{\frac{2(x_0+y_0)}{2}}\log\frac{\frac{x_0+y_0}{2}+\left[a-\frac{x_0-y_0}{2}\right]}{\frac{x_0+y_0}{2}-\left[a-\frac{x_0-y_0}{2}\right]}$$

$$Kt+C=\frac{1}{x_0+y_0}\log\frac{a+y_0}{(x_0-a)}$$

at t = 0, a = 0

$$C = \frac{1}{x_0 + y_0}\log\frac{y_0}{x_0}$$

$$\therefore \qquad Kt = \frac{1}{x_0 + y_0}\log\frac{a + y_0}{(x_0 - a)}.\frac{x_0}{y_0} = \frac{1}{x_0 + y_0}\log\frac{y - x_0}{x - y_0}$$

$$= \frac{2.303}{(x_0 + y_0)}\log\frac{y - x_0}{x - y_0}$$

20. Derive an expression for the rate of reaction:

$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

With the help of following mechanism

$$N_2O_5 \xrightarrow{K_a} NO_2 + NO_3$$

$$NO_3 + NO_2 \xrightarrow{K_{-a}} N_2O_5$$

$$NO_2 + NO_3 \xrightarrow{K_b} NO_2 + O_2 + NO$$

$$NO + NO_3 \xrightarrow{K_c} 2NO_2$$

Sol. $\text{Rate} = \frac{k_a \times k_b}{k_{-a} + 2k_b}[N_2O_5]$

$$N_2O_5 \xrightarrow{K_a} NO_2 + NO_3$$

$$NO_2 + NO_3 \xrightarrow{k_b} NO_2 + O_2 + NO$$

$$NO + NO_3 \xrightarrow{k_c} 2NO_2$$

$$\frac{-d[N_2O_5]}{dt} = k_a[N_2O_5] - k_{-a}[NO_2][NO_3] \quad ......(i)$$

$$\frac{d[NO_3]}{dt} = k_a[N_2O_5] - k_{-a}[NO_2][NO_3] - k_b[NO_2]$$

$[NO_3] - k_c\,[NO][NO_3] = 0$ ....(ii)

$$\frac{d[NO]}{dt} = k_b[NO_2][NO_3] - k_c[NO][NO_3] = 0 \; ....(iii)$$

From equation (iii)

$$[NO] = \frac{k_b}{k_c}[NO_2]$$

putting this in equation (i)

$$\frac{-d[N_2O_5]}{dt} = k_a[N_2O_5] - \frac{k_a k_{-a}[N_2O_5]}{k_{-a} + 2k_b}$$

$$\frac{-d[N_2O_5]}{dt} = \frac{2k_a k_b[N_2O_5]}{k_{-a} + 2k_b}$$

$$r = \frac{-1}{2}\frac{d[N_2O_5]}{dt} = \frac{k_a k_b[N_2O_5]}{k_{-a} + 2k_b}$$

21. For the reaction

$A \rightleftharpoons P$

Following data is produced

Time/Hr.	0	1	2	3	4	∞
%A	100	72.5	56.8	45.6	39.5	30

Find k_1, k_{-1} and Keq.

Sol. $k_1 = 9.74 \times 10^{-5}\ \text{sec}^{-1}$, $k^{-1} = 4.16 \times 10^{-5}\ \text{sec}^{-1}$

At t = ∞ when equilibrium is established

$$k = \frac{[P]}{[A]} = \frac{7}{3} = 2.33$$

$$\frac{k_1}{k_{-1}} = 2.33 \Rightarrow k_1 = 2.33k_{-1}$$

$$[A] = \frac{k_2[A]_0}{k_1 + k_{-1}}\left[1 - e^{-(k_1+k_{-1})t}\right]$$

$$0.725 = \frac{1}{3.33}\left[1 + 2.33e^{-3.33k_{-1}\times 3600}\right]$$

$k_{-1} = 4.16 \times 10^{-5}\text{sec}^{-1}$

$k_1 = 2.33k_{-1} = 9.7 \times 10^{-5}\text{sec}^{-1}$

22. The decomposition of a compound P, at temperature T according to the equation

$2P_{(g)} \rightarrow 4Q_{(g)} + R_{(g)} + S_{(l)}$

is the first order reaction. After 30 minutes from the start of decomposition in a closed vessel, the total pressure developed is found to be 317 mm Hg and after a long period of time the total pressure observed to be 617 mm Hg. Calculate the total pressure of the vessel after 75 minute, if volume of liquid S is supposed to be negligible. Also calculate the time fraction $t_{7/8}$.
Given: Vapour pressure of $S_{(l)}$ at temperature T = 32.5 mm Hg.

Sol. $P_t = 379.55$ mm Hg, $t_{7/8} = 399.96$ min

$$2P_{(g)} \rightarrow 4Q_{(g)} + R_{(g)} + S_{(l)}$$

t = 0 P_0
t = 30 min. $P_0 – P$ $2P$ $P/2$
t = ∞ –2 P_0 $P_0/2$

so $P_0 – P + 2P + P/2 = 317 – 32.5$

i.e. $P_0 + 1.5\,P = 284.5$ ....(i)

& $2.5\,P_0 = 617 – 32.5 = 584.5$

so $P_0 = 233.8$

$P = 33.8$

$$k \times 30 = \ln\frac{233.8}{200} \Rightarrow k = 0.0052$$

At t = 75 min

$$0.0052 \times 75 = \ln\frac{233.8}{P^{o} - P}$$

$P° – P = 158.23 \Rightarrow P = 75.57$

$P_T = 32.5 + P_0 + 1.5\ P = 347.155 + 32.5$

$P_T = 379.65$ mm Hg

(ii) $0.0052 \times t = \ln 8$

t = 399.89 min.

23. The acid catalysed hydrolysis of an organic compound A at 30°C has a time for half change of 100 minutes, when carried out in a buffer solution at pH 5 and of 10 minutes, when carried out at pH 4. Both times of half change are independent of the initial concentration of A. If the rate of reaction is given by $\frac{-d[A]}{dt} = k[A]^a[H^+]^b$, what are the values of a and b?

Ans. **(a = 1, b = 2)**

Sol. Independency of half-life on initial concentration is a characteristic of first order rxn. Since halflife doesn't change with change in conc. of A. Also, half-life is inversely proportional to the concentration of H^+. $\therefore$ $a = 1$ & $b = 2$

24. Derive an expression for the rate of reaction:

$H_2\ (g) + Br_2\ (g) \rightarrow 2HBr\ (g)$

With the help of following mechanism

$Br_2 \xrightarrow{k_1} 2Br$; $Br + H_2 \xrightarrow{k_2} HBr + H$

$H + Br_2 \xrightarrow{k_3} HBr + Br$; $H + HBr \xrightarrow{k_4} H_2 + Br$; $Br + Br \xrightarrow{k_5} Br_2$

Sol. $$\frac{d[HBr]}{dt} = \frac{2k_2(k_1/k_5)^{1/2}[Br_2]^{1/2}[H_2]}{1 + (k_4/k_3)[HBr]/[Br_2]}$$

The rate law of the above reaction can be conveniently derived by using the steady-state approximation. The rate of formation of HBr is given by

$$\frac{d[HBr]}{dt} = k_2[Br][H_2] + k_3[H][Br_2] - k_4[H][HBr] \quad .....(1)$$

Applying the steady-state approximation to H and Br, we get

$$\frac{d[H]}{dt} = 0 = k_2[Br][H_2] - k_3[H][Br_2] - k_4[H][HBr] \quad .....(2)$$

$$\frac{d[Br]}{dt} = 0 = 2k_1[Br_2] - k_2[Br][H_2] + k_3[H][Br_2] + k_4[H][HBr] - 2k_5[Br]^2 \quad ......(3)$$

Making use if Eq. (2) in Eq. (2), we get

$$2k_1[Br_2] - 2k_5[Br]^2 = 0$$

$$\text{or} \quad [Br] = \left(\frac{k_1}{k_5}[Br_2]\right)^{1/2} \quad ......(4)$$

From Eq. (2), we get

$$[H]=\frac{k_2[Br][H_2]}{k_3[Br_2]+k_4[HBr]}$$

Substituting [Br] from Eq. (4) in the above relation, we get

$$[H]=\frac{k_2(k_1/k_5)^{1/2}[Br]^{1/2}[H_2]}{k_3[Br_2]+k_4[HBr]} \text{......(5)}$$

Invoking Eq. (2) in Eq. (1), we get

$$\frac{d[HBr]}{dt}=2k_3[H][Br_2]$$

Substituting [H] from Eq. (5) in the above expression, we get

$$\frac{d[HBr]}{dt}=2k_3\left(\frac{k_2(k_1/k_5)^{1/2}[Br_2]^{1/2}[H_2]}{k_3[Br_2]+k_4[HBr]}\right)[Br_2]$$

$$\frac{2k_2(k_1/k_5)^{1/2}[Br_2]^{1/2}[H_2]}{1+(k_4/k_3)[HBr]/[Br_2]}$$

25. For the reaction A → B, the rate law expression is $-\frac{d[A]}{dt}$ = K$[A]^{1/2}$. If initial concentration of A is A_0.

Calculate : (a) integrated form of the rate law expression

(b) nature of plot of $[A]^{1/2}$ vs time.

(c) half life period.

Sol. **(a)** $A \longrightarrow B$

$$\frac{-d[A]}{dt} = K\,[A]^{\frac{1}{2}}$$

$A \longrightarrow B$

$t = 0\ a = C_O$

$t = t\ (a-x) = C_t$

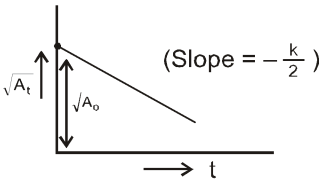
$$\frac{-d[A]}{dt} = K\ \ [A]^{\frac{1}{2}}$$

$$\int_{A_0}^{A_t}\frac{1}{(A_t)^{\frac{1}{2}}}.dA_t = -\int_0^t K\,dt$$

$$\left[\frac{(A_t)^{\frac{1}{2}}}{\left(\frac{1}{2}\right)}\right]_{C_O}^{C_t} = -kt \qquad 2[(C_t)^{\frac{1}{2}}-(C_O)^{\frac{1}{2}}] = -kt$$

$$(A_t)^{\frac{1}{2}}-(A_0)^{\frac{1}{2}} = \frac{kt}{2} \qquad = \sqrt{A_t}-\sqrt{A_0}-\frac{kt}{2} \qquad \sqrt{A_t}=\sqrt{A_0}-\frac{kt}{2}$$

(b) $$\sqrt{A_t}=\left(\frac{-k}{2}\right)t+\sqrt{A_0}$$



(c) For Half life $A_t = \left(\frac{A_0}{2}\right)$

$$\sqrt{\frac{A_0}{2}} = \sqrt{A_0} - \frac{kt_{1/2}}{2} \Rightarrow \frac{kt_{1/2}}{2} = \sqrt{A_0} - \sqrt{\frac{A_0}{2}}$$

$$t_{\frac{1}{2}} = \frac{2}{k}\left[\frac{\sqrt{2}\sqrt{A_0} - \sqrt{A_0}}{\sqrt{2}}\right] \Rightarrow \qquad t_{\frac{1}{2}} = \frac{2}{k}\left[\frac{\sqrt{2}-1}{\sqrt{2}}\right]\sqrt{A_0} = \frac{\sqrt{2}\left(\sqrt{2}-1\right)\sqrt{A_0}}{k} = t_{1/2}$$

26. **(a)** Let there be as first-order reaction of the type, A → B + C. Let us assume that all three species are gases. We are required to calculate the value of rate constant based on the following data.

Time	0	T	∞
Partial pressure of A	P_0	P_t	–

(b) Let there be a first order reaction, A → B + C. Let us assume all three are gases. We are required to calculate the value of rate constant based on the following data

Time	0	t	∞
Total pressure	P_0	P_t	–

Calculate the expression of rate constant.

(c) $A(g) \rightarrow B(g) + C(g)$

Time	0	t	∞
Total pressure of B + C	–	P_t	P_∞

Calculate the expression of rate constant.

(d) $A(g) \rightarrow B(g) + C(s)$

Time	0	t	∞
Total pressure of B	–	P_t	P_∞

Calculate the expression of rate constant.

Sol. **(a)** $A \longrightarrow B + C$

t = 0   a   0   0 $a \propto P_0$

t = t   a - x   x   x $(a-x) \propto P_t$

$$Kt = \ln\left(\frac{a}{a-x}\right) \Rightarrow \quad k = \frac{1}{t}\ln\left(\frac{P_0}{P_t}\right)$$

(b) $A \longrightarrow B + C$

t=0   a   0   0 $a \propto P_0$

t=t   a-x   x   x $(a+x) \propto P_t \quad \Rightarrow \quad x \propto (P_t - P_0)$

$$Kt = \ln\left(\frac{a}{a-x}\right) \Rightarrow \quad k = \frac{1}{t}\ln\left(\frac{P_0}{P_0-(P_t-P_0)}\right) \quad \Rightarrow \quad k = \frac{1}{t}\ln\left(\frac{P_0}{2P_0-P_t}\right)$$

(c) $A \longrightarrow B + C$

t = 0   a   0   0

t = t   a-x   x   x $2x \propto P_t \quad \Rightarrow \quad x \propto \frac{P_t}{2}$

t = ∞   0   a   a $2a \propto P\infty \quad \Rightarrow \quad a \propto \frac{P_\infty}{2}$

$$Kt = \ln\left(\frac{a}{a-x}\right) \quad \Rightarrow \quad K = \frac{1}{t}\ln\left(\frac{P_\infty}{P_\infty - P_t}\right)$$

(d) $A(g) \longrightarrow B(g) + C(s)$

t = 0   a   0   0

$t = t$	$a-x$	x	x
$t = \infty$	0	a	a

$P_t = x$; $P_\infty = a$

$$k = \frac{1}{t}\ln\left[\frac{a}{a-x}\right] \quad ; \quad k = \frac{1}{t}\ln\left[\frac{P_\infty}{P_\infty - P_t}\right]$$