Class: XIIth
Date :

## Topic :- Chemical Kinetics

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(a)

For zero order reaction, $t_{1 / 2} \propto[R]_{0}$
(b)

Let, initial concentration $=\mathrm{a}$
Final concentration $=\mathrm{a}-\frac{2}{3} \mathrm{a}=\frac{a}{3}$
$t_{\frac{2}{3}}=\frac{2.303}{k} \log \frac{a}{a / 3}$
$=\frac{2.303}{5.48 \times 10^{-14}} \log 3$
$=2.01 \times 10^{13} \mathrm{~s}$
6
(b)
$k=A e^{-E_{a} / R T}$
(b)

This is Arrhenius equation.
(c)

Effect of temperature on reaction rate is given by Arrhenius equation

Let the order with respect to $A$ and $B$ is $x$ and $y$ respectively.
Hence,
Rate $r=[A]^{x}[B]^{y}$
On doubling the concentration of A , rate increases 4 times,
$4 r=[A]^{x}[B]^{y}$
From Eqs. (i) and (ii)
$\frac{1}{4}=\left(\frac{1}{2}\right)^{x}$
$\therefore \mathrm{X}=2$
$\therefore$ order with respect to A is 2
If concentration of $A$ and $B$ both are doubled,
$8 r=[2 A]^{x}[2 B]^{y} \ldots$ (iii)
From Eqs. (i) and (iii), we get
$\frac{1}{8}=\frac{1}{(2)^{x}} \cdot \frac{1}{(2)^{y}} \quad[\because x=2]$
$\frac{1}{8}=\frac{1}{(2)^{2}} \cdot \frac{1}{(2)^{y}}$
$\frac{1}{8}=\frac{1}{4 \times 2^{y}}$
$2^{y}=2$
$\therefore \mathrm{Y}=1$
Hence, differential rate equation is
$r \propto[A]^{2}[B]^{1}$ or $\frac{d C}{d t}=k C_{A}^{2} \times C_{B}$
[Where, $C_{A}$ and $C_{B}=$ concentrations of A and B ]
(d)
$r=k[A]^{n}$
When concentration is doubled then

$$
\begin{equation*}
4 r=k(2 A)^{n} \tag{ii}
\end{equation*}
$$

Divide Eq. (ii) by (i)

$$
\begin{aligned}
& 4=2^{n} \\
& n=2
\end{aligned}
$$

(a)

$$
\begin{aligned}
t & =\frac{0.693}{k} \log \frac{[A]_{0}}{[A]} \\
& =\frac{2.303}{60} \log \frac{a}{\frac{a}{16}}=\frac{2.303}{60} \log 16 \\
& =\frac{2.303}{60} \times 1.204 \\
& =0.0462 \mathrm{~s} \\
& =4.6 \times 10^{-2} \mathrm{~s}
\end{aligned}
$$

(a)

From the unit of rate constant (i.e., $\mathrm{s}^{-1}$ ), it is clear that the reaction is of first order.
$2 \mathrm{~N}_{2} \mathrm{O}_{5} \rightarrow 4 \mathrm{NO}_{2}+\mathrm{O}_{2}$
Hence, for first order reaction ,
$k=\frac{2.303}{t} \log \frac{p_{0}}{p_{t}}$
$\therefore 3.38 \times 10^{-5}=\frac{2.303}{10 \times 60} \log \frac{500}{p_{t}}$
Or $\log \frac{500}{p_{t}}=0.00880$
$\therefore \quad \frac{500}{p_{t}}=a n t i \log 0.00880$
$=1.02$
$p_{t}=\frac{500}{1.02}=490 \mathrm{~atm}$
(b)

$$
\begin{aligned}
& t=\frac{2.303}{k} \log \frac{a}{a-x} \\
& \because x=\frac{3}{4} a \\
& \therefore t=\frac{2.303}{k} \log \frac{a}{a-\frac{3}{4} a} \\
& =\frac{2.303}{k} \log 4
\end{aligned}
$$

(b)
$2 \mathrm{~N}_{2} \mathrm{O}_{5} \rightarrow 4 \mathrm{NO}_{2}+\mathrm{O}_{2}$
Rate of decomposition of $N_{2} O_{5}=-\frac{1 k\left[N_{2} O_{5}\right]}{d t}$
Rate of formation of $N O_{2}=\frac{1 k\left[N O_{2}\right]}{d t}$
$\therefore \frac{\text { rate of decompsition of } \mathrm{N}_{2} \mathrm{O}_{5}}{\text { rate of formation of } \mathrm{NO}_{2}}=\frac{\frac{1}{2} \mathrm{k} \frac{\left[\mathrm{N}_{2} \mathrm{O}_{5}\right]}{\mathrm{dt}}}{\frac{1}{4} \mathrm{k} \frac{\left[\mathrm{NO}_{2}\right]}{\mathrm{dt}}}$
or $\quad \frac{1}{2} k \frac{\left[\mathrm{~N}_{2} \mathrm{O}_{5}\right]}{d t} \times \frac{4}{1} \frac{d t}{k\left[\mathrm{NO}_{2}\right]}$
$=\frac{4}{2}=\frac{2}{1}=2: 1$
(a)

$$
k=\frac{2.303}{t} \log \frac{a}{a-x}
$$

Given, reaction is $75 \%$ completed is 32 min

$$
\begin{align*}
& \mathrm{A}=100, \mathrm{x}=75 \\
& \therefore \quad k=\frac{2.303}{32} \log _{\frac{100}{100-75}} \tag{1}
\end{align*}
$$

For $50 \%$ completion of reaction

$$
A=100, x=50
$$

$$
\begin{equation*}
\therefore \quad k=\frac{2.303}{t} \log ^{\frac{100}{100-50}} \tag{2}
\end{equation*}
$$

$\because \quad$ LHSof Eq.(1) $=$ Eq. $(2)$
$\therefore \quad$ RHSof Eq.(1) $=$ Eq. $(2)$
$\therefore \quad \frac{2.303}{32} \log \frac{100}{100-75}=\frac{2.303}{t} \log \frac{100}{100-50}$
or $\frac{2.303}{32} \log 4=\frac{2.303}{t} \log 2$
Or $\frac{t}{32}=\frac{\log 2}{\log 4}$ or $t=\frac{32 \times \log 2}{2 \log 2}$
$\therefore \quad t=16 \mathrm{~min}$
$\therefore$ reaction will be $50 \%$ completed in 16 min
(b)

Rate $\left(\frac{+d[C]}{d t}\right)=k[A][B]$

Thus, the order of reaction w.r.t. $\mathrm{A}=1$
The order of reaction w.r.t. $B=1$
Total order of reaction $=1+1=2$
(a)

The intersection point indicates that half of the reactant $X$ is converted into $Y$.
(b)

At $T_{1}=200 K, T_{2}=400 K, k_{1}=k, k_{2}=10 k$
$\because \log \frac{k_{2}}{k_{1}}=\frac{E_{a}}{2.303 R}\left(\frac{T_{2}-T_{1}}{T_{1} \cdot T_{2}}\right)$
$\log \frac{10 k}{k}=\frac{E_{a}}{2.303 R}\left(\frac{400-200}{400 \times 200}\right)$
$E_{a}=921.2 R$
(c)

Zero order reactions occur with constant rate.
(a)
$t=\frac{2.303}{K} \log \frac{a}{(a-x)}$;
Thus, $K=\frac{2.303}{10} \log 8=(2.303 \times 3 \log 2) / 10$
(c)

For the reaction $A \rightarrow B$
On increasing the concentration of reactant (i.e.,A) by 4 times , the rate of reaction becomes double , hence order of reaction is $\frac{1}{2}$.
(b)

The rate of chemical reaction always decreases with time as reaction proceeds due to decrease in number of reactant molecules. Only for zero order reactions the rate of chemical reaction remains same.

| ANSWER-KEY |  |  |  |  |  |  |  |  |  |  |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Q. | $\mathbf{1}$ | $\mathbf{2}$ | $\mathbf{3}$ | $\mathbf{4}$ | $\mathbf{5}$ | $\mathbf{6}$ | $\mathbf{7}$ | $\mathbf{8}$ | $\mathbf{9}$ | $\mathbf{1 0}$ |
| A. | $\mathbf{A}$ | $\mathbf{A}$ | $\mathbf{B}$ | $\mathbf{B}$ | $\mathbf{B}$ | $\mathbf{C}$ | $\mathbf{D}$ | $\mathbf{A}$ | A | $\mathbf{D}$ |
|  |  |  |  |  |  |  |  |  |  |  |
| Q. | $\mathbf{1 1}$ | $\mathbf{1 2}$ | $\mathbf{1 3}$ | $\mathbf{1 4}$ | $\mathbf{1 5}$ | $\mathbf{1 6}$ | $\mathbf{1 7}$ | $\mathbf{1 8}$ | $\mathbf{1 9}$ | $\mathbf{2 0}$ |
| A. | $\mathbf{B}$ | $\mathbf{B}$ | A | B | A | B | C | A | C | B |
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