

 $\square \mathrm{m}$
$3 \mathrm{H}_{2}(\mathrm{~g})+\mathrm{N}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{NH}_{3}(\mathrm{~g})$
CBSE (AI) 2007
ㅁㅁำ
Rate $=-\frac{1}{3} \frac{\left.d / H_{2}\right]}{\mathrm{dt}}=-\frac{\left.d / N_{2}\right]}{\mathrm{dt}}=\frac{1}{2} \frac{d / \mathrm{NH}_{3} /}{\mathrm{dt}}$
Rate of disappearance of $H_{2}=-\frac{d / H_{2} /}{\mathrm{dt}}=-3 \frac{d / N_{2} /}{\mathrm{dt}}=\frac{3}{2} \frac{d / \mathrm{NH}_{3} /}{\mathrm{dt}}$
Q.2. Define 'order of a reaction'.

$2 \square \square \square ा$
$\square \square \square$ Order of a reaction may be defined as the sum of the powers of the concentration terms of the reactants in the rate law expression.

$\square \square \square R a t e=k[A]^{0}[B]^{0}$ or Rate $=k$.
 r $\square \square \square \square \square \square \square$

## 

Let the rate law for the reaction be

$$
\begin{equation*}
r=k[A]^{n} \tag{i}
\end{equation*}
$$

According to the question,

$$
\begin{equation*}
27 r=k[3 A]^{n} \tag{ii}
\end{equation*}
$$

Dividing equation (ii) by equation (i), we get

$$
\frac{27 r}{r}=\frac{k / 3 A /^{n}}{k / A /^{n}}
$$

or $3^{3}=3^{n} \quad \therefore n=3$
$r=k[A]^{3} \quad \therefore$ Order of reaction, $\boldsymbol{n}=3$.


 collision.

```
\square||
```




```
\square
\square口
```

CBSE (F) 2010 ㅁ
Second order.

CBSE (AI) 2005 ${ }^{11}$
First order.
Define 'activation energy' of a reaction.

प activation energy. Activation energy = Threshold energy - Average energy of the reactants

dd


$\square \square$ Decreases
Gibbs energy ( $\Delta \mathbf{G}$ ) of a reaction?
CBSE (AI) 2017
$\square \square$ No effect


## Q. 1. What do you understand by 'Rate of reaction'? $\square$

메The change in the concentration of any one of the reactants or products per unit time is termed as the rate of reaction.

$\square \square \square$ Average rate becomes equal to instantaneous rate when the interval, $\Delta t$, approaches zero, i.e., it becomes infinitesimally small. Thus, $r_{\text {inst }}$, i.e., $\left(\frac{\mathrm{dx}}{\mathrm{dt}}\right)=\lim _{\Delta t \rightarrow 0} \frac{\Delta x}{\Delta t}$.

d
$\square \square \square \square \square \square ा \square \square \square \square \square \square \square \square \square \square \square \square \square$

$\square \square \square$ Instantaneous rate is measured over a very small interval of time, hence, it does not change when a part of solution is taken out.



Rate $=-\frac{d\left[X_{2}\right]}{\mathrm{dt}}=-\frac{1}{3} \frac{\left.d / Y_{2}\right]}{\mathrm{dt}}=+\frac{1}{2} \frac{d / \mathrm{XY}_{3} /}{\mathrm{dt}}$

Rate of disappearance of $Y_{2}=-\frac{d / Y_{2} /}{\mathrm{dt}}=-3 \frac{d / X_{2} /}{\mathrm{dt}}=+\frac{3}{2} \frac{d / \mathrm{XY}_{3} /}{\mathrm{dt}}$


## $\square \square \square ा$

Acid catalysed hydrolysis of ethyl acetate:

$$
\begin{gathered}
\mathrm{CH}_{3} \mathrm{COOC}_{2} \mathrm{H}_{5}+\mathrm{H}_{2} \mathrm{O} \xrightarrow{\text { n+ }} \mathrm{CH}_{3} \mathrm{COOH}+\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH} \\
\text { Rate }=k\left[\mathrm{CH}_{3} \mathrm{COOC}_{2} \mathrm{H}_{5}\right]
\end{gathered}
$$


$\pi \square \square \square \square \square \square \square \square \square \mathbf{r} \square$
पानी the reaction is an elementary reaction, order is same as molecularity.
 Tl|l|l $\mathbf{r d} \square \mathbf{r} \rightarrow \square \square \square \square$

NCERT Exemplar ${ }^{\text {D }}$
ㅁ

Order of reaction $=\frac{1}{2}+2=\frac{5}{2}$
$\square$ ำा $\square$
 $\square \square \square \square \square \square \square \square \square \square \mathbf{r} \square$
$\square \square$ A bimolecular reaction may become kinetically of first order if one of the reactants is in excess.

$\square \square \square R a t e ~ l a w ~ i s ~ a n ~ e x p e r i m e n t a l ~ l a w . ~ O n ~ t h e ~ o t h e r ~ h a n d, ~ l a w ~ o f ~ m a s s ~ a c t i o n ~ i s ~ a ~$ theoretical law based on the balanced chemical reaction.

Specific reaction rate is the rate of reaction when the molar concentration of each of the reactants is unity.
$\square$
HOTS ${ }^{1}$
$\square \square \square \square]$

Let,

$$
\begin{equation*}
r=k[A]^{n} \tag{i}
\end{equation*}
$$

Given, $\quad 3 r=k[9 A]^{n}$
Dividing equation (ii) by (i), we get

$$
\begin{aligned}
& \frac{3 r}{r}=\frac{k / 9 A /^{n}}{k / A J^{n}}=\frac{9^{n} k / A /^{n}}{k / A /^{n}} \\
& 3=9^{n} \quad \text { or } \quad 3^{1}=3^{2 n} \\
& \Rightarrow \quad 2 n=1 \quad \text { or } \quad n=\frac{1}{2} \\
& \therefore \quad \text { Rate, } r=k[A]^{1 / 2}
\end{aligned}
$$

Order of reaction $=\frac{1}{2}$



$\square \square Z$ Zero order reaction, as the rate of reaction is independent of concentration of reactant.


HOTS

- During an elementary reaction, the number of atoms or ions colliding to react is referred to as molecularity. Had this been an elementary reaction the order of reaction with respect to $B$ would have been 1 , but in the given rate law it is $\frac{3}{2}$. This indicates that the reaction is not an elementary reaction.

$\square$ THI $\square \square$

``` \(\qquad\)
``` \(\square 1 \mathrm{ll}\)
```



``` \(\cdots \square 1 / \mathbb{r}\)
```



HOTS
)
Therefore, it is a first order reaction.


## NCERT Exemplar

At higher temperatures, larger fraction of colliding particles can cross the energy barrier (i.e., the activation energy), which leads to faster rate.
 $\mathbf{r} \square \square \square$

## NCERT Exemplarㅍ

 small. Hence, possibility of molecularity being three is very low.


$\square \square \square$ Thermodynamically the conversion of diamond to graphite is highly feasible but this reaction is very slow because its activation energy is high.

[^0]$\square \square$. This implies that every collision results into a chemical reaction which cannot be true. Hence, a reaction cannot have zero activation energy.

 molecules in order to undergo effective collision which leads to formation of product molecules.



 elementary reaction. For example,
$\mathrm{N}_{2}(g)+\mathrm{O}_{2}(g) \rightarrow 2 \mathrm{NO}(g)$

CBSE (AI) 2009; (F) 2010
 concentration of reactant or increase in concentration of product per unit time.

For a hypothetical reaction, $\mathrm{R} \rightarrow \mathrm{P}$
Rate of reaction $=\frac{-\Delta / R]}{\Delta t}=\frac{+\Delta / P]}{\Delta t}$


ㅁㅔㅣ

Qullifferences between order and molecularity of reaction:

| - | $\square \mathbf{r d} \square \mathbf{r}$ |  |
| :---: | :---: | :---: |
| i $\square^{\text {l }}$ | It is the sum of the powers of the concentration of the reactants in the rate law expression. | It is the number of reacting species taking part in an elementary reaction, which must collide simultaneously so as to result into a chemical reaction. |
| ii $]^{\text {l }}$ | It is determined experimentally. | It is a theoretical concept. |
| iii] | It can be zero or a fraction. | It cannot be zero or a fraction. |
| iv ${ }^{1}$ | Order is applicable to elementary as well as complex reactions. | Molecularity is applicable only for elementary reactions. For complex reactions it has no meaning. |



For a reaction: $2 \mathrm{NH}_{3}(\mathrm{~g}) \xrightarrow{\mathrm{pm}} \mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g})$

$$
\text { Rate }=k
$$

i. Write the order and molecularity of this reaction.
ii. Write the unit of $k$.

CBSE South 2016

Zero order, bimolecular $\mathrm{mol} \mathrm{L}^{-1} \mathrm{~s}^{-1}$


A reaction which is not truely of first order but under certain conditions becomes a reaction of first order is called pseudo first order reaction, e.g., acid hydrolysis of ethyl acetate.
$\mathrm{CH}_{3} \mathrm{COOC}_{2} \mathrm{H}_{5}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{H}+\mathrm{CH}_{3} \mathrm{COOH}+\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}$
Rate $\propto\left[\mathrm{CH}_{3} \mathrm{COOC}_{2} \mathrm{H}_{5}\right]$ as $\mathrm{H}_{2} \mathrm{O}$ is in excess.


CBSE Delhi 2014
and The half life ( $t_{1 / 2}$ ) of a reaction is the time in which the concentration of reactant is reduced to one half of its initial concentration $[R]$.

For a first order reaction, $t_{1 / 2}=\frac{0.693}{k}$, i.e., independent of $[R]_{0}$.
For a zero order reaction, $t_{1 / 2}=\frac{I R / 0}{2 k}$, i.e., $t_{1 / 2} \propto[R]_{0}$.

For a reaction $A+B \rightarrow P$, the rate law is given by,

$$
r=k[A]^{1 / 2}[B]^{2} .
$$

What is the order of this reaction?
Order of reaction $=\frac{1}{2}+2=\frac{5}{2}$


Radioactive decay follows first order kinetics.

$$
t_{1 / 2}=\frac{0.693}{k}=\frac{0.693}{5.5 \times 10^{-14}} \mathrm{~s}=1.26 \times 10^{13} \mathrm{~s}
$$

CBSE (AI) 2011 미
$\square \square C$ Consider the reaction $n R \rightarrow$ Products

As the reaction is of second order
$\therefore$ Rate, $r=k[R]^{2}$
If the concentration of the reactant reduced to half, then

$$
\begin{equation*}
\text { Rate, } r^{\prime}=k\left[\frac{R}{2}\right]^{2} \tag{ii}
\end{equation*}
$$

Dividing equation (ii) by (i), we get

$$
\begin{aligned}
& \frac{r^{\prime}}{r}=\frac{k / R /^{2}}{4 k / R]^{2}}=\frac{1}{4} \\
& r^{\prime}=\frac{1}{4} r, \text { i.e., rate of reaction becomes } \frac{1}{4^{\mathrm{th}}} \text { of the initial rate. }
\end{aligned}
$$

The unit of rate constant is $\mathrm{mol}^{-1} \mathrm{~L} \mathrm{~s}^{-1}$.

## 


$\square \square D$ Due to high activation energy for the reaction.



CBSE (AI) 2017 피
$\square \square \square$ Rate $=k\left[A_{2}\right]^{0}\left[B_{2}\right]^{0}$ or Rate $=k \square$



CBSE (F) 2016 피
$\square \square \square \square \square$
$t=\frac{2.303}{k} \log \frac{[R]_{0}}{[R]}$

$$
\begin{aligned}
& \frac{t_{99.9 \%}}{t_{50 \%}}=\frac{\frac{2.303}{k} \log \frac{100}{100-99.9}}{\frac{2.303}{k} \log \frac{100}{100-50}}=\frac{\log \frac{100}{0.1}}{\log \frac{100}{50}} \\
& =\frac{\log 10^{3}}{\log 2}=\frac{3 \log 10}{0.3010} \\
& \frac{t_{99.9 \%}}{t_{50 \%}}=\frac{30}{3.01} \simeq 10 \\
& t_{99.9 \%}=10 t_{50 \%}
\end{aligned}
$$





CBSE (AI) 2014
$\square \square \square \square^{\circ}$
i. Order of the reaction is zero.
ii. Slope $=\frac{d / R /}{\mathrm{dt}}=-k$



CBSE (AI) $2011 \square$



An experimentally determined expression which relates the rate of reaction with the concentration of reactants is called rate law while the rate of reaction when concentration of each reactant is unity in a rate law expression is called rate constant.

Comparing power of mole in $\mathrm{L}^{-1} \mathrm{~mol} \mathrm{~s}^{-1}$ and $\left(\mathrm{mol} \mathrm{L}^{-1}\right)^{1-n} \mathrm{~s}^{-1}$, We get

$$
1=I-n \Rightarrow n=0 \text { i.e., zero order reaction }
$$

Again comparing power of mole in $\mathrm{L} \mathrm{mol}^{-1} \mathrm{~s}^{-1}$ and (molL-1)1-ns-1, we get

$$
-1=1-n \Rightarrow n=2 \text {, i.e., second order reaction }
$$



$$
\begin{aligned}
t & =\frac{2.303}{k} \log \frac{/ R /_{0}}{\mid R /} \quad \text { as } \quad[R]=\frac{/ R /_{0}}{10} \\
\therefore \quad t & =\frac{2.303}{k} \log \frac{/ R /_{0}}{\frac{\mid R b_{0}}{10}}=\frac{2.303}{60} \times \log 10=\frac{2.303}{60} \times 1=3.838 \times 10^{-2} s
\end{aligned}
$$


CBSE (F) 2010 피
$\square \square \square \square$

Given: $\left[R_{0}\right]=0.10 \mathrm{M} \quad[R]=0.075 \mathrm{M}$

$$
k=0.0030 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1}, t=?
$$

We know that $k=\frac{\left[R_{0} /-/ R /\right.}{t}$
or

$$
t=\frac{/ R_{0} /-/ R /}{k}=\frac{0.10-0.075}{0.0030}=8.33 \mathrm{~s} .
$$

पाराThe rate of reaction depends on the concentration of reactants. As the reaction progresses, reactants start getting converted to products so the concentration of reactants decreases hence the rate of reaction decreases.

```
2 
```



## NCERT Exemplar

넨A complex reaction proceeds through several elementary reactions. Number of molecules involved in each elementary reaction may be different, i.e., the molecularity of each step may be different. Therefore, discussion of molecularity of overall complex reaction is meaningless. On the other hand, order of a complex reaction is determined
by the slowest step in its mechanism and is not meaningless even in the case of complex reactions.


## NCERT Exemplar ${ }^{\text {D }}$

No, the molecularity can never be equal to zero or a fractional number.
Molecularity is the number of molecules involved in each elementary reaction which may be different, i.e., the molecularity of each step may be different.



| प | प $\square$ ¢ |  |
| :---: | :---: | :---: |
| [ $]^{\text {d }}$ | Rate of reaction is the change in concentration of a reactant or product in a unit interval of time. | It is the rate of reaction when the molar concentration of each of the reactants is unity. |
| ii $]^{\text {l }}$ | The rate of reaction at any instant of time depends upon the molar concentrations of the reactants at that time. | The rate constant does not depend upon the concentrations of the reactants. |
| [iii ${ }^{\text {d }}$ | Its units are always mol litre ${ }^{-1}$ time $^{-1}$. | Its units depend upon the order of reaction. |





Order with respect to $\mathrm{Cl}_{2}=1$, Order with respect to $\mathrm{NO}=2$,
Overall order $=1+2=3$



```
|||l \a|m|k
```

$\square \square \square \square ा$
i. Order $=\frac{1}{2}+\frac{3}{2}=2$, i.e., second order.
ii. Order $=\frac{3}{2}+(-1)=\frac{1}{2}$, i.e., half order.


Im Pseudo unimolecular
IIII Order $=1$.

## 

##   $\square \square 1 \mathrm{D} \square$

$\square \square \square \square]$

$$
\begin{align*}
\text { Rate } & =k[X]^{2} \\
r_{1} & =k[X]^{2}  \tag{i}\\
r_{2} & =k[3 X]^{2} \tag{ii}
\end{align*}
$$

Dividing (ii) by (i),

$$
\frac{r_{2}}{r_{1}}=\frac{9 k / X]^{2}}{k / X]^{2}} \quad \text { or } \quad r_{2}=9 r_{1}
$$

Thus, rate of formation of $Y$ will increase by nine times.
$\square$
 $\square \mathbf{r d} \square \mathbf{r} \square \square \mathbf{r} \square \square \square \square \square \square \square \square$

Comparing the unit of $k$, with the general unit $\left(\mathrm{mol} \mathrm{L}^{-1}\right)^{1-n} \mathrm{~s}^{-1}$, we get

$$
\begin{gathered}
\mathrm{mol}^{1-n}=\mathrm{mol}^{1} \\
1-n=1 \\
\Rightarrow \quad n=0, \text { i.e., zero order reaction. }
\end{gathered}
$$

$\frac{\mathrm{dx}}{\mathrm{dt}}=k[$ Ester $]\left[\mathrm{H}^{+}\right]^{0}$



내⒤ The rate of reaction will be doubled. (ii) No effect on rate.
 r $\square \square \square \square \square \square$

NCERT Exemplar $\square$
$\square \square \square \square ा$
$t=\frac{\mid R / 0-[R]}{k}$
For completion, $[R]=0$
$\therefore \quad t=\frac{l R / 0}{k}$


$$
k=0.0030 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1},[R]_{0}=0.10 \mathrm{M},[R]=0.075 \mathrm{M}
$$

We know that

$$
\begin{aligned}
{[R] } & =-k t+[R]_{0} \\
0.075 & =-0.0030 t+0.10 \\
\Rightarrow \quad 3 t & =100-75 \Rightarrow t=\mathbf{8 . 3 3} \text { seconds }
\end{aligned}
$$




|  |  |  |
| :---: | :---: | :---: |
| 1 | 0 | 0.4 |
| 2 | 100 | 0.7 |


ㄴ
HOTS
ㅁㅁㅔㅔ

$$
k=\frac{2.303}{t} \log \frac{P_{0}}{2 P_{0}-P_{t}}
$$

Here, $P_{0}=0.4 \mathrm{~atm}, t=100 \mathrm{~s}, P_{t}=0.7 \mathrm{~atm}$

$$
\begin{aligned}
\therefore \quad k & =\frac{2.303}{100} \log \frac{0.4}{2 \times 0.4-0.7} \\
& =\frac{2.303}{100} \log \frac{0.4}{0.1}=\frac{2.303}{100} \log 4=\frac{2.303}{100} \times 0.6021 \\
k & =1.386 \times 10^{-2} \mathrm{~s}^{-1}
\end{aligned}
$$




## 

$\left(\frac{1}{2}\right)^{n}=\frac{12.5}{100}$ because $87.5 \%$ has disintegrated, amount left is $12.5 \%$.
$\left(\frac{1}{2}\right)^{n}=\left(\frac{1}{8}\right)$
$\Rightarrow$
$\left(\frac{1}{2}\right)^{n}=\left(\frac{1}{2}\right)^{3}$

Number of half lives $=3$

$$
t_{1 / 2}=\frac{45}{3}=15 \text { minutes }
$$


$\square \square \square ा ⿴ 囗 十$

From the graph
Case I：Rate $=k[A]$

$$
\begin{aligned}
& 1 \times 10^{-2} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1} & =k\left(0.1 \mathrm{~mol} \mathrm{~L}^{-1}\right) \\
\therefore \quad & k & =\frac{1 \times 10^{-2} \mathrm{~mol} \mathrm{~L} L^{-1} s^{-1}}{0.1 \mathrm{~mol}^{-1}}=0.1 \mathrm{~s}^{-1}
\end{aligned}
$$

## Case II：

$$
\begin{aligned}
3 \times 10^{-2} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1} & =k\left(0.3 \mathrm{~mol} \mathrm{~L}^{-1}\right) \\
k & =\frac{3 \times 10^{-2} \mathrm{~mol} \mathrm{~L}}{}{ }^{-1} \mathrm{~s}^{-1} \\
0.3 \mathrm{~mol} L^{-1} & =0.1 \mathrm{~s}^{-1}
\end{aligned}
$$

Hence，

$$
k=0.1 \mathrm{~s}^{-1}
$$


$\square \square \square \square]$
i. Threshold energy for the reaction $=300 \mathrm{~kJ} \mathrm{~mol}^{-1}$
ii. Activation energy for the forward reaction $=300-150$

$$
=150 \mathrm{~kJ} \mathrm{~mol}^{-1}
$$

iii. Activation energy for the backward reaction $=300-100$

$$
=200 \mathrm{~kJ} \mathrm{~mol}^{-1}
$$

iv. Enthalpy change for the forward reaction $\Delta_{r} H=100-150$

$$
=-50 \mathrm{~kJ} \mathrm{~mol}^{-1}
$$







According to Arrhenius equation, $\ln k=-\frac{\mathrm{E}_{a}}{\mathrm{RT}}+\ln A$
i. Slope $=-\frac{\mathrm{OB}}{\mathrm{OA}}=-\frac{b}{a}=-\frac{E_{a}}{R} \quad$ or $\quad E_{a}=\frac{b}{a} R$
ii. Intercept on $y$-axis $=O B=b=\ln A$ or $A=e^{b}$

CBSE Sample Paper 2013
$\square \square \square \square ा$

$$
\begin{align*}
& t=\frac{2.303}{k} \log \frac{/ R / 0}{[R]}  \tag{i}\\
& k=2.54 \times 10^{-3} s^{-1} ;[R]=\frac{/ R / 0}{4}
\end{align*}
$$

Substituting these values in equation (i), we get

$$
\begin{aligned}
& t_{3 / 4}=\frac{2.303}{2.54 \times 10^{-3}} \log \frac{/ R h_{0}}{\frac{/ R_{0}}{4}}=0.9066 \times 10^{3} \log 4 \\
& t_{3 / 4}=0.9066 \times 10^{3} \times 0.6021 \mathrm{~s}=5.46 \times 10^{2} \mathrm{~s}
\end{aligned}
$$

Here, $[R]_{0}=1 \mathrm{~g},[R]=0.125 \mathrm{~g}, t=24 \mathrm{~h}$

$$
\begin{aligned}
& k=\frac{2.303}{t} \log \frac{\mid R]_{0}}{[R \mid} \\
& k=\frac{2.303}{24} \log \frac{1}{0.125}
\end{aligned}
$$

$$
\begin{aligned}
k & =\frac{2.303}{24} \log 8 \\
k & =\frac{2.303}{24} \times 0.9031 \\
k & =0.0866 h^{-1} \\
t_{1 / 2} & =\frac{0.693}{k} \\
t_{1 / 2} & =\frac{0.693}{0.0866 h^{-1}} \text { or } t_{1 / 2}=8 h
\end{aligned}
$$






$$
k=\frac{2.303}{t} \log \frac{/ R_{/}}{[R]}
$$

$2.0 \times 10^{-4} s^{-1}=\frac{2.303}{900} \log \frac{/ R / 0}{[R]}$

$$
\log \frac{\mid R /_{0}}{|R|}=\frac{2.0 \times 10^{-4} \times 900}{2.303}=0.0781
$$

$$
\log \frac{|R|}{\mid R l_{0}}=-0.0781
$$

$$
\begin{aligned}
& \frac{\mid R /}{\mid R /_{0}}=\text { Antilog } \overline{1} .9219 \\
& \frac{/ R /}{\mid R /_{0}}=0.835
\end{aligned}
$$

$[R]=0.835[R]_{0}$
If $[R] 0=100$, then
$[R]=83.5$
$R]_{0}-[R]=100-83.5=16.5$, i.e., $16.5 \%$ of initial concentration has changed into products.


$$
2 \mathrm{H}_{2} \mathrm{O}_{2} \xrightarrow{\text { ö }} 2 \mathrm{H}_{2} \mathrm{O}+\mathrm{O}_{2}
$$

This reaction takes place in two steps as given below:

Step-I $\quad \mathrm{H}_{2} \mathrm{O}_{2}+\mathrm{I}^{-} \rightarrow \mathrm{H}_{2} \mathrm{O}+\mathrm{IO}^{-}$(slow)

Step-II $\mathrm{H}_{2} \mathrm{O}_{2}+\mathrm{IO}^{-} \rightarrow \mathrm{H}_{2} \mathrm{O}+\mathrm{I}^{-}+\mathrm{O}_{2}$ (fast)
i. Write the rate law expression and determine the order of reaction w.r.t. $\mathrm{H}_{2} \mathrm{O}_{2}$.
ii. What is the molecularity of each individual step?
$\square \square \square \square ा$
i. Rate $=k\left[\mathrm{H}_{2} \mathrm{O}_{2}\right]^{1}\left[\mathrm{I}^{-}\right]^{1}$

Order of reaction w.r.t $\mathrm{H}_{2} \mathrm{O}_{2}=1$
ii. Molecularity of step $\mathrm{I}=2$ and step $\mathrm{II}=2$.

CBSE (F) 2014



민 The half life ( $t_{1 / 2}$ ) of a reaction is the time in which the concentration of a reactant is reduced to one half of its initial concentration.
i. $t_{1 / 2}$ for a zero order reaction $=\frac{/ R /_{0}}{2 k}$ where $[R]_{0}=$ initial concentration, $k=$ rate constant ii. $t_{1 / 2}$ for a first order reaction $=\frac{0.693}{k}$


| $\mathrm{N}_{2}+\mathrm{O}_{2} \rightarrow$ |  |  |  |
| :--- | :---: | :---: | :---: |
| Initial conc. in $\mathrm{mol} \mathrm{L}^{-1}$ | 0.8 | 0.2 | 0 |
| Change in conc. in $\mathrm{mol} \mathrm{L}^{-1}$ | $-x$ | $-x$ | $+2 x$ |
| Equilibrium conc. in $\mathrm{mol} \mathrm{L}^{-1}$ | $0.8-x$ | $0.2-x$ | $2 x$ |

$$
K_{C}=\frac{l \mathrm{NO} /^{2}}{\left[N_{2} / / O_{2} /\right.} \quad \therefore \quad 1 \times 10^{-5}=\frac{(2 x)^{2}}{(0.8-x)(0.2-x)}
$$

As $x \ll 0.2$, therefore $0.8-x \approx 0.8$ and $0.2-x \approx 0.2$

$$
\begin{aligned}
\therefore & 1 \times 10^{-5}=\frac{4 x^{2}}{0.16} \Rightarrow 4 x^{2}=16 \times 10^{-7} \\
& x=6.324 \times 10^{-4} \mathrm{~mol} \mathrm{~L}^{-1}
\end{aligned}
$$

Thus at equilibrium,

$$
\begin{aligned}
{[\mathrm{NO}] } & =2 x=2 \times 6.324 \times 10^{-4} \\
& =12.648 \times 10^{-4} \mathrm{~mol} \mathrm{~L}^{-1} \\
{\left[\mathrm{~N}_{2}\right] } & =0.8-6.324 \times 10^{-4} \mathrm{~mol} \mathrm{~L}^{-1} \\
& =0.799 \mathrm{~mol} \mathrm{~L}
\end{aligned}
$$



$\log k=14.2-\frac{1.0 \times 10^{4}}{T} \mathrm{~K}$



## CBSE Delhi 2016 피

## 매ำ

Comparing the equation, $\log k=14.2-\frac{1.0 \times 10^{4}}{T} \mathrm{~K}$ with the equation, $\log k=\log A-\frac{E_{a}}{2.303 \mathrm{RT}}$, we get

$$
\begin{aligned}
& \frac{E_{a}}{2.303 \mathrm{RT}}=\frac{1.0 \times 10^{4} \mathrm{~K}}{T} \text { or } E_{a}=1.0 \times 10^{4} \mathrm{~K} \times 2.303 \times \mathrm{R} \\
& \begin{aligned}
E_{a} & =1.0 \times 10^{4} \mathrm{~K} \times 2.303 \times 8.314 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1} \\
& =19.1471 \times 10^{4} \mathrm{~J} \mathrm{~mol}^{-1} \\
& =191.47 \mathrm{~kJ} \mathrm{~mol}
\end{aligned}
\end{aligned}
$$

For a first order reaction, $t_{1 / 2}=\frac{0.693}{k}$ or $k=\frac{0.693}{t_{1 / 2}}$
$\therefore k=\frac{0.693}{200 \mathrm{~min}}=3.465 \times 10^{-3} \mathrm{~min}^{-1}$

$\mathrm{N}_{2} \mathrm{O}_{5} \rightarrow 2 \mathrm{NO}_{2}+\frac{1}{2} \mathrm{O}_{2}$

| $\square \\| \square$ | $\square$ | $\square \square \square$ | $\square \square \square$ |
| :--- | :--- | :--- | :--- |
| $\square \mathbf{2} \square \square \\| \square \square \square \square^{-}$ | $\square \square \square \square \square^{\mathbf{2}}$ | $\square \square \square \square \square^{\mathbf{2}}$ | $\square \square \square \square \square^{\mathbf{2}}$ |




CBSE Delhi 2017 ㅍ
$\square \square \square \square \square$
i. At 300 s ,

$$
\begin{aligned}
& k=\frac{2.303}{t} \log \frac{\left[R /_{0}\right.}{[R]} \\
&=\frac{2.303}{300} \log \frac{1.6 \times 10^{-2}}{0.8 \times 10^{-2}}=\frac{2.303}{300} \log 2 \\
& k=\frac{2.303}{300} \times 0.3010=2.31 \times 10^{-3} \mathrm{~s}^{-1} \\
& \text { At } 600 \mathrm{~s} \\
& k=\frac{2.303}{t} \log \frac{[R / 0}{[R]} \\
&=\frac{2.303}{600} \log \frac{1.6 \times 10^{-2}}{0.4 \times 10^{-2}}=\frac{2.303}{600} \log 4 \\
& k=\frac{2.303}{600} \times 0.6021=2.31 \times 10^{-3} \mathrm{~s}^{-1}
\end{aligned}
$$

$k$ is constant and is equal to $2.31 \times 10^{-3} \mathrm{~s}^{-1}$ when we use first order equation. Hence, it follows first order reaction.
ii. $t_{1 / 2}=\frac{0.693}{k}$

$$
=\frac{0.693}{2.31 \times 10^{-3} s^{-1}}=300 \mathrm{~s}
$$

## 

Substituting $k_{1}=2 \times 10^{-2}, k_{2}=4 \times 10^{-2}, T_{1}=300 \mathrm{~K}, T_{2}=310 \mathrm{~K}, R=8.314 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$ in the expression

$$
\log \frac{k_{2}}{k_{1}}=\frac{E_{a}}{2.303 \times R}\left(\frac{T_{2}-T_{1}}{T_{1} T_{2}}\right) \text {, we get }
$$

$\log \frac{4 \times 10^{-2}}{2 \times 10^{-2}}=\frac{E_{a}}{2.303 \times 8.314}\left(\frac{310-300}{300 \times 310}\right)$

$$
\begin{aligned}
\log 2 & =\frac{E_{a}}{19.147} \times \frac{10}{300 \times 310} \\
E_{a} & =0.3010 \times 19.147 \times 300 \times 31=53598 \mathrm{~J} \mathrm{~mol}^{-1} \\
E_{a} & =53.598 \mathrm{~kJ} \mathrm{~mol}^{-1}
\end{aligned}
$$ $\square \square \square$




## $\square \square \square$

i. As $\frac{-d / B /}{d t}=1 \times 10^{-2} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1}$

$$
\therefore \quad \text { Rate }=-\frac{1}{2} \frac{d / B /}{\mathrm{dt}}=\frac{1}{2} \times 1 \times 10^{-2}=0.5 \times 10^{-2} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1}
$$

ii. Rate $=-\frac{d / A /}{\mathrm{dt}}=-\frac{1}{2} \frac{d / B /}{\mathrm{dt}}=+\frac{1}{3} \frac{d / C /}{\mathrm{dt}}$

Rate of change in concentration of $A$

$$
\begin{aligned}
& =-\frac{d / A /}{\mathrm{dt}}=-\frac{1}{2} \frac{d / B]}{\mathrm{dt}} \\
& =0.5 \times 10^{-2} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1}
\end{aligned}
$$

Rate of change in concentration of $C$

$$
\begin{aligned}
& =+\frac{d / C]}{\mathrm{dt}}=-\frac{3}{2} \frac{d / B /}{\mathrm{dt}}=\frac{3}{2} \times 1 \times 10^{-2} \\
& =1.5 \times 10^{-2} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1}
\end{aligned}
$$


HOTS
$2 \mathrm{NO}(g)+\mathrm{O}_{2}(g) \rightarrow 2 \mathrm{NO}_{2}(g)$
The rate law for this reaction is:

$$
\text { Rate }=k[\mathrm{NO}]^{2}\left[\mathrm{O}_{2}\right]
$$

Propose a mechanism for the reaction.

## 

The probable proposed mechanism may be,

$$
\begin{array}{ll}
\mathrm{NO}+\mathrm{O}_{2} \rightarrow \mathrm{NO}_{3} \text { (fast) } & \text { Step I } \\
\mathrm{NO}_{3}+\mathrm{NO} \xrightarrow{\mathrm{k}_{1}} \mathrm{NO}_{2}+\mathrm{NO}_{2} \text { (slow) } & \text { Step II }
\end{array}
$$

Since slowest reaction is the rate determining step, therefore

$$
\begin{aligned}
\text { Rate } & =k_{1}\left[\mathrm{NO}_{3}\right][\mathrm{NO}] \\
K & =\frac{/ \mathrm{NO}_{3} /}{/ \mathrm{NO} / / O_{2} /}
\end{aligned}
$$

$$
\begin{aligned}
{\left[\mathrm{NO}_{3}\right] } & =K[\mathrm{NO}]\left[\mathrm{O}_{2}\right] \\
\text { Rate } & =k_{1} K[\mathrm{NO}]\left[\mathrm{O}_{2}\right][\mathrm{NO}]=K[\mathrm{NO}]^{2}\left[\mathrm{O}_{2}\right], \text { where } K^{K}=k_{1} \cdot K
\end{aligned}
$$






$$
\begin{align*}
& 2 r=k[\mathrm{NO}]^{x}\left[2 \mathrm{Cl}_{2}\right]^{y}  \tag{ii}\\
& 8 r=k[2 \mathrm{NO}]^{x}\left[2 \mathrm{Cl}_{2}\right]^{y}
\end{align*}
$$

Dividing (iii) by (ii), we get

$$
\begin{aligned}
\frac{8 r}{2 r} & =\frac{k / 2 \mathrm{NO} J^{x} / 2 \mathrm{Cl}_{2} /^{y}}{\left.k / \mathrm{NO} J^{x} / 2 \mathrm{Cl}_{2}\right]^{y}} \\
2^{2} & =[2]^{x} \\
x & =2
\end{aligned}
$$

Putting the value of $x$ in (i) and (ii), we get

$$
\begin{gathered}
r=k[\mathrm{NO}]^{2}\left[\mathrm{Cl}_{2}\right]^{y} \\
2 r=k[\mathrm{NO}]^{2}\left[2 \mathrm{Cl}_{2}\right]^{y} \\
\frac{2 r}{r}=\frac{/ 2 \mathrm{Cl}_{2} /^{y}}{/ \mathrm{Cl}_{2} /^{y}} \\
2=[2]^{y} \\
y=1 \\
\text { Rate }=k[\mathrm{NO}]^{2}\left[\mathrm{Cl}_{2}\right]^{1}
\end{gathered}
$$

Overall order of reaction $=x+y=2+1=$ $\qquad$



|  | $\square$ | $\square \square$ | 2 |
| :---: | :---: | :---: | :---: |
|  | $2 \square$ | $\square \square \square$ | $\square \square$ |


ㅁㅁำ
i. $k=\frac{2.303}{10} \log \frac{23.8}{14.7}=\frac{2.303}{10} \times 0.2093=0.048 \mathrm{~min}^{-1}$
ii. $k=\frac{2.303}{20} \log \frac{23.8}{9.1}=\frac{2.303}{20} \times 0.4176=0.048 \mathrm{~min}^{-1}$

Since the value of $k$ comes out to be constant in both the cases, therefore the reaction is of first order.

$2 \mathrm{NO}(g)+\mathrm{O}_{2}(g) \rightarrow 2 \mathrm{NO}_{2}(g)$




$$
\text { Rate }=k[\mathrm{NO}]^{2}\left[\mathrm{O}_{2}\right]
$$

Let initially, moles of $\mathrm{NO}=a$, moles of $\mathrm{O}_{2}=b$, volume of the vessel $=V$. Then

$$
\begin{align*}
& {[\mathrm{NO}]=\frac{a}{V} \mathrm{M},\left[\mathrm{O}_{2}\right]=\frac{b}{V} \mathrm{M} } \\
\therefore & \text { Rate }\left(r_{1}\right)=k\left(\frac{a}{V}\right)^{2}\left(\frac{b}{V}\right)=k \frac{a^{2} b}{V^{3}} \tag{i}
\end{align*}
$$

Now, new volume $=\frac{V}{3}$
$\therefore$ New concentrations: $[\mathrm{NO}]=\frac{a}{V / 3}=\frac{3 a}{V}$

$$
\begin{array}{cc} 
& {\left[\mathrm{O}_{2}\right]=\frac{b}{V / 3}=\frac{3 b}{V}} \\
\therefore & \text { New rate }\left(r_{2}\right)=k\left(\frac{3 a}{V}\right)^{2}\left(\frac{3 b}{V}\right)=\frac{27 \mathrm{ka}^{2} b}{V^{3}}  \tag{ii}\\
\therefore & \frac{r_{2}}{r_{1}}=27
\end{array} \text { or } \quad r_{2}=27 r_{1}, \text { i.e., rate becomes } 27 \text { times. } .
$$

Thus, there is no effect on the order of reaction.




|  | 메 [1] |  |
| :---: | :---: | :---: |
| $\square \square$ | $\square$ | $\square \square$ |
| 2 | $\square \square$ | $\square 1 \square^{2}$ |

$\square \square \square L e t ~ t h e ~ p r e s s u r e ~ o f ~ \mathrm{~N}_{2} \mathrm{O}_{5}(g)$ decrease by $2 x$ atm. As two moles of
$\mathrm{N}_{2} \mathrm{O}_{5}$ decompose to give two moles of $\mathrm{N}_{2} \mathrm{O}_{4}(g)$ and one mole of $\mathrm{O}_{2}(g)$, the pressure of $\mathrm{N}_{2} \mathrm{O}_{4}(g)$ increases by $2 x$ atm and that of $\mathrm{O}_{2}(g)$ increases by $x$ atm.

| $2 \mathrm{~N}_{2} \mathrm{O}_{5}(g) \rightarrow 2 \mathrm{~N}_{2} \mathrm{O}_{4}(g)+\mathrm{O}_{2}(g)$ |  |  |  |
| :--- | :---: | :---: | :---: |
| At $t=0$ | 0.5 atm | 0 atm | 0 atm |
| At time $t$ | $(0.5-2 x) \mathrm{atm}$ | $2 x \mathrm{~atm}$ | xatm |

$$
\begin{aligned}
& p_{t}=p_{N_{2} O_{5}}+p_{N_{2} O_{4}}+p_{O_{2}} \\
& \quad=(0.5-2 x)+2 x+x=0.5+x \\
& x=p_{t}-0.5 \\
& p_{N_{2} O_{5}}=0.5-2 x=0.5-2\left(p_{t}-0.5\right)=1.5-2 p_{t} \\
& =(0.5-2 x)+2 x+x=0.5+x
\end{aligned}
$$

$x=p_{t}-0.5$

$$
p_{N_{2} O_{5}}=0.5-2 x=0.5-2\left(p_{t}-0.5\right)=1.5-2 p_{t}
$$

At $t=100 \mathrm{~s} ; p_{t}=0.512 \mathrm{~atm}$,
$p_{N_{2} O_{5}}=1.5-2 \times 0.512=0.476 \mathrm{~atm}$

Thus, $k=\frac{2.303}{t} \log \frac{p_{i}}{p_{A}}$
$=\frac{2.303}{100 \mathrm{~s}} \log \frac{0.5 \mathrm{~atm}}{0.476 \mathrm{~atm}}$
$=\frac{2.303}{100 s} \times 0.0216=4.98 \times 10^{-4} s^{-1}$


प $\square \square$

Given $T_{1}=280 \mathrm{~K}, k_{1}=1.6 \times 10^{6} \mathrm{~s}^{-1}, k_{2}=?, E_{a}=0, T_{2}=300 \mathrm{~K}$.
By Arrhenius equation,

$$
\log \frac{k_{2}}{k_{1}}=\frac{E_{a}}{2.303 R}\left[\frac{T_{2}-T_{1}}{T_{2} T_{1}}\right]
$$

As, $E_{a}=0$
$\therefore \quad \log \frac{k_{2}}{k_{1}}=0$
or

$$
\frac{k_{2}}{k_{1}}=1 \quad \text { or } \quad k_{2}=k_{1}
$$

Thus, the rate constant at 300 K is $1.6 \times 10^{6} \mathrm{~s}^{-1}$.

We know that,
$\log k_{2}-\log k_{1}=\frac{E_{a}}{2.303 R}\left[\frac{1}{T_{1}}-\frac{1}{T_{2}}\right]$
$\log k_{2}=\log k_{1}+\frac{E_{a}}{2.303 R}\left[\frac{1}{T_{1}}-\frac{1}{T_{2}}\right]$
$\log k_{2}=\log \left(1.60 \times 10^{-5} \mathrm{~s}\right)+\frac{209000 \mathrm{~J} \mathrm{~mol}}{} \mathrm{~mol}^{-1}-303 \times 8.314 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1} \quad\left[\frac{1}{600 \mathrm{~K}}-\frac{1}{700 \mathrm{~K}}\right]$
$\log k_{2}=-4.796+2.599=-2.197$ or $k_{2}=\operatorname{Antilog}(\overline{3} .803)$

$$
k_{2}=6.36 \times 10^{-3} \mathrm{~s}^{-1}
$$

 $\qquad$

## 

For a first order reaction, $k=\frac{0.693}{t_{1 / 2}}$
$T_{1}=300 \mathrm{~K}, \quad k_{1}=\frac{0.693}{20}=3.456 \times 10^{-2} \mathrm{~min}^{-1}$
$T_{2}=350 \mathrm{~K}, \quad k_{2}=\frac{0.693}{5}=1.386 \times 10^{-1} \mathrm{~min}^{-1}$

$$
\begin{gathered}
\log \frac{k_{2}}{k_{1}}=\frac{E_{a}}{2.303 R}\left[\frac{T_{2}-T_{1}}{T_{2} T_{1}}\right] \\
\log \frac{1.386 \times 10^{-1}}{3.465 \times 10^{-2}}=\frac{E_{a}}{2.303 \times 8.314}\left(\frac{350-300}{350 \times 300}\right) \\
\log 4=\frac{E_{a}}{2.303 \times 8.314}\left(\frac{50}{350 \times 300}\right)
\end{gathered}
$$

$$
\begin{aligned}
0.602 & =\frac{E_{a}}{19.147}\left(\frac{50}{350 \times 300}\right) \\
E_{a} & =\frac{0.602 \times 19.147 \times 350 \times 300}{50} \\
& =24205.63 \mathrm{~J} \mathrm{~mol}^{-1}=24.206 \mathrm{~kJ} \mathrm{~mol}^{-1}
\end{aligned}
$$

## $\square \square \square \square ा$

${ }_{92}^{238} U$ changes to ${ }_{92}^{206} \mathrm{~Pb}$ by successive radioactive decay. A sample of uranium ore was analysed and found to contain 1.0 g of ${ }^{238} \mathrm{U}$ and 0.1 g of ${ }^{206} \mathrm{~Pb}$ had accumulated due to decay of ${ }^{238} \mathrm{U}$, find out the age of the ore. (Half-life of ${ }^{238} \mathrm{U}=4.5 \times 10^{9}$ years)
[HOTS]
$[A]_{0}=$ Initial amount of ${ }^{238} \mathrm{U}=$ amount of ${ }^{238} \mathrm{U}$ left at time $t+$ amount of ${ }^{238} \mathrm{U}$ decayed $[A]_{0}=1.0+$ amount of ${ }^{238} \mathrm{U}$ decayed

Now, amount of ${ }^{238} \mathrm{U}$ decayed $=\frac{0.1 \times 238}{206} \mathrm{~g}=0.1155 \mathrm{~g}$
$\therefore[A]_{0}=1.0 \mathrm{~g}+0.1155 \mathrm{~g}=1.1155 \mathrm{~g}$
Determination of $k$. $k=\frac{0.693}{t_{1 / 2}}=\frac{0.693}{4.5 \times 10^{9}}=0.154 \times 10^{-9} \mathrm{year}^{-1}$
Determination of time: $t=\frac{2.303}{k} \log \frac{\mid A / 0}{|A|}$
Substituting the values of $[A]_{0}=1.1155 \mathrm{~g}$ and $k=0.154 \times 10^{-9} \mathrm{year}^{-1}$
$t=\frac{2.303}{0.154 \times 10^{9}} \log \frac{1.1155}{1}$
$=0.7099 \times 10^{9}$ year
$=7.099 \times 10^{8}$ year

# CBSE Sample Paper 2017 





i. $\quad$ Slope $=-\frac{k}{2.303}$ or $k=-2.303 \times$ Slope

$$
\left.\begin{array}{rl}
\therefore \quad k & =-2.303 \times\left(-2.0 \times 10^{-6} \mathrm{~s}^{-1}\right) \\
& k
\end{array}\right)=4.606 \times 10^{-6} \mathrm{~s}^{-1}
$$

ii. For a zero order reaction

$$
\begin{aligned}
t & =\frac{\left[R h_{0}-[R]\right.}{k} \\
\text { At } t & =t_{1 / 2},[R]=\frac{/ R / 6}{2} \\
\therefore \quad t_{1 / 2} & =\frac{\left[R_{6}-\frac{\left[R_{0}\right.}{2}\right.}{k} \quad \text { or } \quad t_{1 / 2}=\frac{/ R /_{0}}{2 k}
\end{aligned}
$$


$2 \mathrm{NO}(g)+\mathrm{Cl}_{2}(g) \rightarrow 2 \mathrm{NOCl}(g)$,


|  |  |  | $\qquad$ |
| :---: | :---: | :---: | :---: |
| $\square$ | $\square$ | [1] | $\square \mathrm{m}$ |
| 2 | $\square \square$ | प | $\square \mathbf{2}$ |
| $\square$ | $\square \square$ | $\square \square$ | 2 피 |
| $\square$ | $\square 2$ | $\square 2$ | $\square$ |




CBSE Delhi 2012피
$\square \square$ Suppose order w.r.t. NO is $m$ and order w.r.t. $\mathrm{Cl}_{2}$ is $n$. Then the rate will be

$$
\text { Rate }=k\left[\mathrm{NO}^{m}\left[\mathrm{Cl}_{2}\right]^{n}\right.
$$

Substituting the values of experiment 1 to 3 in the rate expression, we get

$$
\begin{align*}
& 0.60=k(0.15)^{m}(0.15)^{n}  \tag{i}\\
& 1.20=k(0.15)^{m}(0.30)^{n}  \tag{ii}\\
& 2.40=k(0.30)^{m}(0.15)^{n} \tag{iii}
\end{align*}
$$

Dividing equation (iii) by (i), we get
$\frac{2.40}{0.60}=\frac{k(0.30)^{m}(0.15)^{n}}{k(0.15)^{m}(0.15)^{n}}$

$$
4=2^{m} \text { or } 22=2^{m} \text { or } m=2
$$

Dividing equation (ii) by (i), we get

$$
\begin{aligned}
\frac{1.20}{0.60} & =\frac{k(0.15)^{m}(0.30)^{n}}{k(0.15)^{m}(0.15)^{n}} \\
2 & =2^{n} \text { or } n=1
\end{aligned}
$$

i. Rate law expression is, Rate $=k[\mathrm{NO}]^{2}\left[\mathrm{Cl}_{2}\right]$
ii. $0.60 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~min}^{-1}=k\left(0.15 \mathrm{~mol} \mathrm{~L}^{-1}\right)^{2}\left(0.15 \mathrm{~mol} \mathrm{~L}^{-1}\right)$

$$
k=177.77 \mathrm{~mol}^{-2} \mathrm{~L}^{2} \mathrm{~min}^{-1}
$$

iii. Rate $=177.77 \mathrm{~mol}^{-2} \mathrm{~L}^{2} \mathrm{~min}^{-1} \times\left(0.25 \mathrm{~mol} \mathrm{~L}^{-1}\right)^{2}\left(0.25 \mathrm{~mol} \mathrm{~L}^{-1}\right)$

$$
=2.778 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~min}^{-1}
$$







पac|manate, $r=k[A][B]^{2}$
If concentration of $B$ is doubled, then
$r^{\prime}=k[A][2 B]^{2}$

As $A$ is present in large excess therefore, order of the reaction w.r.t. A will be zero.
Rate $=k[A]^{0}[B]^{2}=k[B]^{2}$
$\therefore$ Order of reaction $=\mathbf{2}$
$t_{1 / 2}=30 \mathrm{~min}$.

$$
\begin{aligned}
& {[R]=[R]_{0}-90 \% \text { of }[R]_{0}=[R]_{0}-\frac{\mathbf{9 0} / R /_{0}}{100}} \\
& {[R]=\frac{/ R /_{0}}{10}}
\end{aligned}
$$

$$
\begin{aligned}
& k=\frac{0.693}{t_{1 / 2}}=\frac{0.693}{30}=0.0231 \mathrm{~min}^{-1} \\
& t=\frac{2.303}{k} \log \frac{/ R / 0}{\mid R /} \\
& t=\frac{2.303}{0.0231} \log \frac{/ R / 0}{\frac{/ R_{0}}{10}}=\frac{2.303}{0.0231} \log 10 \\
& t=99.7 \mathrm{~min} .
\end{aligned}
$$


 $\square \square \square \square \square \square \square$

| $\square \mathbf{2} \square \square \mathbf{M} \square$ | $\square \square \square \square \square \square \square$ |
| :--- | :--- |
| 0.400 | 0.00 |
| 0.289 | 20.0 |
| 0.209 | 40.0 |
| 0.151 | 60.0 |
| 0.109 | 80.0 |





## CBSE Delhi 2011 피

$\square \square \square \mathrm{T}$ When $t=20 \mathrm{~min},[R]=0.289 \mathrm{~mol} \mathrm{~L}^{-1}$
Also,

$$
[R] 0=0.400 \mathrm{~mol} \mathrm{~L}^{-1}
$$

For a first order reaction

$$
\begin{array}{ll} 
& k=\frac{2.303}{t} \log \frac{/ R / 0}{l R /} \\
\therefore & k=\frac{2.303}{20} \log \frac{0.400}{0.289} \\
\Rightarrow & k=\frac{2.303}{20} \log \frac{4.00}{2.89} \\
\Rightarrow & k=\frac{2.303}{20}[\log 4.00-\log 2.89] \\
\Rightarrow & k=\frac{2.303}{20}[0.6021-0.4609] \\
\Rightarrow & k=\frac{2.303}{20} \times 0.1412 \\
\Rightarrow & k=2.303 \times 0.00706=0.016259 \mathrm{~min}^{-1} \\
\Rightarrow & t=\frac{2.303}{k} \log \frac{\mid R / 0}{[R]}
\end{array}
$$

Here, $[R]_{0}=0.400 \mathrm{~mol}^{-1}, t=100 \mathrm{~min}, k=1.626 \times 10^{-2} \mathrm{~min}^{-1}$

$$
\begin{gathered}
100=\frac{2.303}{1.626 \times 10^{-2}} \log \frac{0.400}{\mid R /} \\
\frac{100 \times 1.626 \times 10^{-2}}{2.303}=\log \frac{0.4}{|R|} \Rightarrow 0.7060=\log \frac{0.4}{\mid R /}
\end{gathered}
$$

Antilog $(0.7060)=\frac{0.4}{[R]}$

$$
5.082=\frac{0.4}{|R|} \quad \Rightarrow \quad[R]=\frac{0.4}{5.082}=0.0787 \mathrm{M}
$$

iii. Initial rate, i.e., rate of reaction when $t=0$

When,

$$
t=0.00 \mathrm{~min},[R]=0.400 \mathrm{~mol} \mathrm{~L}^{-1}
$$

Also,

$$
k=1.626 \times 10^{-2} \mathrm{~min}^{-1}
$$

$\therefore \quad$ Initial rate $=k[R]$

$$
\begin{aligned}
& =1.626 \times 10^{-2} \mathrm{~min}^{-1} \times 0.400 \mathrm{~mol} \mathrm{~L}^{-1} \\
& =6.504 \times 10^{-3} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~min}^{-1}
\end{aligned}
$$

 $\square \square \mathbf{r} \square \lim _{\square} \square \mathbf{d} \square$

| W | $\square$ | $\square \square$ | $\square \square$ |
| :---: | :---: | :---: | :---: |
| ㄴำ | [1]1] | $\square \square$ | $\square \square$ |



CBSE Delhi 2015 피
ㅁㅐㅣㅔ
i. $\quad k=\frac{2.303}{t} \log \frac{/ R /_{0}}{\mid R /}$

Substituting $[R]_{0}=0.60 \mathrm{~mol} \mathrm{~L}^{-1},[R]=0.30 \mathrm{~mol} \mathrm{~L}^{-1}$ and $t=30 \mathrm{~s}$ in equation (i), we get

$$
\begin{aligned}
& k=\frac{2.303}{30} \log \frac{0.60}{0.30} \\
& k=\frac{2.303}{30} \log 2=\frac{2.303}{30} \times 0.3010 \quad k=0.0231 \mathrm{~s}^{-1}
\end{aligned}
$$

Again substituting, $[R]_{0}=0.60 \mathrm{~mol} \mathrm{~L}^{-1},[R]=0.15 \mathrm{~mol} \mathrm{~L}^{-1}$ and $t=60$ in equation ( $i$ ), we get

$$
\begin{aligned}
& k=\frac{2.303}{60} \log \frac{0.60}{0.15} \\
& k=\frac{2.303}{60} \times \log 4=\frac{2.303}{60} \times 0.6021 \quad k=0.0231 \mathrm{~s}^{-1}
\end{aligned}
$$

As the value of $k$ is same in both the cases, therefore, hydrolysis of methylacetate in aqueous solution follows pseudo first order reaction.
ii. Average rate $=-\frac{\Delta / \mathrm{CH}_{3} \mathrm{COOCH}_{3} /}{\Delta t}$

$$
=\frac{-/ 0.15-0.30 /}{60-30}=\frac{0.15}{30}
$$





## $\square \square \square \square]$

For a first order reaction, $\quad t=\frac{2.303}{k} \log \frac{[R]_{0}}{[R]}$
$\therefore \quad \frac{t_{3 / 4}}{t_{1 / 2}}=\frac{\frac{2.303}{k} \log \frac{100}{25}}{\frac{2.303}{k} \log \frac{100}{50}}=\frac{\log 4}{\log 2}=\frac{0.6021}{0.3010}$

$$
\frac{40 \mathrm{~min}}{t_{1 / 2}}=2 \quad \text { or } \quad t_{1 / 2}=20 \mathrm{~min}
$$

## $\square \square$

(a)

(b)

$\square \square \mathbf{r} \square \boldsymbol{R}$



ㄴำ $2 \square \square$
$\square \square \boldsymbol{a}$ First order
b Zero order

## 



## HOTS



$\square \square \square \square ा$
i. The reaction $R \rightarrow P$ is a zero order reaction.
ii. For the reaction $R \xrightarrow{k} P$
rate $=\frac{-d / R /}{\mathrm{dt}}=k$
$d[R]=-k d t$
Integrating both sides,
$[R]=-k t+C$, where $C=$ constant of integration
At $t=0,[R]=[R]_{0}$
Substituting this in equation (i)

$$
C=[R]_{0}
$$

Substituting the value of $C$ in equation (i)
$[R]=-k t+[R]_{0}$
$k t=[R]_{0}-[R]$
$\Rightarrow t=\frac{\left[R h_{0}-[R]\right.}{k}$
On completion of reactions, $[R]=0$
$\therefore t=\frac{l R]_{0}}{k}$
iii. From equation (ii), we have slope of curve

$$
\text { Slope }=\frac{d / R]}{\mathrm{dt}}=-k
$$

$$
2 \square \square ा \square \rightarrow \square \square
$$

the rate of appearance of $C$ at time ' $t$ ' is $1.3 \times 10^{-1 / m}$




a. Rate $=\frac{1}{3} \frac{d / C /}{\mathrm{dt}}$

$$
=\frac{1}{3} \times 1.3 \times 10^{-4} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1}=0.43 \times 10^{-4} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1}
$$

b. Rate $=\frac{-d / A /}{\mathrm{dt}}=\frac{2}{3} \times \frac{d / C /}{\mathrm{dt}}$

$$
=\frac{2}{3} \times 1.3 \times 10^{-4} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1}=0.86 \times 10^{-4} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1}
$$






## 

$$
[R]_{0}=0.25 \mathrm{M}, t=2 \mathrm{~min}=2 \times 60 \mathrm{~s}=120 \mathrm{~s}, k=5.0 \times 10^{-4} \mathrm{~s}^{-1}
$$

For a first order reaction,

$$
k=\frac{2.303}{t} \log \frac{\mid R / 0}{\mid R /}
$$

$5.0 \times 10^{-4}=\frac{2.303}{120} \log \frac{0.25}{[R]}$ or $\log \frac{0.25}{[R]}=0.026$
$\log \frac{[R]}{0.25}=-0.026$ or $\frac{[R]}{0.25}=\operatorname{Antilog}(1.974)$

$$
\begin{aligned}
& \quad \frac{\mid R /}{0.25}=0.9419 \text { or }[R]=0.235 \mathrm{~m} \\
& t_{1 / 2}=\frac{0.693}{k}=\frac{0.693}{5 \times 10^{-4} s^{-1}}=1386 \mathrm{~s}
\end{aligned}
$$

```
\square\square\mathbf{rmull|}|\square\square|||
```







i．First order
ii．time ${ }^{-1}\left(\mathrm{~s}^{-1}\right)$
iii．$k=\frac{0.693}{t_{1 / 2}}$
iv．slope $=-k$（rate constant）

$\square \square ा ⿴ 囗 十 \square \square \square$



 $\square \square \square \square \square$ d

 which colloide with energies greater than $E_{a}$ ．It is clear from the graph below that with $10^{\circ} \mathrm{C}$ rise in temperature the area showing the fraction of molecules having energy equal to or greater than activation energy gets almost double leading to almost to doubling the rate constant．Quantitatively the effect of temperature on rate constant $(k)$ is given by Arrhenius equation．

$$
k=A e^{-E_{a} / \mathrm{RT}} \text { or } k=A \frac{1}{e^{B_{a} / \mathrm{RT}}}
$$

where $A$ is the frequency factor，$R$ is the gas constant and $E_{a}$ is the activation energy．


Thus, from Arrhenius equation we find that increasing the temperature or decreasing the activation energy will result in an exponential increase in rate constant.

$k=\left(4.5 \times 10^{11} s^{-1}\right) e^{-28000 K / T}$


ㄴㅁㅔㅣㄴ
Comparing with Arrhenius equation $k=\mathrm{Ae}^{-E_{a} / \mathrm{RT}}$, we get

$$
\begin{aligned}
& \quad-\frac{E_{a}}{\mathrm{RT}}=-\frac{28000 \mathrm{~K}}{T} \text { or } E_{a}=28000 \mathrm{~K} \times R \\
& E_{a}=28000 \mathrm{~K} \times 8.314 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}=232792 \mathrm{~J} \mathrm{~mol}^{-1} \\
& E_{a}=232.79 \mathrm{~kJ} \mathrm{~mol}^{-1}
\end{aligned}
$$




매Consider the first order reaction,

$$
R \rightarrow P
$$

For this reaction, rate law which relates the rate of reaction to the concentration of reactants can be given as

Rate $\left.=\frac{-d / R /}{\mathrm{dt}}=k / R\right]$
For a first order reaction,
$t=\frac{2.303}{k} \log \frac{/ R / 0}{[R]}$, where $[R]_{0}=$ initial concentration, $[R]=$ concentration at time $t$.

At $t_{1 / 2},[R]=[R]_{0} / 2$
So, the above equation becomes

$$
\begin{aligned}
& t_{1 / 2}=\frac{2.303}{k} \log \frac{\mid R /_{0}}{[R]_{0} / 2} \\
& t_{1 / 2}=\frac{2.303}{k} \log 2 \quad \text { or } \quad t_{1 / 2}=\frac{2.303}{k} \times 0.3010 \\
& t_{1 / 2}=\frac{0.693}{k}
\end{aligned}
$$





According to Arrhenius equation,

$$
\log k=\log A-\frac{E_{a}}{2.303 \mathrm{RT}}
$$

For uncatalysed reaction, For catalysed reaction,

$$
\log k_{1}=\log A-\frac{E_{a_{1}}}{2.303 \mathrm{RT}} \ldots(i) \quad \log k_{2}=\log A-\frac{E_{a_{2}}}{2.303 \mathrm{RT}} \ldots(i i)
$$

$A$ is equal for both reactions.
Subtracting equation (i) from equation (ii),

$$
\begin{aligned}
\log \frac{k_{2}}{k_{1}} & =\frac{E_{a_{1}}-E_{a_{2}}}{2.303 \mathrm{RT}}=\frac{(75.2-50.14) \mathrm{kJ} \mathrm{~mol}^{-1}}{2.303 \times 8.314 \mathrm{JK}^{-1} \mathrm{~mol}^{-1} \times 298 \mathrm{~K}}=4.39 \\
\frac{k_{2}}{k_{1}} & =\text { anti } \log (4.39)=2.45 \times 10^{4}
\end{aligned}
$$

Rate of reaction increases by $2.45 \times 10^{4}$ times.


For reactant $Q$, t99\% $=2 \times$ t90\%
Therefore, order of reaction w.r.t. reactant $Q=1$.
From the graph, order of reaction w.r.t. reactant, $R=0$.
So, overall order of reaction $=1+0=1$
Unit of rate constant, $k=$ time $^{-1}$
Rate $=k\left[Q[R]^{0}\right.$
Rate $=k[Q]$



## ㄴㅁㅔㅔ

$[R]=[R]_{0}-\frac{3}{4}[R]_{0}=\frac{/ R /_{0}}{4}$
Substituting $[R]=\frac{/ R h_{0}}{4}, k=2.54 \times 10^{-3} s^{-1}$ in the expression $t=\frac{2.303}{k} \log \frac{/ R / 0}{[R]}$, we get
$t=\frac{2.303}{2.54 \times 10^{-3}} \log \frac{/ R /_{0}}{\left[R / h_{0} / 4\right.}=\frac{2.303 \times 10^{3}}{2.54} \log 4$
$t=\frac{2.303 \times 10^{3}}{2.54} \times 0.6021=545.92 \mathrm{~s}$

## Alternative Method:

For a first order reaction, $t_{3 / 4}=2 \times t_{1 / 2}$
$\therefore \quad t_{3 / 4}=2 \times \frac{0.693}{k}$

$$
t_{3 / 4}=\frac{2 \times 0.693}{2.54 \times 10^{-3} \mathrm{~s}}=545.67 \mathrm{~s}
$$


[^0]:    

