Class: XIIth

Solutions
Subject : CHEMISTRY
DPP No. : 1

## Topic :- Chemical Kinetics

1

2
(a)

It is the definition of molecularity.
(c)
$\left(\frac{d x}{d t}\right)=k[N O]^{2}\left[o_{2}\right]$
$=k\left(\frac{n_{N O}}{V}\right)^{2}\left(\frac{n_{O_{2}}}{V}\right)$
$\left(\frac{d x}{d t}\right)=\frac{k}{V^{3}}\left(n_{N o}\right)^{2}\left(n_{O_{2}}\right)$
$\left(\frac{d x}{d t}\right)=\frac{k\left(n_{N o}\right)^{2}\left(n_{O_{2}}\right)}{\left(\frac{V}{2}\right)^{3}}$
$=8\left(\frac{d x}{d t}\right)$
3

4
(a)

$$
\begin{array}{ll}
\text { Rate }=-\left[\frac{d c}{d t}\right]=\left[-\frac{d n}{d t}\right] \frac{1}{V} & {\left[\because c=\frac{n}{V}\right]} \\
\therefore & -\left[\frac{d c}{d t}\right]=-\frac{1}{R T}\left[\frac{d P}{d t}\right] .
\end{array}\left[\begin{array}{ll} 
& {\left[c=\frac{P}{R T}\right]}
\end{array}\right.
$$

(a)

For zero order reaction
Rate $=[A]^{0}=k$
$\frac{\mathrm{mol} L^{-1}}{s}=k$
$\mathrm{K}=\operatorname{mol}^{-1} \mathrm{~S}^{-1}$
6
(b)
$A \xrightarrow{k_{1}} B$,
$A \xrightarrow{k_{2}} C$,
By Arrhenius equation,
$R_{1}=A^{\prime} e^{-E_{a} 1 / R T}$ and $k_{2}=A^{\prime} e^{-E_{a} 2 / R T}$
( $A^{\prime}$ is Arrhenius constant) (Since, $E_{a 2}=2 E_{a 1}$ )
$\therefore k_{2}=A^{\prime} e^{-2 E_{\alpha} \mid R T}$
$\frac{k_{1}}{k_{2}}=\frac{A^{\prime} e^{-E_{a} 1 \mid R T}}{A^{\prime} e^{-2 E_{a} \mid R T}}=e^{E_{a} 1 \mid R T}$
$\therefore k_{1}=k_{2} e^{E_{a} 1 / R T}$
(d)

For the reaction, $2 A+B \rightarrow A_{2} B$
According to rate laws,
Rate $\propto$ concentration of reactants
rate $=k[A]^{2}[B]$
Where, $\mathrm{k}=$ rate constant
(d)

This is activation state and orientation concept for mechanism of reactions.
(b)

Rate depends upon the slowest step. Hence, from equation
$\mathrm{O}+\mathrm{O}_{3} \rightarrow 2 \mathrm{O}_{2}$
$r=k\left[\mathrm{O}_{3}\right][\mathrm{O}]$
And from equation $\mathrm{O}_{3} \rightleftharpoons \mathrm{O}_{2}+0$

$$
\begin{aligned}
& K_{\mathrm{eq}}=\frac{\left[\mathrm{O}_{2}\right][\mathrm{O}]}{\left[\mathrm{O}_{3}\right]} \\
& {[\mathrm{O}]=\frac{K_{\mathrm{eq}}\left[\mathrm{O}_{3}\right]}{\left[\mathrm{O}_{2}\right]}} \\
& \therefore r=k\left[\mathrm{O}_{3}\right] \frac{K_{\mathrm{eq}}\left[\mathrm{O}_{3}\right]}{\left[\mathrm{O}_{2}\right]} \\
& =k^{\prime}\left[\mathrm{O}_{3}\right]^{2}\left[\mathrm{O}_{2}\right]^{-1}
\end{aligned}
$$


(a)

Amount of $A$ left in $n_{1}$ halves $=\frac{\left[A_{0}\right]}{2^{n_{1}}}$
Amount of $B$ left in $n_{2}$ halves $=\frac{\left[B_{0}\right]}{2^{n_{2}}}$
Also if $\frac{\left[A_{0}\right]}{2^{n_{1}}}=\frac{\left[B_{0}\right]}{2^{n_{2}}}$ when $A$ decays to $n_{1}$ halves and $B$ decays to $n_{2}$ halves.
$\because \quad\left[A_{0}\right]=4\left[B_{0}\right]$
$\therefore \quad 4=\frac{2^{n_{1}}}{2^{n_{2}}}=(2)^{n_{1}-n_{2}}$
or $\quad\left(n_{1}-n_{2}\right)=2$
$\therefore \quad n_{2}=n_{1}-2$
Now, $\quad T=n_{1} \times t_{1 / 2 A}$ and $T=n_{2} \times t_{1 / 2 B}$
$\therefore \quad \frac{n_{1} \times t_{1 / 2 A}}{n_{2} \times t_{1 / 2 B}}=1$
or $\quad \frac{n_{1} \times 5}{n_{2} \times 15}=1$
or $\quad \frac{n_{1}}{n_{2}}=3$
$\therefore$ By Eqs. (i) and (ii) $n_{1}=3, n_{2}=1$
Thus,
$T=3 \times 5=15$ minute
(c)
$\because$ On doubling the concentration of A , the rate of reaction becomes two times.
$\therefore$ The order of reaction w.r.t. A is 1
$\because$ On doubling the concentration of B , the rate of reaction does not change.
$\therefore$ the order of reaction respect to B is 0
$\because$ on doubling the concentration of C , the rate of reaction becomes four times
$\therefore$ the order of reaction w.r.t. C is 2
$\therefore$ the overall order of reaction $=1+0+2=3$
(c)

For $n$th order; unit of rate constant may be derived by
$K=\frac{\text { rate }}{[\text { reactant }]^{n}}$
(c)
$r=K\left[\mathrm{~N}_{2} \mathrm{O}_{5}\right]=6.2 \times 10^{-4} \times 1.25=7.75 \times 10^{-4} \mathrm{M} / \mathrm{s}$
(c)

A $\rightarrow$ product
Initially a
After time $\mathrm{t} \quad(\mathrm{a}-\mathrm{x}) \quad \mathrm{x}$
After $t_{1 / 4} \quad\left(a-\frac{a}{4}\right) \quad \frac{a}{4}$
For the first order kinetics ,
$k=\frac{2.303}{t} \log \left(\frac{a}{a-x}\right)$
$k=\frac{2.303}{t_{1 / 4}} \log \frac{a}{\frac{3 a}{4}}$
$t_{1 / 4}=\frac{2.303 \log \frac{4}{3}}{k}$
$=\frac{0.29}{k}$
(a)

The order of reaction is zero. Suppose the following reaction take place.
$A+B \rightarrow$ product
$\therefore$ rate $=[A][B]^{-1}$
$\therefore$ order $=1+(-1)=0$
(d)

Pseudo first order reactions are those reactions which are not truly first order but show first order kinetics under specific conditions. For examples, acidic hydrolysis of an ester and hydrolysis of cane sugar.
(d)

The differential rate law for the reaction,
$4 \mathrm{NH}_{3}(\mathrm{~g})+5 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow 4 \mathrm{NO}(\mathrm{g})+6 \mathrm{H}_{2} \mathrm{O}(\mathrm{g})$ is
Rate $=-\frac{1}{4} \frac{d\left[\mathrm{NH}_{3}\right]}{d t}=-\frac{1}{5} \frac{d\left[\mathrm{O}_{2}\right]}{d t}$
$=+\frac{1}{4} \frac{d[N O]}{d t}=+\frac{1}{6} \frac{d\left[\mathrm{H}_{2} \mathrm{O}\right]}{d t}$
(a)
${ }_{79} \mathrm{Au}^{198} \xrightarrow{-B}{ }_{80} \mathrm{Hg}^{198}$
$k=\frac{0.693}{t_{1 / 2}}=\frac{0.693}{65}$
After 260 hr ,
$k=\frac{2.303}{260} \log \frac{a}{a-x}$
$\frac{0.693}{65}=\frac{2.303}{260} \log \frac{a}{a-x}$
$\frac{a}{a-x}=16$
$\frac{1}{1-x}=16$
$x=\frac{15}{16} \mathrm{~g}=0.9375 \mathrm{~g}$

20
(d)

Rate $=k\left[\mathrm{NO}_{2} \mathrm{Cl}\right]$
Hence ,rate determining step is
$\mathrm{NO}_{2} \mathrm{CL} \rightarrow \mathrm{NO}_{2}+\mathrm{CL}$
(b)
$R \mathrm{Cl}+\mathrm{NaOH} \rightarrow \mathrm{ROH}+\mathrm{NaCl}$
Rate $=k[R \mathrm{Cl}]$
For this reaction rate of reaction is depends upon the concentration of RCl
It means, the rate of reaction is halved by reducing the concentration of $R \mathrm{Cl}$ by one half

| ANSWER-KEY |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Q. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| A. | A | C | C | A | A | B | D | D | B | A |
| Q. | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
| A. | C | C | C | C | A | D | D | A | D | B |
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