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## NCERT Solutions for Class 12 Chemistry Part 1 Chapter 4

## Chemical Kinetics Class 12

Chapter 4 Chemical Kinetics Exercise Solutions
In text : Solutions of Questions on Page Number : 98
Q1 :
For the reaction $R \rightarrow P$, the concentration of a reactant changes from 0.03 M to 0.02 M in 25 minutes. Calculate the average rate of reaction using units of time both in minutes and seconds.

Answer :

$$
\begin{aligned}
& \text { Average rate of reaction }=-\frac{\Delta[\mathrm{R}]}{\Delta t} \\
& =-\frac{[\mathrm{R}]_{2}-[\mathrm{R}]_{1}}{t_{2}-t_{1}} \\
& =-\frac{0.02-0.03}{25} \mathrm{M} \mathrm{~min}^{-1} \\
& =-\frac{-0.01}{25} \mathrm{M} \mathrm{~min}^{-1} \\
& =4 \times 10^{-4} \mathrm{M} \mathrm{~min}^{-1} \\
& =\frac{4 \times 10^{-4}}{60} \mathrm{M} \mathrm{~s}^{-1} \\
& =6.67 \times 10^{-6} \mathrm{M} \mathrm{~s}^{-1}
\end{aligned}
$$

Q2 :
In a reaction, $2 \mathrm{~A} \rightarrow$ Products, the concentration of $A$ decreases from $0.5 \mathrm{~mol} \mathrm{~L}^{-1}$ to $0.4 \mathrm{~mol} \mathrm{~L}-1 \mathrm{in} 10$ minutes. Calculate the rate during this interval?

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Average rate $=-\frac{1}{2} \frac{\Delta[\mathrm{~A}]}{\Delta t}$
$=-\frac{1}{2} \frac{[\mathrm{~A}]_{2}-[\mathrm{A}]_{1}}{t_{2}-t_{1}}$
$=-\frac{1}{2} \frac{0.4-0.5}{10}$
$=-\frac{1}{2} \frac{-0.1}{10}$
$=0.005 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~min}^{-1}$
$=5 \times 10-3 \mathrm{M} \mathrm{min}_{-1}$

Q3 :
For a reaction, $\mathbf{A}+\mathbf{B}$ Ãфâ€ 'Product; the rate law is given by, $r=k[\mathrm{~A}]^{1 / 2}[\mathrm{~B}]^{2}$. What is the order of the reaction?

## Answer :

The order of the reaction $=\frac{1}{2}+2$
$=2 \frac{1}{2}$
$=2.5$

Q4 :

The conversion of molecules $X$ to $Y$ follows second order kinetics. If concentration of $X$ is increased to three times how will it affect the rate of formation of $Y$ ?

## Answer :

The reaction $\mathrm{X} \rightarrow \mathrm{Y}$ follows second order kinetics.
Therefore, the rate equation for this reaction will be:
Rate $=k[X]^{2}(1)$

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Let $[\mathrm{X}]=a \mathrm{~mol} \mathrm{~L}^{-1}$, then equation (1) can be written as:
Rate $_{1}=k .(a)^{2}$
$=k a^{2}$
If the concentration of $X$ is increased to three times, then $[X]=3 \mathrm{amol}^{-1}$
Now, the rate equation will be:
Rate $=k(3 a)^{2}$
$=9\left(k a^{2}\right)$
Hence, the rate of formation will increase by 9 times.

Q5 :

A first order reaction has a rate constant $1.151^{-3} \mathbf{s}^{-1}$. How long will 5 g of this reactant take to reduce to 3 g ?

## Answer :

From the question, we can write down the following information:
Initial amount $=5 \mathrm{~g}$
Final concentration $=3 \mathrm{~g}$

Rate constant $=1.1510^{-3} \mathrm{~s}^{-1}$
We know that for a $1^{\text {storder reaction, }}$

$$
\begin{aligned}
& t=\frac{2.303}{k} \log \frac{[\mathrm{R}]_{0}}{[\mathrm{R}]} \\
&=\frac{2.303}{1.15 \times 10^{-3}} \log \frac{5}{3} \\
&=\frac{2.303}{1.15 \times 10^{-3}} \times 0.2219 \\
&= 444.38 \mathrm{~s}= \\
& 444 \mathrm{~s}(\text { approx })
\end{aligned}
$$

## Q6 :

Time required to decompose $\mathrm{SO}_{2} \mathrm{Cl}_{2}$ to half of its initial amount is 60 minutes. If the decomposition is a first order reaction, calculate the rate constant of the reaction.

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## Answer:

We know that for a $1^{\text {storder }}$ reaction,
$t_{1 / 2}=\frac{0.693}{k}$
It is given that $\mathrm{t}_{1 / 2}=60 \mathrm{~min}$
$\therefore k=\frac{0.693}{t_{1 / 2}}$
$=\frac{0.693}{60}$
$=0.01155 \mathrm{~min}^{-1}$
$=1.155 \mathrm{~min}^{-1}$

Or $k=1.925 \times 10^{-4} \mathrm{~s}^{-1}$

Q7 :

What will be the effect of temperature on rate constant?

## Answer :

The rate constant of a reaction is nearly doubled with a $10^{\circ}$ rise in temperature. However, the exact dependence of the rate of a chemical reaction on temperature is given by Arrhenius equation,
$k=\mathrm{Ae}^{-\mathrm{Ea} / R T}$
Where,
A is the Arrhenius factor or the frequency factor
Tis the temperature
Ris the gas constant $E_{\mathrm{a}}$ is
the activation energy

Q8 :

The rate of the chemical reaction doubles for an increase of 10 K in absolute temperature from 298 K .
Calculate $E_{\text {a }}$

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## Answer:

It is given that $T_{1}=298 \mathrm{~K}$
$\therefore T_{2}=(298+10) \mathrm{K}$
$=308 \mathrm{~K}$
We also know that the rate of the reaction doubles when temperature is increased by $10^{\circ}$.
Therefore, let us take the value of $k_{1}=k$ and that of $k_{2}=2 k$
Also, $R=8.314 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$
Now, substituting these values in the equation:
$\log \frac{k_{2}}{k_{1}}=\frac{E_{\mathrm{a}}}{2.303 R}\left[\frac{T_{2}-T_{1}}{T_{1} T_{2}}\right]$
We get:
$\log \frac{2 k}{k}=\frac{E_{\mathrm{a}}}{2.303 \times 8.314}\left[\frac{10}{298 \times 308}\right]$
$\Rightarrow \log 2=\frac{E_{\mathrm{a}}}{2.303 \times 8.314}\left[\frac{10}{298 \times 308}\right]$
$\Rightarrow E_{\mathrm{a}}=\frac{2.303 \times 8.314 \times 298 \times 308 \times \log 2}{10}$
$=52897.78 \mathrm{~J} \mathrm{~mol}^{-1}$
$=52.9 \mathrm{~kJ} \mathrm{~mol}^{-1}$
Note: There is a slight variation in this answer and the one given in the NCERT textbook.

Q9 :

The activation energy for the reaction
$2 \mathrm{HI}_{(g)} \rightarrow \mathrm{H}_{2}+\mathrm{I}_{2(g)}$
is $209.5 \mathrm{~kJ} \mathrm{~mol}^{-1}$ at 581 K . Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy?

## Answer :

In the given case:

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$E_{\mathrm{a}}=209.5 \mathrm{~kJ} \mathrm{~mol}^{-1}=209500 \mathrm{~J} \mathrm{~mol}^{-1}$
$T=581 \mathrm{~K}$
$R=8.314 \mathrm{JK}^{-1} \mathrm{~mol}^{-1}$ Now, the fraction of molecules of reactants having energy equal to or greater than activation energy is given as:
$x=e-E_{a} / \mathrm{R} T \Rightarrow \operatorname{In} x=-E$

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Exercise : Solutions of Questions on Page Number : 117
Q1 :
From the rate expression for the following reactions, determine their order of reaction and the dimensions of the rate constants.
(i) $3 \mathrm{NO}(\mathrm{g})$ Ã $\notin a ̂ €, \mathrm{~N}_{2} \mathrm{O}(\mathrm{g})$ Rate $=k\left[\mathrm{NO}^{2}\right.$
(ii) $\mathrm{H}_{2} \mathrm{O}_{2}(\mathrm{aq})+3 \mathrm{I} \cdot(\mathrm{aq})+2 \mathrm{H}+\tilde{A} \not \subset \mathrm{â}{ }^{\prime} 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{I})+\mathrm{I}_{3}^{-}$Rate $=k\left[\mathrm{H}_{2} \mathrm{O}_{2}\right][\mathrm{I}-]$
(iii) $\mathrm{CH}_{3} \mathrm{CHO}(\mathrm{g})$ Ãĉâ€ ${ }^{\prime} \mathrm{CH}_{4}(\mathrm{~g})+\mathrm{CO}(\mathrm{g})$ Rate $=k\left[\mathrm{CH}_{3} \mathrm{CHO}\right]^{3 / 2}$
(iv) $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{Cl}(\mathrm{g})$ Ã孔̧â€ ${ }^{\prime} \mathrm{C}_{2} \mathrm{H}_{4}(\mathrm{~g})+\mathrm{HCl}(\mathrm{g})$ Rate $=k\left[\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{Cl}\right]$

## Answer:

(i) Given rate $=k[\mathrm{NO}]^{2}$

Therefore, order of the reaction $=2$

Dimension of

$$
k=\frac{\text { Rate }}{[\mathrm{NO}]^{2}}
$$

$=\frac{\mathrm{mol} \mathrm{L}^{-1} \mathrm{~s}^{-1}}{\left(\mathrm{~mol} \mathrm{~L}^{-1}\right)^{2}}$
$=\frac{\mathrm{mol} \mathrm{L}^{-1} \mathrm{~s}^{-1}}{\mathrm{~mol}^{2} \mathrm{~L}^{-2}}$
$=\mathrm{Lmol}^{-1} \mathrm{~s}^{-1}$
(ii) Given rate $=k\left[\mathrm{H}_{2} \mathrm{O}_{2}\right]\left[\mathrm{I}^{-}\right]$

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Therefore, order of the reaction $=2$
Dimension of $k=\frac{\text { Rate }}{\left[\mathrm{H}_{2} \mathrm{O}_{2}\right]\left[\mathrm{I}^{-}\right]}$
$=\frac{\mathrm{mol} \mathrm{L}^{-1} \mathrm{~s}^{-1}}{\left(\mathrm{~mol} \mathrm{~L}^{-1}\right)\left(\mathrm{mol} \mathrm{L}^{-1}\right)}$
$=\mathrm{Lmol}^{-1} \mathrm{~s}^{-1}$
(iii) Given rate $=k\left[\mathrm{CH}_{3} \mathrm{CHO}\right]^{3 / 2}$

Therefore, order of reaction $=\frac{3}{2}$

$$
k=\frac{\text { Rate }}{\left[\mathrm{CH}_{3} \mathrm{CHO}\right]^{\frac{3}{2}}}
$$

imension of

$$
\frac{3}{2}
$$

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

(iv) Given rate $=k\left[\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{Cl}\right]$

Therefore,order of the reaction $=1$
Dimension of $k=\frac{\text { Rate }}{\left[\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{Cl}\right]}$
$=\frac{\mathrm{mol} \mathrm{L}^{-1} \mathrm{~s}^{-1}}{\mathrm{~mol} \mathrm{~L}^{-1}}$
$=\mathrm{s}^{-1}$

Q2 :

For the reaction:
$2 \mathrm{~A}+\mathrm{B} \rightarrow \mathrm{A}_{2} \mathrm{~B}$
the rate $=k[A][B]^{2}$ with $k=2.0 \times 10^{-6} \mathrm{~mol}^{-2} \mathrm{~L}^{2} \mathrm{~S}^{-1}$. Calculate the initial rate of the reaction when $[A]=0.1 \mathrm{~mol} \mathrm{~L}^{-1}$, $[B]$ $=0.2 \mathrm{~mol} \mathrm{~L}^{-1}$. Calculate the rate of reaction after [A] is reduced to $0.06 \mathrm{~mol} \mathrm{~L}^{-1}$.

## Answer :

The initial rate of the reactionis
Rate $=k[\mathrm{~A}][\mathrm{B}]^{2}$
$=\left(2.0 \times 10-6 \mathrm{~mol}_{-2 \mathrm{~L}_{2} \mathrm{~S}-1}\right)\left(0.1 \mathrm{~mol} \mathrm{~L}_{-1}\right)(0.2 \mathrm{~mol} \mathrm{~L}-1)_{2}$
$=8.0 \times 10-\mathrm{mmol}-\mathrm{L}^{2} 2 \mathrm{~S}-1$
When $[A]$ is reduced from $0.1 \mathrm{~mol}^{-1}$ to $0.06 \mathrm{~mol}^{-1}$, the concentration of $A$ reacted $=(0.1-0.06) \mathrm{mol} \mathrm{L}^{-1}=0.04 \mathrm{~mol} \mathrm{~L}$

Therefore, concentration of B reacted $=\frac{1}{2} \times 0.04 \mathrm{~mol} \mathrm{~L}^{-1}=0.02 \mathrm{~mol} \mathrm{~L}^{-1}$
Then, concentration of $B$ available, $[B]=(0.2-0.02) \mathrm{mol} \mathrm{L}^{-1}$
$=0.18 \mathrm{~mol} \mathrm{~L}^{-1}$
After [A] is reduced to $0.06 \mathrm{~mol} \mathrm{~L}^{-1}$, the rate of the reaction is given by,
Rate $=k[A][B]^{2}$
$=\left(2.0 \times 10^{-6} \mathrm{~mol}^{-2} \mathrm{~L}^{2} \mathrm{~s}^{-1}\right)\left(0.06 \mathrm{~mol} \mathrm{~L}^{-1}\right)\left(0.18 \mathrm{~mol} \mathrm{~L}^{-1}\right)^{2}$
$=3.89 \mathrm{~mol}$ L- s - t

Q3 :

The decomposition of $\mathrm{NH}_{3} \mathrm{O}$ platinum surface is zero order reaction. What are the rates of production of $\mathrm{N}_{2}$ and $\mathrm{H}_{2}$ if $k=2.5 \times 10^{-4} \mathrm{~mol}^{-1} \mathrm{~L} \mathrm{~s}^{-1}$ ?

## Answer :

The decomposition of $\mathrm{NH}_{3}$ on platinum surface is represented by the following equation.
$2 \mathrm{NH}_{3(\mathrm{~g})} \xrightarrow{\mathrm{Pt}} \mathrm{N}_{2(\mathrm{~g})}+3 \mathrm{H}_{2(\mathrm{~g})}$
Therefore,
Rate $=-\frac{1}{2} \frac{d\left[\mathrm{NH}_{3}\right]}{d t}=\frac{d\left[\mathrm{~N}_{2}\right]}{d t}=\frac{1}{3} \frac{d\left[\mathrm{H}_{2}\right]}{d t}$
However, it is given that the reaction is of zero order.

Therefore,

$$
\begin{aligned}
-\frac{1}{2} \frac{d\left[\mathrm{NH}_{3}\right]}{d t}=\frac{d\left[\mathrm{~N}_{2}\right]}{d t}=\frac{1}{3} \frac{d\left[\mathrm{H}_{2}\right]}{d t} & =k \\
& =2.5 \times 10^{-4} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1}
\end{aligned}
$$

Therefore, the rate of production of $\mathrm{N}_{2}$ is

$$
\frac{d\left[\mathrm{~N}_{2}\right]}{d t}=2.5 \times 10^{-4} \mathrm{molLL}^{-1} \mathrm{~s}^{-1}
$$

And, the rate of production of $\mathrm{H}_{2}$ is
$\frac{d\left[\mathrm{H}_{2}\right]}{d t}=3 \times 2.5 \times 10^{-4} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1}$
$=7.5 \times 10^{-4} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~S}^{-1}$

## Q4 :

The decomposition of dimethyl ether leads to the formation of $\mathrm{CH}_{4}, \mathrm{H}_{2}$ and CO and the reaction rate is given by

Rate $=k\left[\mathrm{CH}_{3} \mathrm{OCH}_{3}\right]^{3 / 2}$
The rate of reaction is followed by increase in pressure in a closed vessel, so the rate can also be expressed in terms of the partial pressure of dimethyl ether, i.e.,

$$
\text { Rate }=k\left(p_{\mathrm{CH}_{3} \mathrm{OCH}_{3}}\right)^{3 / 2}
$$

If the pressure is measured in bar andtime in minutes, then what are the units of rate and rate constants?

## Answer :

If pressure is measured in bar and time in minutes, then
Unit of rate $=$ bar min ${ }^{-1}$
Rate $=k\left(p_{\mathrm{CH}_{3} \mathrm{OCH}_{3}}\right)^{3 / 2}$
$\Rightarrow k=\frac{\text { Rate }}{\left(p_{\mathrm{CH}_{3} \mathrm{OCH}_{3}}\right)^{3 / 2}}$
Therefore, unit of rate constants $(k)=\frac{\mathrm{bar} \mathrm{min}^{-1}}{\mathrm{bar}^{3 / 2}}$

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$=\operatorname{bar}^{-1 / 2} \mathrm{~min}^{-1}$

Q5 :

Mention the factors that affect the rate of a chemical reaction.

## Answer :

The factors that affect the rate of a reaction areas follows.
(i) Concentration of reactants (pressure in case of gases)
(ii) Temperature
(iii) Presence of a catalyst

Q6 :

A reaction is second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is
(i) doubled (ii) reduced to half?

Answer:
Letthe concentration of the reactant be $[\mathrm{A}]=a$
Rate of reaction, $\mathrm{R}=k[\mathrm{~A}]^{2}$
$=k a^{2}$
(i)If the concentration of the reactant is doubled, i.e. $[A]=2 a$, then the rate of the reaction would be
$\mathrm{R}^{\prime}=k(2 a)^{2}$
$=4 k a^{2}$
$=4 \mathrm{R}$
Therefore, the rate of the reaction would increase by 4 times.
(ii) If the concentration of the reactant is reduced to half, i.e. $[\mathrm{A}]=\frac{1}{2} a$, then the rate of the reaction would be
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$R=k\left(\frac{1}{2} a\right)^{2}$
$=\frac{1}{4} k a^{2}$
$=\frac{1}{4} R$

Therefore, the rate of the reaction would be reduced to $\frac{1}{4}^{\text {th }}$.

Q7 :

What is the effect of temperature on the rate constant of a reaction? How can this temperature effect on rate constant be represented quantitatively?

## Answer :

The rate constant is nearly doubled with a rise in temperature by $10^{\circ}$ for a chemical reaction.
The temperature effect on the rate constant can be represented quantitatively by Arrhenius equation,
$k=\mathrm{A} e^{-E_{3} / \mathrm{R} T}$
where, kis the rate constant,
A is the Arrhenius factor or the frequency factor,
$R$ is the gas constant,
Tis the temperature, and
Eais the energy of activation for the reaction

Q8 :

In a pseudo first order hydrolysis of ester in water, the following results were obtained:

Answer :
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| $\mathrm{t} / \mathrm{s}$ | 0 | 30 | 60 | 90 |
| :---: | :---: | :---: | :---: | :---: |
| $[$ Ester]mol L-1 | 0.55 | 0.31 | 0.17 | 0.085 |

(i) Calculate the average rate of reaction between the time interval 30 to 60 seconds.
(ii) Calculate the pseudo first order rate constant for the hydrolysis of ester.
(i) Average rate of reaction between the time interval, 30 to 60 seconds,

$$
=\frac{d[\text { Ester }]}{d t}
$$

$=\frac{0.31-0.17}{60-30}$
$=\frac{0.14}{30}$

$$
=4.67
$$

$\times 10-3 \mathrm{~mol} \mathrm{~L}-1 \mathrm{~S}-1$
(ii) For a pseudo first order reaction,
$k=\frac{2.303}{t} \log \frac{[\mathrm{R}]_{0}}{[\mathrm{R}]}$
For $t=30 \mathrm{~s}, \quad k_{1}=\frac{2.303}{30} \log \frac{0.55}{0.31}$
$=1.911 \times 10^{-2} \mathrm{~s}^{-1}$
For $t=60 \mathrm{~s}, \quad k_{2}=\frac{2.303}{60} \log \frac{0.55}{0.17}$
$=1.957 \times 10^{-2} \mathrm{~s}^{-1}$
For $t=90 \mathrm{~s}, \quad k_{3}=\frac{2.303}{90} \log \frac{0.55}{0.085}$
$=2.075 \times 10^{-2} \mathrm{~s}^{-1}$

$$
k=\frac{k_{1}+k_{2}+k_{3}}{3}
$$

$=\frac{\left(1.911 \times 10^{-2}\right)+\left(1.957 \times 10^{-2}\right)+\left(2.075 \times 10^{-2}\right)}{3}$
$=1.98 \times 10^{-2} \mathrm{~s}^{-1}$

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A reaction is first order in A and second order in $B$.
(i) Write the differential rate equation.
(ii) How is the rate affected on increasing the concentration of $B$ three times?
(iii) How is the rate affected when the concentrations of both $A$ and $B$ are doubled?

## Answer :

(i) The differential rate equation will be

$$
\begin{aligned}
& \begin{aligned}
&-\frac{d[\mathrm{R}]}{d t}=k[\mathrm{~A}][\mathrm{B}]^{2} \\
&-\frac{d[\mathrm{R}]}{d t}=k[\mathrm{~A}][3 \mathrm{~B}]^{2} \\
&=9 \cdot k[\mathrm{~A}][\mathrm{B}]^{2} \\
&\text { ii }) \text { If the concentration of } \mathrm{B} \text { is increased three times, then }
\end{aligned} \\
&
\end{aligned}
$$

Therefore, the rate of reaction will increase 9 times.
(iii) When the concentrations of both A and B are doubled,

$$
\begin{aligned}
-\frac{d[\mathrm{R}]}{d t} & =k[\mathrm{~A}][\mathrm{B}]^{2} \\
& =k[2 \mathrm{~A}][2 \mathrm{~B}]^{2} \\
& =8 \cdot k[\mathrm{~A}][\mathrm{B}]^{2}
\end{aligned}
$$

Therefore, the rate of reaction will increase 8 times.

Q10 :
In a reaction between $A$ and $B$, the initial rate of reaction ( $r_{0}$ ) was measured for different initial concentrations of $A$ and $B$ as given below:

| $\mathrm{A} / \mathrm{mol} \mathrm{L}^{-1}$ | 0.20 | 0.20 | 0.40 |
| :---: | :---: | :---: | :---: |
| $\mathrm{~B} / \mathrm{mol} \mathrm{L}^{-1}$ | 0.30 | 0.10 | 0.05 |
| $\mathrm{r} / \mathrm{mol} \mathrm{L}_{-1} \mathrm{~S}^{-1}$ | $5.07 \times 10^{-5}$ | $5.07 \times 10^{-5}$ | $1.43 \times 10^{-4}$ |

What is the order of the reaction with respect to $A$ and $B$ ?

Answer:

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Let the order of the reaction with respect to $A$ be xand with respect to $B$ be $y$.
Therefore,
$\mathrm{r}_{0}=k[\mathrm{~A}]^{x}[\mathrm{~B}]^{y}$
$5.07 \times 10^{-5}=k[0.20]^{x}[0.30]^{y}$
$5.07 \times 10^{-5}=k[0.20]^{x}[0.10]^{y}$
$1.43 \times 10^{-4}=k[0.40]^{x}[0.05]^{y}$
Dividing equation (i) by (ii), we obtain
$\frac{5.07 \times 10^{-5}}{5.07 \times 10^{-5}}=\frac{k[0.20]^{x}[0.30]^{y}}{k[0.20]^{x}[0.10]^{y}}$
$\Rightarrow 1=\frac{[0.30]^{v}}{[0.10]^{y}}$
$\Rightarrow\left(\frac{0.30}{0.10}\right)^{0}=\left(\frac{0.30}{0.10}\right)^{y}$
$\Rightarrow y=0$
Dividing equation (iii) by (ii), we obtain
$\frac{1.43 \times 10^{-4}}{5.07 \times 10^{-5}}=\frac{k[0.40]^{x}[0.05]^{v}}{k[0.20]^{v}[0.30]^{v}}$
$\Rightarrow \frac{1.43 \times 10^{-4}}{5.07 \times 10^{-5}}=\frac{[0.40]^{x}}{[0.20]^{x}} \quad\left[\begin{array}{l}\text { Since } y=0, \\ {[0.05]^{y}=[0.30]^{y}=1}\end{array}\right]$
$\Rightarrow 2.821=2^{x}$
$\Rightarrow \log 2.821=x \log 2 \quad$ (Taking log on both sides)
$\Rightarrow x=\frac{\log 2.821}{\log 2}$
$=1.496$
$=1.5$ (approximately)
Hence, the order of the reaction with respect to $A$ is 1.5 and with respect to $B$ is zero.

Q11 :
The following results have been obtained during the kinetic studies of the reaction:
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2A + B Ãধâ€ ' C + D

| Experiment | $\mathrm{A} / \mathrm{mol} \mathrm{L}^{-1}$ | $\mathrm{~B} / \mathrm{mol} \mathrm{L}^{-1}$ | Initial rate of formation of D/mol L. $\mathrm{min}^{-1}$ |  |
| :---: | :---: | :---: | :---: | :---: |
| I | 0.1 | 0.1 | $6.0 \times 10^{-3}$ | $7.2 \times 10^{-2}$ |
| II | 0.3 | 0.2 | $2.88 \times 10^{-1}$ |  |
| III | 0.3 | 0.4 | $2.40 \times 10^{-2}$ |  |
| IV | 0.4 | 0.1 |  |  |

Determine the rate law and the rate constant for the reaction.

## Answer:

Let the order of the reaction with respect to $A$ be xand with respect to $B$ be $y$.
Therefore, rate of the reaction is given by,

$$
\text { Rate }=k[\mathrm{~A}]^{x}[\mathrm{~B}]^{v}
$$

According to the question,
$6.0 \times 10^{-3}=k[0.1]^{x}[0.1]^{y}$
$7.2 \times 10^{-2}=k[0.3]^{x}[0.2]^{y}$
$2.88 \times 10^{-1}=k[0.3]^{x}[0.4]^{y}$
$2.40 \times 10^{-2}=k[0.4]^{x}[0.1]^{y}$

Dividing equation (iv) by (i), we obtain
$\frac{2.40 \times 10^{-2}}{6.0 \times 10^{-3}}=\frac{k[0.4]^{x}[0.1]^{y}}{k[0.1]^{x}[0.1]^{y}}$
$\Rightarrow 4=\frac{[0.4]^{x}}{[0.1]^{x}}$
$\Rightarrow 4=\left(\frac{0.4}{0.1}\right)^{x}$
$\Rightarrow(4)^{1}=4^{x}$
$\Rightarrow x=1$
Dividing equation (iii) by (ii), we obtain

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Therefore, the rate law is
Rate $=k[\mathrm{~A}][\mathrm{B}]^{2}$

$$
\Rightarrow k=\frac{\text { Rate }}{[\mathrm{A}][\mathrm{B}]^{2}}
$$

From experiment I, we obtain

$$
k=\frac{6.0 \times 10^{-3} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~min}^{-1}}{\left(0.1 \mathrm{~mol} \mathrm{~L}^{-1}\right)\left(0.1 \mathrm{~mol} \mathrm{~L}^{-1}\right)^{2}}
$$

$=6.0 \mathrm{~L}^{2} \mathrm{~mol}^{-2} \mathrm{~min}^{-1}$
From experiment II, weobtain

$$
\begin{aligned}
& k=\frac{7.2 \times 10^{-2} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~min}^{-1}}{\left(0.3 \mathrm{~mol} \mathrm{~L}^{-1}\right)\left(0.2 \mathrm{~mol} \mathrm{~L}^{-1}\right)^{2}} \\
& =6.0 \mathrm{~L}_{2 \mathrm{~mol}-2 \mathrm{~min}-1}
\end{aligned}
$$

From experiment III, we obtain

$$
\begin{aligned}
& k=\frac{2.88 \times 10^{-1} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~min}^{-1}}{\left(0.3 \mathrm{~mol} \mathrm{~L}^{-1}\right)\left(0.4 \mathrm{~mol} \mathrm{~L}^{-1}\right)^{2}} \\
& =6.0 \mathrm{~L}_{2 \mathrm{~mol}-2 \mathrm{~min}-1}
\end{aligned}
$$

From experiment IV, we obtain

$$
\begin{aligned}
& k=\frac{2.40 \times 10^{-2} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~min}^{-1}}{\left(0.4 \mathrm{~mol} \mathrm{~L}^{-1}\right)\left(0.1 \mathrm{~mol} \mathrm{~L}^{-1}\right)^{2}} \\
& =6.0 \mathrm{~L}_{2} \mathrm{~mol}-2 \mathrm{~min} .1
\end{aligned}
$$

Therefore, rate constant, $k=6.0 \mathrm{~L}^{2} \mathrm{~mol}^{-2} \mathrm{~min}^{-1}$

Q12 :
The reaction between $A$ and $B$ is first order with respect to $A$ and zero order with respect to $B$. Fill in the blanks in the following table:

| Experiment | $\mathrm{A} / \mathrm{mol} \mathrm{L}^{-1}$ | $\mathrm{~B} / \mathrm{mol} \mathrm{L}^{-1}$ | Initial rate/mol L-1 $\mathrm{min}^{-1}$ |
| :---: | :---: | :---: | :---: |
| I | 0.1 | 0.1 | $2.0 \times 10^{-2}$ |

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| II | -- | 0.2 | $4.0 \times 10^{-2}$ |  |
| :---: | :---: | :---: | :---: | :---: |
| III | 0.4 | 0.4 | -- |  |
| IV | -- | 0.2 | $2.0 \times 10^{-2}$ |  |

## Answer :

The given reaction is of the first order with respect to $A$ and of zero order with respect to $B$.
Therefore, the rate of the reaction is given by,
Rate $=k[\mathrm{~A}]^{1}[\mathrm{~B}]^{0}$
$\Rightarrow$ Rate $=k[A]$
From experiment I, we obtain
$2.0 \times 10^{-2} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~min}^{-1}=\mathrm{k}\left(0.1 \mathrm{~mol} \mathrm{~L}^{-1}\right) \Rightarrow k=$
$0.2 \mathrm{~min}^{-1}$

From experiment II, we obtain
$4.0 \times 10^{-2} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~min}^{-1}=0.2 \mathrm{~min}^{-1}[\mathrm{~A}]$
$\Rightarrow[A]=0.2 \mathrm{~mol} \mathrm{~L}^{-1}$
From experiment III, we obtain
Rate $=0.2 \mathrm{~min}^{-1} \times 0.4 \mathrm{~mol} \mathrm{~L}^{-1}$
$=0.08 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~min}^{-1}$
From experiment IV, we obtain
$2.0 \times 10^{-2} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~min}^{-1}=0.2 \mathrm{~min}^{-1}[\mathrm{~A}]$
$\Rightarrow[A]=0.1 \mathrm{~mol} \mathrm{~L}^{-1}$

Q13 :

Calculate the half-life of a first order reaction from their rate constants given below: (i)
$200 \mathrm{~s}^{-1}$ (ii) 2 min $^{-1}$ (iii) 4 years ${ }^{-1}$
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Answer:
(i) Half life, $t_{1 / 2}=\frac{0.693}{k}$
$=\frac{0.693}{200 \mathrm{~s}^{-1}}$
$=3.47 \times 10^{-3} \mathrm{~s}$ (approximately)
(ii) Half life, $t_{1 / 2}=\frac{0.693}{k}$
$=\frac{0.693}{2 \min ^{-1}}$
$=0.35 \mathrm{~min}$ (approximately)
(iii) Half life, $t_{1 / 2}=\frac{0.693}{k}$
$=\frac{0.693}{4 \text { years }^{-1}}$
$=0.173$ years (approximately)

Q14 :

The half-life for radioactive decay of ${ }^{14} \mathrm{C}$ is 5730 years. An archaeological artifact containing wood had only $80 \%$ of the ${ }^{14} \mathrm{C}$ found in a living tree. Estimate the age of the sample.

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## Answer :

Here,

$$
k=\frac{0.693}{t_{1 / 2}}
$$

$$
=\frac{0.693}{5730} \text { years }^{-1}
$$

It is known that,

$$
\begin{aligned}
t & =\frac{2.303}{k} \log \frac{[\mathrm{R}]_{0}}{[\mathrm{R}]} \\
& =\frac{2.303}{\frac{0.693}{5730}} \log \frac{100}{80}
\end{aligned}
$$

$=1845$ years (approximately)
Hence, the age of the sample is 1845 years.

Q15 :
The experimental data for decomposition of $\mathrm{N}_{2} \mathrm{O}_{5}$
$\left[2 \mathrm{~N}_{2} \mathrm{O}_{5} \longrightarrow 4 \mathrm{NO}_{2}+\mathrm{O}_{2}\right]$
in gas phase at 318 K are given below:

| $t(\mathrm{~s})$ | 0 | 400 | 800 | 1200 | 1600 | 2000 | 2400 | 2800 | 3200 |
| :---: | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $10^{2} \times\left[\mathrm{N}_{2} \mathrm{O}_{5}\right] \mathrm{mol} \mathrm{L}^{-1}$ | 1.63 | 1.36 | 1.14 | 0.93 | 0.78 | 0.64 | 0.53 | 0.43 | 0.35 |

(i) Plot $\left[\mathrm{N}_{2} \mathrm{O}_{5}\right]$ against $t$.
(ii) Find the half-life period for the reaction.
(iii) Draw a graph between $\log \left[\mathrm{N}_{2} \mathrm{O}_{5}\right]$ and $t$.
(iv) What is the rate law?
(v)
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Answer:

(ii) Time corresponding to the concentration, $\frac{1.630 \times 10^{2}}{2} \mathrm{~mol} \mathrm{~L}^{-1}=81.5 \mathrm{~mol} \mathrm{~L}^{-1}$, is the half life. From the graph, the half life is obtained as 1450 s .
(iii)

| $\mathbf{t}(\mathbf{s})$ | $\mathbf{1 0}^{\mathbf{2} \times\left[\mathbf{N}_{\mathbf{2}} \mathbf{O}_{\mathbf{5}}\right] / \mathrm{mol} \mathrm{L}^{-1}}$ | $\log \left[\mathbf{N}_{\mathbf{2}} \mathbf{O}_{5}\right]$ |
| :---: | :---: | :---: |
| 0 | 1.63 | -1.79 |
| 400 | 1.36 | -1.87 |
| 800 | 1.14 | -1.94 |
| 1200 | 0.93 | -2.03 |
| 1600 | 0.78 | -2.11 |
| 2000 | 0.64 | -2.19 |
| 2400 | 0.53 | -2.28 |
| 2800 | 0.43 |  |

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| 3200 | 0.35 | -2.46 |
| :--- | :--- | :--- |


$\log \left[\mathrm{N}_{2} \mathrm{O}_{5}\right]$
(iv) The given reaction is of the first order as the plot, the reaction is $\mathrm{v} / \mathrm{s} t$, is a straight line. Therefore, the rate law of
Rate $=k\left[\mathrm{~N}_{2} \mathrm{O}_{5}\right]$
(v) From the plot, $\log \left[\mathrm{N}_{2} \mathrm{O}_{5}\right]_{\mathrm{v} / \mathrm{s} t}$, we obtain

Slope $=\frac{-2.46-(-1.79)}{3200-0}$

$$
=\frac{-0.67}{3200}
$$

Again, slope of the line of the plot $\log \left[\mathrm{N}_{2} \mathrm{O}_{5}\right]_{\mathrm{v} / \mathrm{s} t}$ is given by
$-\frac{k}{2.303}$.
Therefore, we obtain,
$-\frac{k}{2.303}=-\frac{0.67}{3200}$

Q16 :

The rate constant for a first order reaction is $60 \mathrm{~s}^{-1}$. How much time will it take to reduce the initial concentration of the reactant to its $1 / 16^{\text {th }}$ value?

## Answer :

It is known that,

$$
\begin{aligned}
t & =\frac{2.303}{k} \log \frac{[\mathrm{R}]_{0}}{[\mathrm{R}]} \\
& =\frac{2.303}{60 \mathrm{~s}^{-1}} \log \frac{1}{1 / 16} \\
& =\frac{2.303}{60 \mathrm{~s}^{-1}} \log 16 \\
& =4.6 \times 10^{-2} \mathrm{~s} \text { (approximately) }
\end{aligned}
$$

Hence, the required time is $4.6 \times 10^{-2} \mathrm{~s}$.

Q17 :

During nuclear explosion, one of the products is ${ }^{90} \mathrm{Sr}$ with half-life of 28.1 years. If $1 \mathrm{ÃŽÂA1/4g} \mathrm{of}{ }^{90} \mathrm{Sr}$ was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 10 years and 60 years if it is not lost metabolically.
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## Answer :

Here,

$$
k=\frac{0.693}{t_{1 / 2}}=\frac{0.693}{28.1} \mathrm{y}^{-1}
$$

It is known that,

$$
\begin{aligned}
& t=\frac{2.303}{k} \log \frac{[\mathrm{R}]_{0}}{[\mathrm{R}]} \\
& \Rightarrow 10=\frac{2.303}{\frac{0.693}{28.1}} \log \frac{1}{[\mathrm{R}]} \\
& \Rightarrow 10=\frac{2.303}{\frac{0.693}{28.1}}(-\log [\mathrm{R}])
\end{aligned} \begin{array}{r}
\Rightarrow \log [\mathrm{R}]=-\frac{10 \times 0.693}{2.303 \times 28.1} \\
\Rightarrow[\mathrm{R}]=\operatorname{antilog}(-0.1071) \\
\quad=\operatorname{antilog}(\overline{1} .8929) \\
\quad=0.7814 \mu \mathrm{~g}
\end{array}
$$

Therefore, 0.7814 ÃŽÂA1/4g of ${ }^{90} \mathrm{Sr}$ will remain after 10 years.
Again,

$$
\begin{aligned}
& t=\frac{2.303}{k} \log \frac{[\mathrm{R}]_{0}}{[\mathrm{R}]} \\
& \Rightarrow 60=\frac{2.303}{\frac{0.693}{28.1}} \log \frac{1}{[\mathrm{R}]}
\end{aligned}
$$

$$
\Rightarrow \log [R]=-\frac{60 \times 0.693}{2.303 \times 28.1}
$$

$$
\Rightarrow[\mathrm{R}]=\operatorname{antilog}(-0.6425)
$$

$$
=\operatorname{antilog}(\overline{1} .3575)
$$

$$
=0.2278 \mu \mathrm{~g}
$$

Therefore, 0.2278 ÃŽÂ $1 / 4 \mathrm{~g}$ of ${ }^{90} \mathrm{Sr}$ will remain after 60 years.

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For a first order reaction, show that time required for $99 \%$ completion is twice the time required for the completion of $90 \%$ of reaction.

## Answer:

For a first order reaction, the time required for $99 \%$ completionis

$$
\begin{aligned}
t_{1} & =\frac{2.303}{k} \log \frac{100}{100-99} \\
& =\frac{2.303}{k} \log 100 \\
& =2 \times \frac{2.303}{k} \\
t_{2} & =\frac{2.303}{k} \log \frac{100}{100-90} \\
& =\frac{2.303}{k} \log 10 \\
& =\frac{2.303}{k}
\end{aligned}
$$

For a first order reaction, the time required for $90 \%$ completion i Therefore, $t_{1}=2 t_{2}$
Hence, the time required for $99 \%$ completion of a first order reaction is twice the time required for the completion of $90 \%$ of the reaction.

Q19 :

A first order reaction takes 40 min for $\mathbf{3 0 \%}$ decomposition. Calculate $\boldsymbol{t}_{1 / 2}$.

## Answer:

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For a first order reaction,

$$
\begin{aligned}
t & =\frac{2.303}{k} \log \frac{[\mathrm{R}]_{0}}{[\mathrm{R}]} \\
k & =\frac{2.303}{40 \mathrm{~min}} \log \frac{100}{100-30} \\
& =\frac{2.303}{40 \mathrm{~min}} \log \frac{10}{7} \\
& =8.918 \times 10^{-3} \mathrm{~min}^{-1}
\end{aligned}
$$

Therefore, $t_{1 / 2}$ of the decomposition reaction is

$$
\begin{aligned}
t_{1 / 2} & =\frac{0.693}{k} \\
& =\frac{0.693}{8.918 \times 10^{-3}} \mathrm{~min} \\
= & 77.7 \text { min (approximately) }
\end{aligned}
$$

Q20 :
For the decomposition of azoisopropane to hexane and nitrogen at 543 K , the following data are obtained.

| $t(\mathrm{sec})$ | $\mathrm{P}(\mathrm{mm}$ of Hg$)$ |  |
| :---: | :---: | :---: |
| 0 | 35.0 |  |
| 360 | 54.0 |  |
| 720 | 63.0 |  |

Calculate the rate constant.

## Answer :

The decomposition of azoisopropane to hexane and nitrogen at 543 K is represented by the following equation.

$$
\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CHN}=\mathrm{NCH}\left(\mathrm{CH}_{3}\right)_{2(\mathrm{~g})} \longrightarrow \mathrm{N}_{2(\mathrm{~g})}+\mathrm{C}_{6} \mathrm{H}_{14(\mathrm{~g})}
$$

At $t=0$
At $t=t$
$\mathrm{P}_{0}$
0
0
$\mathrm{P}_{0}-p$
p $p$

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After time, $t$, total pressure, $\mathrm{P}_{t}=\left(\mathrm{P}_{0}-p\right)+p+p$
$\Rightarrow \mathrm{P}_{t}=\mathrm{P}_{0}+p$
$\Rightarrow p=\mathrm{P}_{\mathrm{t}}-\mathrm{P}_{0}$
Therefore, $\mathrm{P}_{\mathrm{o}}-p=\mathrm{P}_{\mathrm{o}}-\left(\mathrm{P}_{\mathrm{t}}-\mathrm{P}_{\mathrm{o}}\right)$
$=2 \mathrm{P}_{0}-\mathrm{P}_{t}$
For a first order reaction,
$k=\frac{2.303}{t} \log \frac{\mathrm{P}_{0}}{\mathrm{P}_{0}-p}$
$=\frac{2.303}{t} \log \frac{\mathrm{P}_{0}}{2 \mathrm{P}_{0}-\mathrm{P}_{t}}$
When $t=360 \mathrm{~s}, \quad k=\frac{2.303}{360 \mathrm{~s}} \log \frac{35.0}{2 \times 35.0-54.0}$
$=2.175 \times 10^{-3} \mathrm{~s}^{-1}$
When $t=720 \mathrm{~s}, \quad k=\frac{2.303}{720 \mathrm{~s}} \log \frac{35.0}{2 \times 35.0-63.0}$
$=2.235 \times 10^{-3} \mathrm{~s}^{-1}$
Hence, the average value of rate constant is

$$
k=\frac{\left(2.175 \times 10^{-3}\right)+\left(2.235 \times 10^{-3}\right)}{2} \mathrm{~s}^{-1}
$$

$=2.21 \times 10_{-3} \mathrm{~S}-1$
Note: There is a slight variation in this answer and the one given in the NCERT textbook.

Q21 :

Answer :

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The following data were obtained during the first order thermal decomposition of $\mathrm{SO}_{2} \mathrm{Cl}_{2}$ at a constant volume.
$\mathrm{SO}_{2} \mathrm{Cl}_{2}(\mathrm{~g}) \longrightarrow \mathrm{SO}_{2}(\mathrm{~g})+\mathrm{Cl}_{2}(\mathrm{~g})$

| Experiment | Time/s ${ }^{-1}$ | Total pressure/atm |  |
| :---: | :---: | :---: | :---: |
| 1 | 0 | 0.5 |  |
| 2 | 100 | 0.6 |  |

Calculate the rate of the reaction when total pressure is 0.65 atm.

The thermal decomposition of $\mathrm{SO}_{2} \mathrm{Cl}_{2}$ at a constant volume is represented by the following equation.

$$
\mathrm{SO}_{2} \mathrm{Cl}_{2(\mathrm{~g})} \longrightarrow \mathrm{SO}_{2(\mathrm{~g})}+\mathrm{Cl}_{2(\mathrm{~g})}
$$

$\begin{array}{llll}\text { At } t=0 & \mathrm{P}_{0} & 0 & 0 \\ \text { At } t=t & \mathrm{P}_{0}-\mathrm{p} & \mathrm{p} & \mathrm{p}\end{array}$
After time, $t$, total pressure, $\mathrm{P}_{t}=\left(\mathrm{P}_{0}-p\right)+p+p$
$\Rightarrow \mathrm{P}_{t}=\mathrm{P}_{0}+p$
$\Rightarrow p=\mathrm{P}_{\mathrm{t}}-\mathrm{P}_{0}$
Therefore, $\mathrm{P}_{\mathrm{o}}-p=\mathrm{P}_{\mathrm{o}}-\left(\mathrm{P}_{\mathrm{t}}-\mathrm{P}_{\mathrm{o}}\right)$
$=2 \mathrm{P}_{0}-\mathrm{P}_{t}$
For a first order reaction,
$k=\frac{2.303}{t} \log \frac{\mathrm{P}_{0}}{\mathrm{P}_{0}-p}$
$=\frac{2.303}{t} \log \frac{\mathrm{P}_{0}}{2 \mathrm{P}_{0}-\mathrm{P}_{t}}$
When $t=100 \mathrm{~s}, \quad k=\frac{2.303}{100 \mathrm{~s}} \log \frac{0.5}{2 \times 0.5-0.6}$
$=2.231 \times 10^{-3} \mathrm{~s}^{-1}$
When $\mathrm{P}_{\mathrm{f}}=0.65 \mathrm{~atm}$,
$\mathrm{P}_{0}+p=0.65 \Rightarrow p=$
$0.65-P_{0}$
$=0.65-0.5$
$=0.15 \mathrm{~atm}$

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Therefore, when the total pressure is 0.65 atm , pressure of $\mathrm{SOCl}_{2}$ is
$p_{\mathrm{SOCl}_{2}}=\mathrm{P}_{0}-\mathrm{p}$
$=0.5-0.15$
$=0.35 \mathrm{~atm}$
Therefore, the rate of equation, when total pressure is 0.65 atm , is given by,
Rate $=k\left(p_{\mathrm{SOCl}_{2}}\right)$
$=\left(2.23 \times 10^{-3} \mathrm{~s}^{-1}\right)(0.35 \mathrm{~atm})=$
$7.8 \times 10^{-4} \mathrm{~atm} \mathrm{~s}^{-1}$

Q22 :
The rate constant for the decomposition of $\mathrm{N}_{2} \mathrm{O}_{5}$ at various temperatures is given below:

| $T /{ }^{\circ} \mathrm{C}$ | 0 | 20 | 40 | 60 | 80 |  |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $10^{5} \times \mathrm{k} / \mathrm{s}^{-1}$ | 0.0787 | 1.70 | 25.7 | 178 | 2140 |  |

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Draw a graph between $\ln k$ and $1 / T$ and calculate the values of $A$ and $E_{\mathrm{a}}$.
Predict the rate constant at $30{ }^{\circ}$ and $50 \cong$.

## Answer :

From the given data, we obtain


According to Arrhenius equation,

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Slope $=-\frac{E_{a}}{\mathrm{R}}$
$\Rightarrow E_{a}=-$ Slope $\times \mathrm{R}$
$=-(-12.301 \mathrm{~K}) \times\left(8.314 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}\right)$
$=102.27 \mathrm{~kJ} \mathrm{~mol}^{-1}$
Again,
$\ln k=\ln A-\frac{E_{a}}{\mathrm{R} T}$
$\ln A=\ln k+\frac{E_{a}}{\mathrm{R} T}$
When $T=273 \mathrm{~K}$,
$\ln k=-7.147$
Then, $\ln A=-7.147+\frac{102.27 \times 10^{3}}{8.314 \times 273}$

$$
=37.911
$$

Therefore, $A=2.91 \times 10^{6}$
When $T=30+273 \mathrm{~K}=303 \mathrm{~K}$,
$\frac{1}{T}=0.0033 \mathrm{~K}=3.3 \times 10^{-3} \mathrm{~K}$
Then, ${ }^{\text {at }} \frac{1}{T}=3.3 \times 10^{-3} \mathrm{~K}$,
$\ln k=-2.8$
Therefore, $k=6.08 \times 10^{-2} \mathrm{~s}^{-1}$
Again, when $T=50+273 \mathrm{~K}=323 \mathrm{~K}$,

Q23 :
The rate constant for the decomposition of hydrocarbons is $2.418 \times 10^{-5} \mathrm{~s}^{-1}$ at 546 K . If the energy of activation is $179.9 \mathbf{k J} / \mathrm{mol}$, what will be the value of pre-exponential factor.
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Answer :
$k=2.418 \times 10-5 \mathrm{~S}-1$
$T=546 \mathrm{~K}$
$E_{\mathrm{a}}=179.9 \mathrm{~kJ} \mathrm{~mol}^{-1}=179.9 \times 10^{3} \mathrm{~J} \mathrm{~mol}^{-1}$
According to the Arrhenius equation,

$$
\begin{aligned}
& k=\mathrm{Ae}^{-E_{a} / \mathrm{R} T} \\
& \begin{aligned}
& \Rightarrow \ln k=\ln \mathrm{A}-\frac{E_{a}}{\mathrm{R} T} \\
& \Rightarrow \log k=\log \mathrm{A}-\frac{E_{a}}{2.303 \mathrm{R} T} \\
& \Rightarrow \log \mathrm{~A}=\log k+\frac{E_{a}}{2.303 \mathrm{R} T} \\
& \quad=\log \left(2.418 \times 10^{-5} \mathrm{~s}^{-1}\right)+\frac{179.9 \times 10^{3} \mathrm{~J} \mathrm{~mol}^{-1}}{2.303 \times 8.314 \mathrm{Jk}^{-1} \mathrm{~mol}^{-1} \times 546 \mathrm{~K}}
\end{aligned}
\end{aligned}
$$

$=(0.3835-5)+17.2082$
$=12.5917$
Therefore, $\mathrm{A}=$ antilog (12.5917)
$=3.9 \times 10^{12} \mathrm{~S}^{-1}$ (approximately)

Q24 :

Consider a certain reaction $\mathrm{A} \rightarrow$ Products with $k=2.0 \times 10^{-2} \mathrm{~s}^{-1}$. Calculate the concentration of $A$ remaining after 100 s if the initial concentration of $A$ is $1.0 \mathrm{~mol} \mathrm{~L}^{-1}$.

## Answer:

$k=2.0 \times 10-2 \mathrm{~S}-1$
$T=100 \mathrm{~s}$
$[\mathrm{A}]_{0}=1.0 \mathrm{moL}^{-1}$
Sincethe unit of kis $^{-1}$, the given reaction is a first order reaction.

Therefore,

$$
k=\frac{2.303}{t} \log \frac{[\mathrm{~A}]_{0}}{[\mathrm{~A}]}
$$

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$\Rightarrow 2.0 \times 10^{-2} \mathrm{~s}^{-1}=\frac{2.303}{100 \mathrm{~s}} \log \frac{1.0}{[\mathrm{~A}]}$
$\Rightarrow 2.0 \times 10^{-2} \mathrm{~s}^{-1}=\frac{2.303}{100 \mathrm{~s}}(-\log [\mathrm{A}])$
$\Rightarrow-\log [\mathrm{A}]=\frac{2.0 \times 10^{-2} \times 100}{2.303}$
$\Rightarrow[\mathrm{A}]=\operatorname{anti} \log \left(-\frac{2.0 \times 10^{-2} \times 100}{2.303}\right)$
$=0.135 \mathrm{~mol} \mathrm{~L}^{-1}$ (approximately)
Hence, the remaining concentration of $A$ is $0.135 \mathrm{~mol} \mathrm{~L}^{-1}$.

Q25 :

Sucrose decomposes in acid solution into glucose and fructose according to the first order rate law, with $t_{1 / 2}=$ 3.00 hours. What fraction of sample of sucrose remains after 8 hours?

## Answer :

For a first order reaction,
$k=\frac{2.303}{t} \log \frac{[\mathrm{R}]_{0}}{[\mathrm{R}]}$
It is given that, $t_{1 / 2}=3.00$ hours
Therefore, $k=\frac{0.693}{t_{1 / 2}}$
$=\frac{0.693}{3} \mathrm{~h}^{-1}$
$=0.231 \mathrm{~h}^{-1}$
Then, $0.231 \mathrm{~h}^{-1}=\frac{2.303}{8 \mathrm{~h}} \log \frac{[\mathrm{R}]_{0}}{[\mathrm{R}]}$

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$\Rightarrow \log \frac{[\mathrm{R}]_{0}}{[\mathrm{R}]}=\frac{0.231 \mathrm{~h}^{-1} \times 8 \mathrm{~h}}{2.303}$
$\Rightarrow \frac{[\mathrm{R}]_{0}}{[\mathrm{R}]}=\operatorname{antilog}(0.8024)$
$\Rightarrow \frac{[R]_{0}}{[R]}=6.3445$
$\Rightarrow \frac{[\mathrm{R}]}{[\mathrm{R}]_{0}}=0.1576$ (approx)
$=0.158$
Hence, the fraction of sample of sucrose that remains after 8 hours is 0.158 .

Q26 :

The decomposition of hydrocarbon follows the equation
$k=\left(4.5 \times 10_{11} \mathrm{~S}_{-1}\right) \mathrm{e}_{-28000} \mathrm{k} / \tau$ Calculate
$E_{\text {a }}$.

## Answer :

The given equation is
$k=\left(4.5 \times 10_{11} \mathrm{~S}-1\right) \mathrm{e}-28000 \mathrm{kT}(\mathrm{i})$
Arrhenius equation is given by,

$$
\begin{equation*}
k=\mathrm{Ae}^{-E_{\alpha} / \mathrm{R} T} \tag{ii}
\end{equation*}
$$

From equation (i) and (ii), we obtain

$$
\begin{aligned}
& \frac{E_{a}}{\mathrm{R} T}=\frac{28000 \mathrm{~K}}{T} \\
& \Rightarrow E_{a}=\mathrm{R} \times 28000 \mathrm{~K} \\
& =8.314 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1} \times 28000 \mathrm{~K} \\
& =232792 \mathrm{~J} \mathrm{~mol}^{-1}= \\
& 232.792 \mathrm{~kJ} \mathrm{~mol}^{-1}
\end{aligned}
$$

Q27 :

The rate constant for the first order decomposition of $\mathrm{H}_{2} \mathrm{O}_{2}$ is given by the following equation:
$\log k=14.34-1.25 \times 10^{4} \mathrm{~K} / T$
Calculate $E_{\mathrm{a}}$ for this reaction and at what temperature will its half-period be 256 minutes?

## Answer :

Arrhenius equation is given by,

$$
\begin{align*}
& k=\mathrm{Ae}^{-E_{a} / \mathrm{R} T} \\
& \Rightarrow \ln k=\ln \mathrm{A}-\frac{E_{a}}{\mathrm{R} T} \\
& \Rightarrow \ln k=\log \mathrm{A}-\frac{E_{a}}{\mathrm{R} T} \\
& \Rightarrow \log k=\log \mathrm{A}-\frac{E_{a}}{2.303 \mathrm{R} T} \tag{i}
\end{align*}
$$

The given equation is

$$
\begin{equation*}
\log k=14.34-1.25 \times 10^{4} \mathrm{~K} / T \tag{ii}
\end{equation*}
$$

From equation (i) and (ii), we obtain

$$
\begin{aligned}
& \frac{E_{a}}{2.303 \mathrm{RT}}=\frac{1.25 \times 10^{4} \mathrm{~K}}{T} \\
& \Rightarrow E_{a}=1.25 \times 10^{4} \mathrm{~K} \times 2.303 \times \mathrm{R} \\
& =1.25 \times 10^{4} \mathrm{~K} \times 2.303 \times 8.314 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1} \\
& =239339.3 \mathrm{~J} \mathrm{~mol}^{-1} \text { (approximately) } \\
& =239.34 \mathrm{~kJ} \mathrm{~mol}^{-1}
\end{aligned}
$$

Also, when $t_{1 / 2}=256$ minutes,

$$
\begin{aligned}
k & =\frac{0.693}{t_{1 / 2}} \\
& =\frac{0.693}{256}
\end{aligned}
$$

$$
=2.707 \times 10^{-3} \mathrm{~min}^{-1}
$$

$$
=4.51 \times 10_{-5 S_{-1}}
$$

It is also given that, $\log k=14.34-1.25 \times 10^{4} \mathrm{~K} / T$
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$$
\begin{aligned}
& \Rightarrow \log \left(4.51 \times 10^{-5}\right)=14.34-\frac{1.25 \times 10^{4} \mathrm{~K}}{T} \\
& \Rightarrow \log (0.654-05)=14.34-\frac{1.25 \times 10^{4} \mathrm{~K}}{T} \\
& \Rightarrow \frac{1.25 \times 10^{4} \mathrm{~K}}{T}=18.686 \\
& \Rightarrow T=\frac{1.25 \times 10^{4} \mathrm{~K}}{18.686}
\end{aligned}
$$

$=668.95 \mathrm{~K}$
$=669 \mathrm{~K}$ (approximately)

Q28 :

The decomposition of $A$ into product has value of $k$ as $4.5 \times 10^{3} \mathrm{~s}^{-1}$ at $10^{\circ} \mathrm{C}$ and energy of activation 60 kJ mol ${ }^{1}$. At what temperature would $k$ be $1.5 \times 10^{4} \mathrm{~s}^{-1}$ ?

Answer:
From Arrhenius equation, we obtain
$\log \frac{k_{2}}{k_{1}}=\frac{E_{a}}{2.303 \mathrm{R}}\left(\frac{T_{2}-T_{1}}{T_{1} T_{2}}\right)$
Also, $k_{1}=4.5 \times 10^{3} \mathrm{~s}^{-1}$
$T_{1}=273+10=283 \mathrm{~K}$
$k_{2}=1.5 \times 10^{4} \mathrm{~s}^{-1}$
$E_{a}=60 \mathrm{~kJ} \mathrm{~mol}^{-1}=6.0 \times 10^{4} \mathrm{~J} \mathrm{~mol}^{-1}$
Then,

$$
\begin{aligned}
& \log \frac{1.5 \times 10^{4}}{4.5 \times 10^{3}}=\frac{6.0 \times 10^{4} \mathrm{~J} \mathrm{~mol}^{-1}}{2.303 \times 8.314 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}}\left(\frac{T_{2}-283}{283 T_{2}}\right) \\
& \Rightarrow 0.5229=3133.627\left(\frac{T_{2}-283}{283 T_{2}}\right) \\
& \Rightarrow \frac{0.5229 \times 283 T_{2}}{3133.627}=T_{2}-283 \\
& \Rightarrow 0.0472 T_{2}=T_{2}-283 \\
& \Rightarrow 0.9528 T_{2}=283 \\
& \Rightarrow T_{2}=297.019 \mathrm{~K} \text { (approximately) }
\end{aligned}
$$

$=297 \mathrm{~K}$
$=24^{\circ} \mathrm{C}$
Hence, $k$ would be $1.5 \times 10^{4} \mathrm{~s}^{-1}$ at $24^{\circ} \mathrm{C}$.
Note: There is a slight variation in this answer and the one given in the NCERT textbook.

Q29 :

The time required for $10 \%$ completion of a first order reaction at 298 K is equal to that required for its $25 \%$ completion at 308 K . If the value of $\boldsymbol{A}$ is $\mathbf{4 x}$ $10^{10} \mathbf{s}^{-1}$. Calculate $k$ at 318 K and $E_{a}$.

## Answer :

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For a first order reaction,
$t=\frac{2.303}{k} \log \frac{a}{a-x}$
At $298 \mathrm{~K}, \quad t=\frac{2.303}{k} \log \frac{100}{90}$
$=\frac{0.1054}{k}$
At $308 \mathrm{~K}, \quad t^{\prime}=\frac{2.303}{k^{\prime}} \log \frac{100}{75}$
$=\frac{2.2877}{k^{\prime}}$
According to the question,
$t=t^{\prime}$
$\Rightarrow \frac{0.1054}{k}=\frac{0.2877}{k^{\prime}}$
$\Rightarrow \frac{k^{\prime}}{k}=2.7296$
From Arrhenius equation, we obtain

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$\log \frac{k^{\prime}}{k}=\frac{E_{a}}{2.303 \mathrm{R}}\left(\frac{T^{\prime}-T}{T T^{\prime}}\right)$
$\log (2.7296)=\frac{E_{a}}{2.303 \times 8.314}\left(\frac{308-298}{298 \times 308}\right)$
$E_{a}=\frac{2.303 \times 8.314 \times 298 \times 308 \times \log (2.7296)}{308-298}$
$=76640.096 \mathrm{~J} \mathrm{~mol}^{-1}$
$=76.64 \mathrm{~kJ} \mathrm{~mol}^{-1}$
To calculate $k$ at 318 K ,
It is given that, $A=4 \times 10^{10} \mathrm{~s}^{-1}, T=318 \mathrm{~K}$
Again, from Arrhenius equation, we obtain

$$
\begin{aligned}
\log k & =\log A-\frac{E_{a}}{2.303 \mathrm{R} T} \\
& =\log \left(4 \times 10^{10}\right)-\frac{76.64 \times 10^{3}}{2.303 \times 8.314 \times 318} \\
& =(0.6021+10)-12.5876 \\
& =-1.9855
\end{aligned}
$$

Therefore, $k=\operatorname{Antilog}(-1.9855)$

$$
=1.034 \times 10^{-2} \mathrm{~s}^{-1}
$$

Q30 :
The rate of a reaction quadruples when the temperature changes from 293 K to 313 K . Calculate the energy of activation of the reaction assuming that it does not change with temperature.

## Answer :

From Arrhenius equation, we obtain
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$\log \frac{k_{2}}{k_{1}}=\frac{E_{a}}{2.303 \mathrm{R}}\left(\frac{T_{2}-T_{1}}{T_{1} T_{2}}\right)$
It is given that, $k_{2}=4 k_{1}$
$T_{1}=293 \mathrm{~K}$
$T_{2}=313 \mathrm{~K}$
Therefore, $\log \frac{4 k_{1}}{k_{2}}=\frac{E_{a}}{2.303 \times 8.314}\left(\frac{313-293}{293 \times 313}\right)$
$\Rightarrow 0.6021=\frac{20 \times E_{a}}{2.303 \times 8.314 \times 293 \times 313}$
$\Rightarrow E_{o}=\frac{0.6021 \times 2.303 \times 8.314 \times 293 \times 313}{20}$
$=52863.33 \mathrm{~J} \mathrm{~mol}^{-1}$
$=52.86 \mathrm{~kJ} \mathrm{~mol}^{-1}$
Hence, the required energy of activation is $52.86 \mathrm{kJmol}^{-1}$.

