## Consequetive or Sequential Reaction

A Typical Example: In many cases, the product formed in one of the elementary reactions acts as the reactant for some other elementary reaction. One of the examples of consecutive reactions involves the following steps.

$$
\mathrm{A} \xrightarrow{\mathrm{k}_{1}} \mathrm{~B} \xrightarrow{\mathrm{k}_{1}^{\prime}} \mathrm{C}
$$

Let the initial concentration of A be $[\mathrm{A}]_{0}$ and let after time t , the concentrations of $\mathrm{A}, \mathrm{B}$ and C be [A], [B] and [C], respectively. It is obvious that

$$
\begin{equation*}
[\mathrm{A}]_{0}=[\mathrm{A}]+[\mathrm{B}]+[\mathrm{C}] \tag{1}
\end{equation*}
$$

Differential Rate Law : The differential rate expressions are

$$
\begin{align*}
& -\frac{\mathrm{d}[\mathrm{~A}]}{\mathrm{dt}}=\mathrm{k}_{1}[\mathrm{~A}]  \tag{2}\\
& \frac{\mathrm{d}[\mathrm{~B}]}{\mathrm{dt}}=\mathrm{k}_{1}[\mathrm{~A}]-\mathrm{k}_{1}^{\prime}[\mathrm{B}]  \tag{3}\\
& \frac{\mathrm{d}[\mathrm{C}]}{\mathrm{dt}}=\mathrm{k}_{1}^{\prime}[\mathrm{B}] \tag{4}
\end{align*}
$$

On integrating equation (2), we get

$$
\begin{equation*}
[\mathrm{A}]=[\mathrm{A}]_{0} \mathrm{e}^{-\mathrm{k}, \mathrm{t}} \tag{5}
\end{equation*}
$$

Substituting [A] from equation (5) into equation (3), we get

$$
\begin{aligned}
& \frac{\mathrm{d}[\mathrm{~B}]}{\mathrm{dt}}=\mathrm{k}_{1}[\mathrm{~A}]_{0} \mathrm{e}^{-\mathrm{k}_{1} \mathrm{t}}-\mathrm{k}_{1}^{\prime}[\mathrm{B}] \\
& \frac{\mathrm{d}[\mathrm{~B}]}{\mathrm{dt}}+\mathrm{k}_{1}^{\prime}[\mathrm{B}]=\mathrm{k}_{1}[\mathrm{~A}]_{0} \mathrm{e}^{-\mathrm{k}_{1} t}
\end{aligned}
$$

Integrated Rate Law : Multiplying the above expression throughout by $\exp \left(\mathrm{k}^{\prime}{ }_{1} \mathrm{t}\right)$, we get

$$
\frac{\mathrm{d}[\mathrm{~B}]}{\mathrm{dt}}+\mathrm{k}_{1}^{\prime}[\mathrm{B}] \mathrm{e}^{\mathrm{k}_{1}^{\prime} \mathrm{t}}=\mathrm{k}_{1}[\mathrm{~A}]_{0} \mathrm{e}^{-\left(\mathrm{k}_{1}-\mathrm{k}_{1}^{\prime}\right) \mathrm{t}}
$$

The left side of the above expression is equal to $\mathrm{d}\left([\mathrm{B}] \mathrm{e}^{\mathrm{k}_{1}^{\prime t}}\right) / \mathrm{dt}$. Hence, the above expression can written as, $\mathrm{d}\left\{[\mathrm{B}] \mathrm{e}^{\mathrm{k}_{1} \mathrm{t}}\right\}=\mathrm{k}_{1}[\mathrm{~A}]_{0} \mathrm{e}^{-\left(\mathrm{k}_{1}-k_{1}^{\prime}\right) \mathrm{t}} \mathrm{dt}$
Integrating the above expression with $[\mathrm{B}]=0$ at $\mathrm{t}=0$, we get

$$
\begin{align*}
& {[B] \mathrm{e}^{\mathrm{k}^{\prime} \mathrm{t}}=\mathrm{k}_{1}[\mathrm{~A}]_{0}\left[\frac{\mathrm{e}^{-\left(\mathrm{k}_{1}-\mathrm{k}_{1}^{\prime}\right) \mathrm{t}}}{-\left(\mathrm{k}_{1}-\mathrm{k}_{1}^{\prime}\right)}+\frac{1}{\mathrm{k}_{1}-\mathrm{k}_{1}^{\prime}}\right]} \\
& {[\mathrm{B}]=\mathrm{k}_{1}[\mathrm{~A}]_{0}\left[\frac{\mathrm{e}^{-k_{1} t}}{-\left(\mathrm{k}_{1}^{\prime}-\mathrm{k}_{1}\right)}+\frac{\mathrm{e}^{-\mathrm{k}_{1}^{\prime} t}}{\mathrm{k}_{1}-\mathrm{k}_{1}^{\prime}}\right]} \\
& {[\mathrm{B}]=\mathrm{k}_{1}[\mathrm{~A}]_{0}\left(\frac{\mathrm{k}_{1}}{\mathrm{k}_{1}^{\prime}-\mathrm{k}_{1}}\right)\left\{\mathrm{e}^{-\mathrm{k}_{1} \mathrm{t}}-\mathrm{e}^{-\mathrm{k}_{1}^{\prime} t}\right\}} \tag{6}
\end{align*}
$$

Substituting equations (5) and (6) in equation (1), we get

$$
[\mathrm{A}]_{0}=[\mathrm{A}]_{0} \mathrm{e}^{-\mathrm{k}_{1} \mathrm{t}}+[\mathrm{A}]_{0}\left(\frac{\mathrm{k}_{1}}{\mathrm{k}_{1}^{\prime}-\mathrm{k}_{1}}\right)\left(\mathrm{e}^{-\mathrm{k}_{1} \mathrm{t}}-\mathrm{e}^{-\mathrm{k}_{1}^{\prime} \mathrm{t}}\right)+[\mathrm{C}]
$$

$[C]=[A]_{0}\left[1-\frac{1}{\mathrm{k}_{1}^{\prime}-\mathrm{k}_{1}}\left(\mathrm{k}_{1}^{\prime} \mathrm{e}^{-\mathrm{k}_{1} \mathrm{t}}-\mathrm{k}_{1} \mathrm{e}^{-\mathrm{k}_{1}^{\prime} \mathrm{t}}\right)\right]$
Figure (1) Illustrates the general appearance of the variations of concentrations of A, B and C


Fig. 1: Typical variations of concentration of A, B and C during the progress of the reaction A? B ? C. The actual variations on the values of $k_{1}$ and $k^{\prime}$.
In general concentration of A decreases exponentially, the concentration of B initially increases upto a maximum and then decreases thereafter, and the concentration of C increases steadily until it reaches its final value $[\mathrm{A}]_{0}$, when all A has changed into C .
Maximum Concentration of B : Equation (6) is

$$
\begin{equation*}
[\mathrm{B}]=[\mathrm{A}]_{0}\left(\frac{\mathrm{k}_{1}}{\mathrm{k}_{1}^{\prime}-\mathrm{k}_{1}}\right)\left\{\mathrm{e}^{-\mathrm{k}_{1} \mathrm{t}}-\mathrm{e}^{-\mathrm{k}_{\mathrm{i}}^{\prime} \mathrm{t}}\right\} \tag{6}
\end{equation*}
$$

At the maximum concentration of $B$, we have

$$
\frac{\mathrm{d}[\mathrm{~B}]}{\mathrm{dt}}=0
$$

Hence, differentiating equation (6) with respect to $t$, we get

$$
\begin{equation*}
\frac{\mathrm{d}[\mathrm{~B}]}{\mathrm{dt}}=[\mathrm{A}]_{0}\left(\frac{\mathrm{k}_{1}}{\mathrm{k}_{1}^{\prime}-\mathrm{k}_{1}}\right)\left\{-\mathrm{k}_{1} \mathrm{e}^{-\mathrm{k}_{1} \mathrm{t}}+\mathrm{k}_{1}^{\prime} \mathrm{e}^{-\mathrm{k}_{1}^{\prime} \mathrm{t}}\right\} \tag{8}
\end{equation*}
$$

Equating equation (8) to zero, we get

$$
-\mathrm{k}_{1} \mathrm{e}^{-\mathrm{k}_{1} \mathrm{t}_{\text {max }}}+\mathrm{k}_{1}^{\prime} \mathrm{e}^{-\mathrm{k}_{1} \mathrm{t}_{\text {max }}}=0
$$

or $\quad \frac{\mathrm{k}_{1}}{\mathrm{k}_{1}^{\prime}}=\mathrm{e}^{\left(\mathrm{k}_{1}-\mathrm{k}_{1}^{\prime}\right) \mathrm{t}_{\text {max }}}$
or $\quad \ln \left(\frac{\mathrm{k}_{1}}{\mathrm{k}_{1}^{\prime}}\right)=\left(\mathrm{k}_{1}-\mathrm{k}_{1}^{\prime}\right) \mathrm{t}_{\text {max }}$
or $\quad \mathrm{t}_{\text {max }}=\frac{1}{\mathrm{k}_{1}-\mathrm{k}_{1}^{\prime}} \ln \left(\frac{\mathrm{k}_{1}}{\mathrm{k}_{1}^{\prime}}\right)$
substituting equation (9) in equation (6), we get

$$
\begin{equation*}
[\mathrm{B}]_{\max }=[\mathrm{A}]_{0}\left(\frac{\mathrm{k}_{1}^{\prime}}{\mathrm{k}_{1}}\right)^{\mathrm{k}_{1}^{\prime} /\left(\mathrm{k}_{1}-\mathrm{k}_{1}^{\prime}\right)} \tag{10}
\end{equation*}
$$

## Catalyst

Berzelius used the term catalyst for the first time for the substances which accelerate the rate of chemical reaction. Now the term catalyst has been used for the foreign substances which influence the rate of a reaction and the phenomenon is known as catalysis. Usually two terms are used for catalysis :
Positive Catalysis : The phenomenon in which presence of catalyst accelerates the rate of reaction.
Negative catalysis : The phenomenon in which presence of catalyst retards the rate of reaction. Such substances are also known as inhibitors or negative catalyst.

## Characteristics Of Catalyst

(i) A catalyst remains unchanged chemically at the end of reaction, however its physical state may change. e.g. $\mathrm{MnO}_{2}$ used as catalyst in granular form for the decomposition of $\mathrm{KClO}_{3}$, is left in powder form at the end of reaction.
(ii) A catalyst never initiate a chemical reaction. It simply influences the rate of reaction. Exception : combination of $\mathrm{H}_{2}$ and $\mathrm{Cl}_{2}$ takes place only when moisture (catalyst) is present.
(iii) A small quantity of catalyst is sufficient to influence the rate of reaction e.g. 1 g atom of Platinum is sufficient to catalyse 108 litre of $\mathrm{H}_{2} \mathrm{O}_{2}$ decomposition.
(iv) A catalyst does not influence the equilibrium constant of reaction. It simply helps in attaining equilibrium earlier. It alters the rate of forward \& backward reactions equally.
(v) A catalyst normally does not alter the nature of products in a reaction. However some exceptions are found to this characteristic.
(a) $\mathrm{HCOOH} \xrightarrow{\mathrm{AlCl}_{3}} \mathrm{H}_{2} \mathrm{O}+\mathrm{CO}$,

(b)

$$
\begin{aligned}
& \mathrm{CO}+3 \mathrm{H}_{2} \xrightarrow{\mathrm{Ni}} \mathrm{CH}_{4}+\mathrm{H}_{2} \mathrm{O} \\
& \mathrm{CO}+\mathrm{H}_{2} \xrightarrow{\mathrm{Cu}} \mathrm{HCHO}
\end{aligned}
$$

$$
\mathrm{CO}+2 \mathrm{H}_{2} \xrightarrow[\mathrm{Cr}_{2} \mathrm{O}_{3}]{\mathrm{ZnO}} \mathrm{CH}_{3} \mathrm{OH}
$$

It may therefore be concluded that in some cases nature of products formed depends upon the presence and nature of catalyst used.
(vi) A catalyst does not make reaction more exothermic
(vii) Catalyst's activity is more or less specific : A catalyst for one reaction is not necessary to catalyse the another reaction.

## Type of catalyst

1. Homogeneous catalysis: The reaction in which catalyst and the reactants have same phase. It includes two types.
(a) Gaseous phase catalysis: When reactants and catalyst are in gaseous phase e.g. chamber process for $\mathrm{H}_{2} \mathrm{SO}_{4}$.

$$
2 \mathrm{SO}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \xrightarrow[\text { catalyst }]{\mathrm{NO}} 2 \mathrm{SO}_{3}(\mathrm{~g})
$$

(b) Solution phase catalysis: The reactions in which catalyst and reactants are in solution phase or liquid phase of miscible nature.

$$
\mathrm{RCOOR}_{(1)}^{\prime}+\mathrm{H}_{2} \mathrm{O}_{(1)} \xrightarrow{\mathrm{H}^{+}} \mathrm{RCOOH}+\mathrm{R}^{\prime} \mathrm{OH}
$$

ester
2. Heterogeneous catalysis : The reactions in which catalyst and reactants form phase $\geq 2$.
(a) Solid-liquid catalysis :
$\left.\begin{array}{l}\text { Reactant : Liquid } \\ \text { Catalyst : Solid }\end{array}\right\}$ Immiscible

$$
2 \mathrm{H}_{2} \mathrm{O}_{2(l)} \xrightarrow[\text { Catalyst }]{\mathrm{Mn}_{2(s)}} 2 \mathrm{H}_{2} \mathrm{O}+\mathrm{O}_{2}
$$

(b) Liquid-Liquid catalysis :: $\left.\quad \begin{array}{l}\text { Reactant : Liquid } \\ \text { Catalyst : Liquid }\end{array}\right\}$ Immiscible

$$
2 \mathrm{H}_{2} \mathrm{O}_{2(l)} \xrightarrow[\text { catalyst }]{\mathrm{Hg}()} 2 \mathrm{H}_{2} \mathrm{O}+\mathrm{O}_{2}
$$

(c) Solid-gas catalysis: $\left.\begin{array}{l}\text { Reactant: gases } \\ \text { Catalyst : solid }\end{array}\right\}$ Immiscible

Two aspects of solid catalyst are more significant, one is activity and the other is selectivity. Activity is the ability of catalyst to accelerate chemical reactions; the degree of acceleration can be as high as $10^{10}$ times in certain reactions. Selectivity is the ability of catalyst to direct reaction to yield particular reaction (excluding others). For example, n-heptane selectivity gives toluene in presence of Pt catalyst. Similarly, $\mathrm{CH}_{3}-\mathrm{CH}=\mathrm{CH}_{2}+\mathrm{O}_{2}$ give $\mathrm{CH}_{2}=\mathrm{CHCHO}$ selectivity over Bismuth molybdate catalyst .

## Arrhenius Theory

In 1889 Arrhenius recognised the temperature dependence of rates or rate constant. He has given an emperical relation which can be written as

$$
\begin{equation*}
\mathrm{k}=\mathrm{Ae}^{-\mathrm{E}_{\mathrm{a}} / \mathrm{RT}} \tag{1}
\end{equation*}
$$

k is the rate constant (of any order other than zero order), A is the pre-exponential factor, $\mathrm{E}_{\mathrm{a}}$ is the activation energy, R is the universal gas constant and T is the absolute temperature. Activation energy $\left(\mathrm{E}_{\mathrm{a}}\right)$ is the minimum energy required by a reactant at a certain temperature to undergo transformation into product. Arrhenius clearly assumed that reactions occur because of collisions between atoms and molecules of the reactant.
He assumed the activation energy to be the least value of energy which the colliding molecules must possess for the collision to yield a product. If we plot graph between activation energy and progress of a reaction (expressed as reaction co-ordinate), we get a graph as shown in figure .


The difference between the energies of the reactant and the transition state $(T S)$ is called $\left(\mathrm{E}_{\mathrm{a}}\right)_{\mathrm{f}}$.

$$
\Delta H=\left(E_{a}\right)_{\mathrm{f}}-\left(\mathrm{E}_{\mathrm{a}}\right)_{\mathrm{b}}
$$

A, the pre-exponential factor or the frequency factor or the Arrhenius constant is the number of effective collisions occurring per unit time. Effective collision is the number of collisions occurring per unit time in which orientation of the colliding molecules is proper. $e^{-E_{a} / R T}$ gives the fraction of the effective collision that have the sufficient activation energy. Therefore the product of $A$ and $e^{-E_{a} / R T}$ gives the number of collisions per unit time that forms the product and is called its number of productive collisions which is the rate constant, k .
For all practical calculations, we shall assume that $\mathrm{E}_{\mathrm{a}}$ and A are temperature independent. Both $A$ and $E_{a}$ are characteristics of the reaction.

## Determination of $A$ and $E_{a}$ <br> First Method :

Taking $\log$ of both sides of equation (1)

$$
\ln \mathrm{k}=\ln \mathrm{A}-\frac{\mathrm{E}_{\mathrm{a}}}{\mathrm{RT}}
$$

Converting (natural $\log$ ) to common $\log , \log \mathrm{k}=\log \mathrm{A}-\frac{\mathrm{E}_{\mathrm{a}}}{2.303 \mathrm{RT}}$
If $\log k$ is plotted against $1 / \mathrm{T}$, a straight line is obtained which is shown as below:
The slope of this line is given by slope $=\frac{-\mathrm{E}_{\mathrm{a}}}{2.303 \mathrm{R}}$
Thus, knowing the slope, the $\mathrm{E}_{\mathrm{a}}$ can be easily calculated. The intercept of the line will give the value of $\log \mathrm{A}$.

## Second Method :

The logarithmic form of Arrhenius equation is rearranged as

$$
\ln \mathrm{k}=-\frac{\mathrm{E}_{\mathrm{a}}}{\mathrm{RT}}+\ln \mathrm{A}
$$

Differentiating with respect to temperature, we get :

$\frac{\mathrm{d} \ln \mathrm{k}}{\mathrm{dT}}=\frac{\mathrm{E}_{\mathrm{a}}}{\mathrm{RT}^{2}}$
Integrating with in the limits of temperature $T_{1}$ and $T_{2}$, we get

$$
\begin{aligned}
& \int_{\mathrm{k}_{1}}^{\mathrm{k}_{2}} \mathrm{~d} \ln \mathrm{k}=\int_{\mathrm{T}_{1}}^{\mathrm{T}_{2}} \frac{\mathrm{E}_{\mathrm{a}}}{\mathrm{RT}^{2}} \mathrm{dT} \\
& \ln \frac{\mathrm{k}_{2}}{\mathrm{k}_{1}}=\frac{\mathrm{E}_{\mathrm{a}}}{\mathrm{R}}\left(\frac{1}{\mathrm{~T}_{1}}-\frac{1}{\mathrm{~T}_{2}}\right)
\end{aligned}
$$

or $\quad \log \frac{\mathrm{k}_{2}}{\mathrm{k}_{1}}=\frac{\mathrm{E}_{\mathrm{a}}}{2.303 \mathrm{R}}\left(\frac{1}{\mathrm{~T}_{1}}-\frac{1}{\mathrm{~T}_{2}}\right)$
Where $k_{1}$ and $k_{2}$ are rate constants at temperatures $\mathrm{T}_{1} \& \mathrm{~T}_{2}$ respectively. Thus, knowing these values $\mathrm{E}_{\mathrm{a}}$ can be calculated. When the value of $\mathrm{E}_{\mathrm{a}}$ is known, the value of A can be calculated by substituting its value in equation $k=A e^{-E_{a} / R T}$. In equation (2), the value of $R$ has to be inserted in the same unit in which $\mathrm{E}_{\mathrm{a}}$ is desired.

Temperature Coefficient : "Temperature coefficient of a chemical reaction is defined as the ratio of rate constants of a reaction at two temperatures differing by $10^{\circ} \mathrm{C}$ ".

$$
\therefore \text { Temperature coefficient }=\frac{\mathrm{k}_{\mathrm{T}+10}}{\mathrm{k}_{\mathrm{T}}} \text { » } 2 \text { to } 3
$$

where $\mathrm{k}_{\mathrm{T}}$ is the rate constant at temperature TK and $\mathrm{k}_{\mathrm{T}+10}$ is the rate constant at temperature $(\mathrm{T}+10) \mathrm{K}$. This ratio generally falls between 2 and 3 which means for most of the chemical reactions, the rate becomes two or three folds for every $10^{\circ} \mathrm{C}$ rise in temperature.

## Example 19 :

The rate of a reaction triple when temperature changes from $20^{\circ} \mathrm{C}$ to $50^{\circ} \mathrm{C}$. Calculate energy of activation for the reaction $\left(R=8.314 \mathbf{~ J K}^{-1} \mathrm{~mol}^{-1}\right)$.

## Solution :

The Arrhenius equation is

$$
\log _{10} \frac{\mathrm{k}_{2}}{\mathrm{k}_{1}}=\frac{\mathrm{E}_{\mathrm{a}}}{\mathrm{R} \times 2.303}\left[\frac{\mathrm{~T}_{2}-\mathrm{T}_{1}}{\mathrm{~T}_{1} \mathrm{~T}_{2}}\right]
$$

Given $\frac{\mathrm{k}_{2}}{\mathrm{k}_{1}}=3 ; \mathrm{R}=8.314 \mathrm{JK}^{-1} \mathrm{~mol}^{-1} ; \mathrm{T}_{1}=20+273=293 \mathrm{~K}$
and

$$
\mathrm{T}_{2}=50+273=323 \mathrm{~K}
$$

Substituting the given vlues in the Arrhenius equation,

$$
\begin{aligned}
\log _{10} 3 & =\frac{\mathrm{E}_{\mathrm{a}}}{8.314 \times 2.303}\left[\frac{323-293}{323 \times 293}\right] \\
\mathrm{E}_{\mathrm{a}} & =\quad \frac{2.303 \times 8.314 \times 323 \times 293 \times 0.477}{30} \\
& =28811.8 \mathrm{~J} \mathrm{~mol}^{-1} \\
& =28.8118 \mathrm{~kJ} \mathrm{~mol}^{-1}
\end{aligned}
$$

## Example 20 :

In Arrhenius equation for a certain reaction, the value of $A$ and $E_{a}$ (activation energy) are $4 \times 10^{13}$ sec $^{-1}$ and $98.6 \mathrm{~kJ} \mathrm{~mol}_{-1}$ respectively. At what temperature, the reaction will have specific rate constant $1.1 \times 10^{-3}$ sec $^{-1}$ ?

## Solution :

According to Arrhenius equation

$$
\mathrm{k}=\mathrm{Ae}^{-\mathrm{E}_{\mathrm{a}} / \mathrm{RT}}
$$

or $\quad \log _{e} k=\log _{e} A-\frac{E_{a}}{R T} \log _{e} e$
$2.303 \log _{10} \mathrm{k}=2.303 \log _{10} \mathrm{~A}-\frac{\mathrm{E}_{\mathrm{a}}}{\mathrm{RT}}$
or $\quad 2.303 \log \left(1.1 \times 10^{-3}\right)=2.303 \log \left(4 \times 10^{13}\right)-\frac{98.6 \times 10^{3}}{8.314 \times \mathrm{T}}$

$$
\mathrm{T}=\frac{98.6 \times 10^{3}}{8.314 \times 2.303 \times 16.56} \mathrm{~K}=311 \mathrm{~K}
$$

## Example 21:

The rate constant is giveny by Arrhenius equation

$$
k=A e^{-E_{a} / R T}
$$

Calculate the ratio of the catalysed and uncatalysed rate constant at $25^{\circ} \mathrm{C}$ if the nergy of activation of a catalysed reaxction is 162 kJ and for the uncatalysed reaction the value is 350 kJ .

## Solution :

Let $\mathrm{k}_{\mathrm{ca}}$ and $\mathrm{k}_{\mathrm{un}}$ be the rate constants for catalysed and uncatalysed reactions.

$$
\begin{equation*}
2.303 \log 10 \mathrm{k}_{\mathrm{ca}}=2.303 \log _{10} \mathrm{~A}-\frac{162 \times 10^{3}}{\mathrm{RT}} \tag{i}
\end{equation*}
$$

and $2.303 \log 10_{u n}=2.303 \log _{10} \mathrm{~A}-\frac{350 \times 10^{3}}{\mathrm{RT}}$
Substracting Eq. (ii) from Eq.(i)

$$
\begin{aligned}
& \log _{10} \frac{\mathrm{k}_{\mathrm{ca}}}{\mathrm{k}_{\mathrm{un}}}=\frac{10^{3}}{2.303 \mathrm{RT}}(350-162) \\
&=\frac{188 \times 10^{3}}{2.303 \times 8.314 \times 298}=32.95 \\
& \frac{\mathrm{k}_{\mathrm{ca}}}{\mathrm{k}_{\mathrm{un}}}=8.88 \times 10^{32}
\end{aligned}
$$

## Example 22 :

At 407 K the rate constant of a chemical reaction is $9.5 \times 10^{-5} \mathrm{~s}^{-1}$ and at 420 K , the rate constant is $1.9 \times 10^{-4} \mathbf{s}^{-1}$. Calculate the frequency factor of the reaction.

## Solution :

The Arrhenius equation is,

$$
\log _{10} \frac{\mathrm{k}_{2}}{\mathrm{k}_{1}}=\frac{\mathrm{E}_{\mathrm{a}}}{2.303 \times \mathrm{R}}\left[\frac{\mathrm{~T}_{2}-\mathrm{T}_{1}}{\mathrm{~T}_{1} \mathrm{~T}_{2}}\right]
$$

Given $\mathrm{k}_{1}=9.5 \times 10^{-5} \mathrm{~s}^{-1} ; \quad \mathrm{k}_{2}=1.9 \times 10^{-3} \mathrm{~s}^{-1}$;
$\mathrm{R}=8.314 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}$;
$\mathrm{T}_{1}=407 \mathrm{~K}$ and $\mathrm{T}_{2}=420 \mathrm{~K}$
Substituting the values in Arrhenius equation.

$$
\begin{aligned}
\log _{10} \frac{1.9 \times 10^{-4}}{9.5 \times 10^{-5}} & =\frac{\mathrm{E}_{\mathrm{a}}}{2.303 \times 8.314}\left[\frac{420-407}{420 \times 407}\right] \\
\mathrm{E}_{\mathrm{a}} & =75782.3 \mathrm{~J} \mathrm{~mol}^{-1}
\end{aligned}
$$

Applying now $\log \mathrm{k}_{1}=\log \mathrm{A}-\frac{\mathrm{E}_{\mathrm{a}}}{2.303 \mathrm{RT}_{1}}$

$$
\log 9.5 \times 10^{-5}=\log \mathrm{A}-\frac{75782.3}{2.303 \times 8.314 \times 407}
$$

or $\quad \log \frac{\mathrm{A}}{9.5 \times 10^{-5}}=\frac{75782.3}{2.303 \times 8.314 \times 407}$

$$
=9.7246
$$

$$
\mathrm{A}=5.04 \times 10^{5} \mathrm{~s}^{-1}
$$

## Example 23 :

The energy of activation for a reaction is $100 \mathrm{~kJ} \mathrm{~mol}^{-1}$. Presence of a catalyst lowers the energy of activation by $\mathbf{7 5 \%}$. What will be effect on rate of reaction at $20^{\circ} \mathrm{C}$, other things being equal?

## Solution :

The arrhenius equation is

$$
\mathrm{k}=\mathrm{Ae}^{-\mathrm{E}_{\mathrm{a}} / \mathrm{RT}}
$$

In absence of catalyst, $\mathrm{k}_{1}=\mathrm{Ae}^{-100 / \mathrm{RT}}$
In presence of catalyst, $\mathrm{k}_{2}=\mathrm{Ae}^{-25 / R T}$
So $\frac{\mathrm{k}_{2}}{\mathrm{k}_{1}}=\mathrm{e}^{75 / \mathrm{RT}} \quad$ or $2.303 \log \frac{\mathrm{k}_{2}}{\mathrm{k}_{1}}=\frac{75}{\mathrm{RT}}$
or $\quad 2.303 \log \frac{\mathrm{k}_{2}}{\mathrm{k}_{1}}=\frac{75}{8.314 \times 10^{-3} \times 293}$
or $\quad \log \frac{\mathrm{k}_{2}}{\mathrm{k}_{1}}=\frac{75}{8.314 \times 10^{-3} \times 293 \times 2.303}$
or $\quad \frac{\mathrm{k}_{2}}{\mathrm{k}_{1}}=2.34 \times 10^{13}$
As the things being equal in presence or absence of a catalyst,

$$
\frac{\mathrm{k}_{2}}{\mathrm{k}_{1}}=\frac{\text { rate in presence of catalyst }}{\text { rate in absence of catalyst }}
$$

i.e.,

$$
\frac{\mathrm{r}_{2}}{\mathrm{r}_{1}}=\frac{\mathrm{k}_{2}}{\mathrm{k}_{1}}=2.34 \times 10^{13}
$$

## Pressure Change Method :

This method is used for gaseous reactions.
As reaction proceeds there is change in pressure.
For a reaction,
Initial pressure at $t=0$


Pressure at time ( t )
$\left(P_{0}-x\right) \quad x \quad x$
(Here x is no. of moles of A which change to produce)
Thus, total pressure $\left(\mathrm{P}_{\mathrm{t}}\right)$ at time $(\mathrm{t})=\mathrm{P}_{0}-\mathrm{x}+\mathrm{x}+\mathrm{x}$
or $\quad P_{t}=P_{0}+x, \quad x=P_{t}-P_{0}$

$$
\mathrm{a}-\mathrm{x}=\mathrm{P}_{0}-\left(\mathrm{P}_{\mathrm{t}}-\mathrm{P}_{0}\right)=2 \mathrm{P}_{0}-\mathrm{P}_{\mathrm{t}}
$$

Thus, $\mathrm{k}=\frac{2.303}{\mathrm{t}} \log \frac{\mathrm{P}_{0}}{\left(2 \mathrm{P}_{0}-\mathrm{P}_{\mathrm{t}}\right)}$

## Example 24 :

The following rate data was obtained for the first order thermal decomposition of $\mathrm{SO}_{2} \mathrm{Cl}_{2(g)}$ at a constant volume.
$\mathrm{SO}_{2} \mathrm{Cl}_{2(\mathrm{~g})} \longrightarrow \mathrm{SO}_{2(\mathrm{~g})}+\mathrm{Cl}_{2(\mathrm{~g})}$
Exp. Time (sec ${ }^{-1}$ Total pressure (atm)

1. $0 \quad 0.5$

2
100
0.6

Calculate the reaction rate when total pressure is 0.65 atmosphere.

## Solution :

Let us say that the pressure of $\mathrm{SO}_{2} \mathrm{Cl}_{2}$ decreases by x atm, then the increase of pressure of $\mathrm{SO}_{2}$ and $\mathrm{Cl}_{2}=\mathrm{x}$ atm each. [Q 1 mole of $\mathrm{SO}_{2} \mathrm{Cl}_{2}$ decomposes to give 1 mole of $\mathrm{SO}_{2}$ and 1 mole of $\left.\mathrm{Cl}_{2}\right]$.

Pressure at $t=0$
Pressure at t ,

Since total pressure

$$
\begin{aligned}
\mathrm{P}_{\mathrm{T}} & =\mathrm{P}_{\mathrm{SO}_{2} \mathrm{Cl}_{2}}+\mathrm{P}_{\mathrm{SO}_{2}}+\mathrm{P}_{\mathrm{Cl}_{2}} \\
& =(0.5-\mathrm{x})+\mathrm{x}+\mathrm{x} \\
\mathrm{P}_{\mathrm{T}} & =0.5+\mathrm{x} \text { or } \mathrm{x}=\mathrm{P}_{\mathrm{T}}-0.5 \\
\mathrm{P}_{\mathrm{SO}_{2} \mathrm{Cl}_{2}} & =0.5-\left(\mathrm{P}_{\mathrm{T}}-0.5\right) \\
& =0.5-\mathrm{P}_{\mathrm{T}}+0.5=1.0-\mathrm{P}_{\mathrm{T}}
\end{aligned}
$$

Since, at $\mathrm{t}=100 \mathrm{sec}, \mathrm{P}_{\mathrm{T}}=0.6 \mathrm{~atm}$

$$
\therefore \quad \mathrm{P}_{\mathrm{So}_{2} \mathrm{Cl}_{2}}=1.0-0.6=0.4 \mathrm{~atm}
$$

(a) Evaluation of k

$$
\begin{aligned}
\mathrm{k} & =\frac{2.303}{\mathrm{t}} \log \frac{\text { Initial pressure }}{\text { Pressure at time } \mathrm{t}} \\
& =\frac{2.303}{100} \log \frac{0.5}{0.4}=\frac{2.303}{100} \log 1.25=\frac{2.303}{100} \times 0.0969=2.23 \times 10^{-3} \mathrm{sec}^{-1}
\end{aligned}
$$

(b) Rate at $\mathrm{P}_{\mathrm{T}}=0.65 \mathrm{~atm}$

$$
\mathrm{P}_{\mathrm{SO}_{2} \mathrm{Cl}_{2}} \text { at total pressure of } 0.65 \mathrm{~atm}=1.0-0.65=0.35 \mathrm{~atm}
$$

$$
\text { Rate }=\mathrm{k}\left[\mathrm{~N}_{2} \mathrm{O}_{5}\right]=2.23 \times 10^{-3} \times 0.35=7.8 \times 10^{-4} \mathrm{~atm} \mathrm{sec}^{-1}
$$

## Example 25 :

For a homogeneous gaseous phase reaction: $2 A \longrightarrow 3 B+C$, the initial pressure of reactant was $P^{\circ}$ while pressure at time ' $t$ ' was $P$. Find the pressure after time $2 t$. Assume I order reaction.

## Solution :

Initial Pressure
Pressure at $\mathrm{t}=\mathrm{t}$
Pressure at $\mathrm{t}=2 \mathrm{t}$
Given

$$
\begin{array}{lcc}
2 \mathrm{~A} \longrightarrow & 3 \mathrm{~B}+ & \mathrm{C} \\
\mathrm{P}^{\circ} & 0 & 0 \\
\mathrm{P}^{\circ}-2 \mathrm{a} & 3 \mathrm{a} & \mathrm{a} \\
\mathrm{P}^{\circ}-2 \mathrm{x} & 3 \mathrm{x} & \mathrm{x} \\
\mathrm{P}^{\circ}-2 \mathrm{a}+3 \mathrm{a}+\mathrm{a}=\mathrm{P}  \tag{1}\\
\mathrm{P}^{\circ}+2 \mathrm{a}=\mathrm{P}
\end{array}
$$

$\therefore \quad \mathrm{P}^{\circ}+2 \mathrm{a}=\mathrm{P}$
Now for I order reaction at time $t$

$$
\begin{equation*}
\mathrm{K}=\frac{2.303}{\mathrm{t}} \log \frac{\mathrm{P}^{0}}{\mathrm{P}^{\mathrm{o}}-2 \mathrm{a}}=\frac{2.303}{\mathrm{t}} \log \frac{\mathrm{P}^{0}}{2 \mathrm{P}^{0}-\mathrm{P}} \tag{2}
\end{equation*}
$$

Let total pressure at $\mathrm{t}=2 \mathrm{t}$ be A , then $\mathrm{P}^{\circ}-2 \mathrm{x}+3 \mathrm{x}+\mathrm{x}=\mathrm{A}$ or $\mathrm{P}^{\circ}+2 \mathrm{x}=\mathrm{A}$

$$
\begin{align*}
& \mathrm{K}=\frac{2.303}{2 \mathrm{t}} \log \frac{\mathrm{P}^{\mathrm{o}}}{\mathrm{P}^{\mathrm{o}}-2 \mathrm{x}}=\frac{2.303}{2 \mathrm{t}} \log \frac{\mathrm{P}^{\mathrm{o}}}{2 \mathrm{P}^{\mathrm{o}}-\mathrm{A}}  \tag{3}\\
& \mathrm{~K}=\frac{2.303}{\mathrm{t}} \log \left[\frac{\mathrm{P}^{\mathrm{o}}}{2 \mathrm{P}^{\circ}-\mathrm{A}}\right]^{1 / 2} \tag{4}
\end{align*}
$$

By equations (2) and (4)

$$
\begin{array}{ll} 
& {\left[\frac{\mathrm{P}^{\circ}}{2 \mathrm{P}^{\circ}-\mathrm{P}}\right]^{2}=\left[\frac{\mathrm{P}^{\circ}}{2 \mathrm{P}^{\circ}-\mathrm{A}}\right]} \\
& {\left[2 \mathrm{P}^{\circ}-\mathrm{A}\right] . \mathrm{P}^{\circ}=\left[2 \mathrm{P}^{\circ}-\mathrm{P}\right]^{2}} \\
\therefore & \mathrm{P}^{\circ} \cdot \mathrm{A}=2\left(\mathrm{P}^{\circ}\right)^{2}-\left(2 \mathrm{P}^{\circ}-\mathrm{P}\right)^{2} \\
\therefore & \mathrm{~A}=2 \mathrm{P}^{\circ}-\frac{\left(2 \mathrm{P}^{\circ}-\mathrm{P}\right)^{2}}{\mathrm{P}^{\circ}} .
\end{array}
$$

## Example 26 :

The decomposition of $\mathrm{Cl}_{2} \mathrm{O}_{7}$ at 400 K in the gas phase to $\mathrm{Cl}_{2}$ and $\mathrm{O}_{2}$ is of I order. After 55 sec at 400 K , the pressure of $\mathrm{Cl}_{2} \mathrm{O}_{7}$ falls from 0.062 to 0.044 atm . Calculate :
(a) The rate constant.
(b) Pressure of $\mathrm{Cl}_{2} \mathrm{O}_{7}$ after 100 sec.

## Solution :

$$
\mathrm{Cl}_{2} \mathrm{O}_{7} \longrightarrow \mathrm{Cl}_{2}+\frac{7}{2} \mathrm{O}_{2}
$$

$$
\begin{array}{lcll}
\text { Mole at } \mathrm{t}=0 & \mathrm{a} & 0 & 0 \\
\text { Mole at } \mathrm{t}=55 \mathrm{sec} . & (\mathrm{a}-\mathrm{x}) & \mathrm{x} & 7 \mathrm{x} / 2
\end{array}
$$

(a) Since Pressure of $\mathrm{Cl}_{2} \mathrm{O}_{7}$ is given and therefore,

$$
\begin{aligned}
& \mathrm{a} \propto 0.062 \\
& \mathrm{a}-\mathrm{x}) \propto 0.044 \\
& \mathrm{Q} \quad \mathrm{~K}=\frac{2.303}{\mathrm{t}} \log _{10} \frac{0.062}{0.044} \\
& \mathrm{~K}=6.23 \times 10^{-3} \mathrm{sec}^{-1} .
\end{aligned}
$$

(b) Let at $\mathrm{t}=100 \sec ,(\mathrm{a}-\mathrm{x}) \propto \mathrm{P}$

$$
\therefore \quad 6.23 \times 10^{-3}=\frac{2.303}{100} \log _{10} \frac{0.062}{\mathrm{P}} \quad=\quad \mathrm{P}=0.033 \mathrm{~atm} .
$$

## Daily Practice Problem 1

1. In the reaction; $\mathrm{A}+2 \mathrm{~B} \longrightarrow 3 \mathrm{C}+\mathrm{D}$ which of the following expressions does not describe changes in the concentration of various species as a function of time:
(A) $\frac{\mathrm{d}[\mathrm{C}]}{\mathrm{dt}}=\frac{-3 \mathrm{~d}[\mathrm{~A}]}{\mathrm{dt}}$
(B) $\frac{3 \mathrm{~d}[\mathrm{D}]}{\mathrm{dt}}=\frac{\mathrm{d}[\mathrm{C}]}{\mathrm{dt}}$
(C) $\frac{3 \mathrm{~d}[\mathrm{~B}]}{\mathrm{dt}}=\frac{-2 \mathrm{~d}[\mathrm{C}]}{\mathrm{dt}}$
(D) $\frac{2 \mathrm{~d}[\mathrm{~B}]}{\mathrm{dt}}=\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{dt}}$
2. Which of the following statement is correct for a reaction $\mathrm{X}+2 \mathrm{Y} \longrightarrow$ prodcuts :
(A) The rate of disappearance of $\mathrm{X}=$ twice the rate of disappearance of Y
(B) The rate of disappearance of $\mathrm{X}=1 / 2$ rate of appearance of products
(C) The rate of appearance of products $=1 / 2$ the rae of disappearance of Y
(D) The rat of appearance of products $=1 / 2$ the rate of disappearance of X
3. For the reaction, $4 \mathrm{~A}+\mathrm{B} \longrightarrow 2 \mathrm{C}+2 \mathrm{D}$, The statement not correct is :
(A) The rate of disppearance of B is one fourth the rate of disappearance of A
(B) The rate of appearance of $C$ is half the rate of disappearance of $B$
(C) The rate of formation of D is half the rate of consumption of A
(D) The rates of formation of C and D are equal
4. For the reaction $2 \mathrm{~A}+\mathrm{B} \longrightarrow \mathrm{C}+\mathrm{D},-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{dt}}=\mathrm{k}[\mathrm{A}]^{2}[\mathrm{~B}]$. The expression for $\frac{-\mathrm{d}[\mathrm{B}]}{\mathrm{dt}}$ will be:
(A) $\mathrm{K}[\mathrm{A}]^{2}[\mathrm{~B}]$
(B) $1 / 2 \mathrm{~K}[\mathrm{~A}]^{2}[\mathrm{~B}]$
(C) $\mathrm{K}[\mathrm{A}]^{2}[2 \mathrm{~B}]$
(D) $\mathrm{K}[2 \mathrm{~A}]^{2}[\mathrm{~B}]$
5. Which is correct relation in between $\frac{\mathrm{dC}}{\mathrm{dt}}, \frac{\mathrm{dn}}{\mathrm{dt}}$ and $\frac{\mathrm{dP}}{\mathrm{dt}}$ where $\mathrm{C}, \mathrm{n}, \mathrm{P}$, represents concentration, mole and pressure terms for gaseous phase reactant $\mathrm{A}(\mathrm{g}) \longrightarrow$ product.
(A) $-\frac{\mathrm{dC}}{\mathrm{dt}}=-\frac{1}{\mathrm{~V}} \frac{\mathrm{dn}}{\mathrm{dt}}=-\frac{1}{\mathrm{RT}} \frac{\mathrm{dP}}{\mathrm{dt}}$
(B) $\frac{\mathrm{dC}}{\mathrm{dt}}=\frac{\mathrm{dn}}{\mathrm{dt}}=-\frac{\mathrm{dP}}{\mathrm{dt}}$
(C) $\frac{\mathrm{dC}}{\mathrm{dt}}=\frac{\mathrm{RT}}{\mathrm{V}} \frac{\mathrm{dn}}{\mathrm{dt}}=-\frac{\mathrm{dP}}{\mathrm{dt}}$
(D) All
6. When ammonia is treated with $\mathrm{O}_{2}$ at elevated temperatures, the rate of disappearance of ammonia is found to be $3.5 \times 10^{-2} \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{~s}^{-1}$ during a measured time interval. Calculate the rate of appearance of nitric oxide and water.
7. The following reaction was carried out at $44^{\circ} \mathrm{C}$

$$
\mathrm{N}_{2} \mathrm{O}_{5} \longrightarrow 2 \mathrm{NO}_{2}+1 / 2 \mathrm{O}_{2}
$$

The concentration of $\mathrm{NO}_{2}$ is $6.0 \times 10^{-3} \mathrm{M}$ after 10 minutes of the start of the reaction. Calculate the rate of production of $\mathrm{NO}_{2}$ over the first ten minutes of the reaction.
8. The oxidation of iodide ion by arsenic acid, $\mathrm{H}_{3} \mathrm{AsO}_{4}$, is described by the balance equation :

$$
3 \mathrm{I}^{-}(\mathrm{aq})+\mathrm{H}_{3} \mathrm{AsO}_{4}(\mathrm{aq})+2 \mathrm{H}^{+}(\mathrm{aq}) \longrightarrow \mathrm{I}_{3}^{-}(\mathrm{aq})+\mathrm{H}_{3} \mathrm{AsO}_{3}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(l)
$$

(a) If $-\Delta\left[\mathrm{I}^{-}\right] / \Delta \mathrm{t}=4.8 \times 10^{-4} \mathrm{M} / \mathrm{s}$, what is the value of $\Delta\left[\mathrm{I}_{3}^{-}\right] / \Delta \mathrm{t}$ during the same time interval?
(b) What is the average rate of consumption of $\mathrm{H}^{+}$during that time interval?
9. In a reaction, the rate expression is, rate $=\mathrm{K}[\mathrm{A}][\mathrm{B}]^{2 / 3}[\mathrm{C}]^{0}$, the order of reaciton is :
(A) 1
(B) 2
(C) $5 / 3$
(D) Zero
10. For the reaction, $\mathrm{H}_{2}\left(\mathrm{~g}+\mathrm{Br}_{2}(\mathrm{~g})=2 \mathrm{HBr}(\mathrm{g})\right.$, the reaction rate $=\mathrm{K}\left[\mathrm{H}_{2}\right]\left[\mathrm{Br}_{2}\right]^{1 / 2}$. Which statement is true about this reaction :
(A) The reaction is of second order
(B) Molecularity of the reaction is $3 / 2$
(C) The unit of K is $\mathrm{sec}^{-1}$
(D) Molecularity of the reacion is 2
11. The dimensions of the rate constant of a sceond order reaction involves :
(A) Neither time nor concentration
(B) Time and concentration
(C) Time and square of concentration
(D) Only time
12. The rate constant for a reaction is $10.8 \times 10^{-5} \mathrm{~mol} \mathrm{litre}^{-1} \mathrm{sec}^{-1}$. The rection obeys :
(A) First order
(B) Zero order
(C) Second order
(D) Half order
13. Which statement about the order of reaction is correct ?
(A) The order of reaction must be a positive integer
(B) A second order reaction is also bimolecular
(C) The order of reaction increases with increasing temperature.
(D) The order of reaction can only be determined by experiment
14. The rate of the reaction $\mathrm{A}+\mathrm{B}+\mathrm{C} \longrightarrow \mathrm{P}$ is given by :

$$
\mathrm{r}=\frac{\mathrm{d}[\mathrm{~A}]}{\mathrm{dt}}=\mathrm{k}[\mathrm{~A}]^{1 / 2}[\mathrm{~B}]^{1 / 2}[\mathrm{C}]^{1 / 4} . \text { The order of the reaction is: }
$$

The reaction is :
(A) 1
(B) 2
(C) $1 / 2$
(D) $5 / 4$
15. Bromomethane is converted to methanol in an alkaline solution :

$$
\mathrm{CH}_{3} \mathrm{Br}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq}) \longrightarrow \mathrm{CH}_{3} \mathrm{OH}(\mathrm{aq})+\mathrm{Br}^{-}(\mathrm{aq})
$$

The reaction is first order in each reactant.
(a) Write the rate law.
(b) How does reaction rate change if the $\mathrm{OH}^{-}$concentration is decreased by factor of 5 ?
(c) What is the change in rate if the concentrations of both reactants are doubled?
16. The oxidation of $\mathrm{Br}^{-}$by $\mathrm{BrO}_{3}^{-}$in acidic solution is described by the equation

$$
5 \mathrm{Br}^{-}(\mathrm{aq})+\mathrm{BrO}_{3}^{-}(\mathrm{aq})+6 \mathrm{H}^{+}(\mathrm{aq}) \longrightarrow 3 \mathrm{Br}_{2}(\mathrm{aq})+3 \mathrm{H}_{2} \mathrm{O}(l)
$$

The reaction is first order in $\mathrm{Br}^{-}$, first order in $\mathrm{BrO}_{3}^{-}$, and second order in $\mathrm{H}^{+}$.
(a) Write the rate law
(b) What is the overall reaction order?
(c) How does the reaction rate change if the $\mathrm{H}^{+}$concentration is tripled?
(d) What is the change in rate if the concentrations of both $\mathrm{Br}^{-}$and $\mathrm{BrO}_{3}^{-}$are halved ?
17. For the reaction: $2 \mathrm{~A}+\mathrm{B}_{2}+\mathrm{C} \longrightarrow \mathrm{A}_{2} \mathrm{~B}+\mathrm{BC}$, the rate law expression has been determined experimentally to be $\mathrm{R}=\mathrm{k}[\mathrm{A}]^{2}[\mathrm{C}]$ with, $\mathrm{k}=3.0 \times 10^{-4} \mathrm{M}^{-2} \mathrm{~min}^{-1}$.
(i) Determine the initial rate of the reaction, started with concentration

$$
[\mathrm{A}]=0.1 \mathrm{M},\left[\mathrm{~B}_{2}\right]=0.35 \mathrm{M} \&[\mathrm{C}]=0.25 \mathrm{M}
$$

(ii) What is the effect on rate of reaction and rate constant on changing the volume to $1 / 4^{\text {th }}$ of initial value.
18. For the reaction $2 \mathrm{NO}+\mathrm{Cl}_{2} \longrightarrow 2 \mathrm{NOCl}$, it is found that doubling the concentration of both reactants increases the rate by the factor of 8 , but doubling the $\mathrm{Cl}_{2}$ concentration alone, only doubles the rate What is the order of the reaction with respect to NO and $\mathrm{Cl}_{2}$ ?
19. For the reaction, $2 \mathrm{~A}+\mathrm{B}+\mathrm{C} \longrightarrow \mathrm{A}_{2} \mathrm{~B}+\mathrm{C}$
the rate $=\mathrm{k}[\mathrm{A}][\mathrm{B}]^{2}$ with $\mathrm{k}=2.0 \times 10^{-6} \mathrm{M}^{-2} \mathrm{~s}^{-1}$. Calculate the initial rate of the reaction when $[\mathrm{A}]=0.1 \mathrm{M},[\mathrm{B}]=0.2 \mathrm{M}$ and $[\mathrm{C}]=0.8 \mathrm{M}$.
20. If the pressure of gaseous reactant is changed by 3 times the rate of reaction changes by 5.2 times. Determine
(i) order of reaction
(ii) unit of rate constant
(iii) effect on rate of reaction if volume of container is reduced to $\frac{1}{16}$ th of the original

## 2. Daily Practice Problem Sheet

1. The rate law for the single-step reaction, $2 \mathrm{~A}+\mathrm{B} \longrightarrow 2 \mathrm{C}$, is given by :
(A) Rate $=\mathrm{K}[\mathrm{A}] \cdot[\mathrm{B}]$
(B) Rate $=\mathrm{K}[\mathrm{A}]^{2} .[\mathrm{B}]$
(C) Rate $=\mathrm{K}[2 \mathrm{~A}] \cdot[\mathrm{B}]$
(D) Rate $=\mathrm{K}[\mathrm{A}]^{2} \cdot[\mathrm{~B}]^{0}$
2. The correct expression the rate of reaction of elementary reaction, $\mathrm{A}+\mathrm{B} \longrightarrow \mathrm{C}$ is
(A) $\frac{\mathrm{d}[\mathrm{C}]}{\mathrm{dt}}=\mathrm{K}[\mathrm{A}]$
(B) $\frac{\mathrm{d}[\mathrm{C}]}{\mathrm{dt}}=\mathrm{K}[\mathrm{B}]$
(C) $\frac{-\mathrm{d}[\mathrm{A}]}{\mathrm{dt}}=\mathrm{K}[\mathrm{A}][\mathrm{B}]$
(D) $\frac{-d[A]}{d t}=K[A]$
3. Select the intermediate in the following reaction mechanism :

$$
\mathrm{O}_{3}(\mathrm{~g}) \underset{ }{\rightleftharpoons} \mathrm{O}_{2}(\mathrm{~g})+\mathrm{O}(\mathrm{~g}), \mathrm{O}_{3}+\mathrm{O} \longrightarrow 2 \mathrm{O}_{2}
$$

(A) $\mathrm{O}_{3}(\mathrm{~g})$
(B) $\mathrm{O}(\mathrm{g})$
(C) $\mathrm{O}_{2}(\mathrm{~g})$
(D) None
4. The elementary step of the reaction, $2 \mathrm{Na}+\mathrm{Cl}_{2} \longrightarrow 2 \mathrm{NaCl}$ is found to follow III order kinetics, its molecularity is :
(A) 1
(B) 2
(C) 3
(D) 4
5. For the reaction $2 \mathrm{NO}_{2}+\mathrm{F}_{2} \longrightarrow 2 \mathrm{NO}_{2} \mathrm{~F}$, following mechanism has been provided :

$$
\begin{aligned}
& \mathrm{NO}_{2}+\mathrm{F}_{2} \xrightarrow{\text { slow }} \mathrm{NO}_{2} \mathrm{~F}+\mathrm{F} \\
& \mathrm{NO}_{2}+\mathrm{F} \xrightarrow{\text { fast }} \mathrm{NO}_{2} \mathrm{~F}
\end{aligned}
$$

Thus rate expression of the above reaction can be written as :
(A) $\mathrm{r}=\mathrm{k}\left[\mathrm{NO}_{2}\right]^{2}\left[\mathrm{~F}_{2}\right]$
(B) $\mathrm{r}=\mathrm{k}\left[\mathrm{NO}_{2}\right]\left[\mathrm{F}_{2}\right]$
(C) $\mathrm{r}=\mathrm{k}\left[\mathrm{NO}_{2}\right]$
(D) $\mathrm{r}=\mathrm{k}\left[\mathrm{F}_{2}\right]$
6. The reaction $2 \mathrm{NO}+\mathrm{Br}_{2} \longrightarrow 2 \mathrm{NOBr}$, Obey's the following mechanism:
$\mathrm{NO}+\mathrm{Br}_{2} \stackrel{\text { fast }}{\rightleftharpoons} \mathrm{NOBr}_{2} ; \quad \mathrm{NOBr}_{2}+\mathrm{NO} \xrightarrow{\text { slow }} 2 \mathrm{NOBr}$
The rate expression of the above reaction can be written as:
(A) $\mathrm{r}=\mathrm{k}[\mathrm{NO}]^{2}\left[\mathrm{Br}_{2}\right]$
(B) $\mathrm{r}=\mathrm{k}[\mathrm{NO}]\left[\mathrm{Br}_{2}\right]$
(C) $\mathrm{r}=\mathrm{k}][\mathrm{NO}]\left[\mathrm{Br}_{2}\right]^{2}$
(D) $\mathrm{r}=\mathrm{k}\left[\mathrm{NOBr}_{2}\right]$
7. The reaction $2 \mathrm{~A} \longrightarrow \mathrm{~B}+\mathrm{C}$ follows zero order kinetics. The differential rate equation for the reaction is:
(A) $\frac{d x}{d t}=K[A]^{0}$
(B) $\frac{\mathrm{dx}}{\mathrm{dt}}=\mathrm{K}[\mathrm{A}]^{2}$
(C) $\frac{\mathrm{dx}}{\mathrm{dt}}=\mathrm{K}[\mathrm{B}][\mathrm{C}]$
(D) $\frac{d x}{d t}=K[A]$
8. For the elementary step, $\left(\mathrm{CH}_{3}\right)_{3} \cdot \mathrm{CBr}(\mathrm{aq}) \longrightarrow\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}^{+}(\mathrm{aq})+\mathrm{Br}^{-}(\mathrm{aq})$ the molecularity is:
(A) Zero
(B) 1
(C) 2
(D) cannot ascertained
9. Following mechanism has been proposed for a reaction,

$$
\begin{aligned}
& 2 \mathrm{~A}+\mathrm{B} \longrightarrow \mathrm{D}+\mathrm{E} \\
& \mathrm{~A}+\mathrm{B} \longrightarrow \mathrm{C}+\mathrm{D} \\
& \mathrm{~A}+\mathrm{C} \longrightarrow \mathrm{C} \longrightarrow \mathrm{E}
\end{aligned}
$$

The rate law expression for the reaction is:
(A) $\mathrm{r}=\mathrm{K}[\mathrm{A}]^{2}[\mathrm{~B}]$
(B) $\mathrm{r}=\mathrm{K}[\mathrm{A}][\mathrm{B}]$
(C) $\mathrm{r}=\mathrm{K}[\mathrm{A}]^{2}$
(D) $\mathrm{r}=\mathrm{K}[\mathrm{A}][\mathrm{C}]$
10. A reaction, $\mathrm{A}_{2}+\mathrm{B}_{2} \longrightarrow 2 \mathrm{AB}$ occurs by the following mechanism;

| $\mathrm{A}_{2} \longrightarrow \mathrm{~A}+\mathrm{A}$ | $\ldots \ldots .$. (slow) |
| :--- | :--- |
| $\mathrm{A}+\mathrm{B}_{2} \longrightarrow \mathrm{AB}+\mathrm{B}$ | $\ldots .$. (fast) |
| $\mathrm{A}+\mathrm{B} \longrightarrow \mathrm{AB}$ | $\ldots \ldots$. (fast) |

Its order would be:
(A) $3 / 2$
(B) 1
(C) zero
(D) 2
11. The chemical reaction, $2 \mathrm{O}_{3} \longrightarrow 3 \mathrm{O}_{2}$ proceeds as follows :

$$
\begin{array}{ll}
\mathrm{O}_{3} \rightleftharpoons \mathrm{O}_{2}+\mathrm{O} & \ldots \ldots . \text { (fast) } \\
\mathrm{O}+\mathrm{O}_{3} \longrightarrow 2 \mathrm{O}_{2} & \ldots \ldots . \text { (slow) }
\end{array}
$$

The rate law expression should be:
(A) $\mathrm{r}=\mathrm{K}\left[\mathrm{O}_{3}\right]^{2}$
(B) $\mathrm{r}=\mathrm{K}\left[\mathrm{O}_{3}\right]^{2}\left[\mathrm{O}_{2}\right]^{-1}$
(C) $\mathrm{r}=\mathrm{K}\left[\mathrm{O}_{3}\right]\left[\mathrm{O}_{2}\right]$
(D) Unpredictable
12. The following two step mechanism has been proposed for the gas-phase decomposition of nitrous oxide ( $\mathrm{N}_{2} \mathrm{O}$ ):
Step I : $\quad \mathrm{N}_{2} \mathrm{O}(\mathrm{g}) \longrightarrow \mathrm{N}_{2}(\mathrm{~g})+\mathrm{O}(\mathrm{g})$
Step II : $\quad \mathrm{N}_{2} \mathrm{O}(\mathrm{g})+\mathrm{O}(\mathrm{g}) \longrightarrow \mathrm{N}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g})$
(a) Write the chemical equation for overall reaction.
(b) Identify any reaction intermediates.
(c) What is the molecularity of each of the elementary reactions?
(d) What is the molecularity of the overall reaction?
13. What is the order of reaction,
$\mathrm{A}_{2}+\mathrm{B}_{2} \longrightarrow 2 \mathrm{AB}$; having following mechanism

$$
\begin{array}{ll}
\mathrm{A}_{2} \rightleftharpoons \mathrm{~A}+\mathrm{A} & \ldots \ldots \ldots . \text { (fast) } \\
\mathrm{A}+\mathrm{B}_{2} \longrightarrow \mathrm{AB}+\mathrm{B} & \ldots \ldots . \text { (slow) } \\
\mathrm{A}+\mathrm{B} \longrightarrow \mathrm{AB} & \ldots \ldots . \text { (fast) }
\end{array}
$$

$$
x-1+x
$$

14. The following reaction has a second-order rate law :

$$
\mathrm{H}_{2}(\mathrm{~g})+2 \mathrm{ICl}(\mathrm{~g}) \longrightarrow \mathrm{I}_{2}(\mathrm{~g})+2 \mathrm{HCl}(\mathrm{~g}) \text { Rate }=\mathrm{k}\left[\mathrm{H}_{2}\right][\mathrm{ICl}]
$$

Devise a possible reaction mechanism.
15. Initial rate data at $25^{\circ} \mathrm{C}$ are listed in the table for the reaction
$\mathrm{NH}_{4}^{+}(\mathrm{aq})+\mathrm{NO}_{2}^{-}(\mathrm{aq}) \longrightarrow \mathrm{N}_{2}(\mathrm{~g})+2 \mathrm{H}_{2} \mathrm{O}$ (1)

| Experiment <br> No. | Initial $\left[\mathbf{N H}_{4}{ }^{+}\right]$ | Initial $\left[\mathbf{N O}_{\mathbf{2}}{ }^{-}\right]$ | Initial rate of consumption <br> of $\mathbf{N H} \mathbf{H}_{4}{ }^{+} \mathbf{( M / s )}$ |
| :---: | :---: | :---: | :---: |
| 1. | 0.24 | 0.10 | $7.2 \times 10^{-6}$ |
| 2. | 0.12 | 0.10 | $3.6 \times 10^{-6}$ |
| 3. | 0.12 | 0.15 | $5.4 \times 10^{-6}$ |

(a) What is the rate law?
(b) What is the value of the rate constant?
(c) What is the reaction rate when the concentrations are $\left[\mathrm{NH}_{4}^{+}\right]=0.39 \mathrm{M}$ and $\left[\mathrm{NO}_{2}^{-}\right]=0.052 \mathrm{M}$ ?
16. Find :
(i) rate law expression
(ii) order of reaction with respect to each reactant and overall order of reaction
(iii) value and unit of rate constant
(iv) effect on rate of reaction on changing the volume to $1 / 8^{\text {th }}$ of the original.

For the reaction, $\mathrm{A}+\mathrm{B}+\mathrm{C} \longrightarrow$ product
given :

| Experiment <br> No. | $[\mathbf{A}]_{\mathbf{0}}$ <br> $\mathbf{1 0}^{-4}(\mathbf{m} / \mathbf{l})$ | $[\mathbf{B}]_{\mathbf{0}}$ <br> $\mathbf{1 0}^{-2}(\mathbf{m} / \mathbf{l})$ | $[\mathbf{C}]_{\mathbf{0}}$ <br> $\mathbf{1 0}^{-1}(\mathbf{m} / \mathbf{l})$ | Initial rate <br> $\times \mathbf{1 0}^{-6}(\mathbf{m} / \mathbf{l} / \mathbf{s})$ |
| :---: | :---: | :---: | :---: | :---: |
| 1 | 7 | 3 | 5 | 9 |
| 2 | 7 | 6 | 5 | 12.7 |
| 3 | 7 | 6 | 2 | 12.7 |
| 4 | 14 | 3 | 5 | 4.51 |

17. Initial rate data at $25^{\circ} \mathrm{C}$ are listed in the table for reaction, $\mathrm{A}_{2}+\mathrm{B}_{2} \longrightarrow 2 \mathrm{AB}$

| Experiment <br> No. | $\left[\mathbf{A}_{\mathbf{2}}\right]_{\mathbf{0}} \mathbf{( m / \mathbf { l } )}$ | $\left[\mathbf{B}_{\mathbf{2}} \mathbf{]}_{\mathbf{0}}(\mathbf{m} / \mathbf{l})\right.$ | Initial rate <br> $\mathbf{( m / / \mathbf { / }} \mathbf{)}$ |
| :---: | :---: | :---: | :---: |
| 1 | $1.5 \times 10^{-3}$ | $3.2 \times 10^{-4}$ | $8.1 \times 10^{-8}$ |
| 2 | $4.5 \times 10^{-3}$ | $9.6 \times 10^{-4}$ | $6.56 \times 10^{-6}$ |
| 3 | $3 \times 10^{-3}$ | $1.6 \times 10^{-4}$ | $3.24 \times 10^{-7}$ |

using that, determine
(i) rate law
(ii) order of reaction with respect to $\mathrm{A}_{2}$ and $\mathrm{B}_{2}$ and overall order of reaction
(iii) value and unit of rate constant
(iv) effect on rate of reaction on doubling the volume of container.
18. The data given below are for the reacion of NO and $\mathrm{Cl}_{2}$ to form NOCl at 295 K .
$\left[\mathrm{Cl}_{2}\right]$
[NO]
Initial rate (mol litre ${ }^{-1} \mathbf{s e c}^{-1}$ )
0.05
0.05
$1 \times 10^{-3}$
0.15
0.05
$3 \times 10^{-3}$
0.05
0.15
$9 \times 10^{-3}$
(a) What is the order w.r.t. NO and $\mathrm{Cl}_{2}$ in the reaction
(b) Write the rate expression
(c) Calculate the rate constant
(d) Determine the reaction rate when conc. of $\mathrm{Cl}_{2}$ and NO are 0.2 M and 0.4 M respectively.
19. The decomposition of $\mathrm{NH}_{3}$ on tungsten surface follows zero order kinetics. The half life is 5 minutes for an initial pressure of 70 torr of $\mathrm{NH}_{3}$. If the initial pressure had been 0.25 atm , what would the total pressure after 3 minutes? What is the half life ?
20. In a reaction, the decrease in reactant's concentration is $20 \%$ in 20 minute and $40 \%$ in 40 minute. Calculate order of reaction and rate constant .

## 3. Daily Practice Problem Sheet

1. Show that for a first order reaction, $\mathrm{R} \longrightarrow \mathrm{P}$ the concentration of product can be represented as a function of time by, $[\mathrm{P}]=\mathrm{at}+\mathrm{bt}^{2}+\mathrm{ct}^{3}+-----$ and express $\mathrm{a}, \mathrm{b}$ and c in terms of $[\mathrm{R}]_{0}$ and K .
2. (i) Substance A decomposes by the first order reaction. Starting initially with $[\mathrm{A}]=2.00 \mathrm{M}$, after 200 minutes [A] $=0.25 \mathrm{M}$. For this reaction what is $\mathrm{t}_{1 / 2}$ and k ?
(ii) A first order reaction is $40 \%$ complete after 8 min . How long will it take before it is $90 \%$ complete? What is the value of the rate constant?
(iii) For a certain reaction it takes 20 minutes for the initial concentrations of $34.8 \mathrm{~mol} \mathrm{~L}^{-1}$ to become $17.4 \mathrm{molL}^{-1}$ and another 20 minutes to become $8.7 \mathrm{~mol} \mathrm{~L}^{-1}$. Calculate the rate constant of the reaction.
(iv) For a first order reaction in which $k=5.48 \times 10^{-1} \sec ^{-1}$. Find : (a) $t_{1 / 3} \quad$ (b) $t_{2 / 3}$
3. Show that for a first order reaction
(i) $\mathrm{t}_{25 \%}=0.415 \mathrm{t}_{1 / 2}$
(ii) $\quad \mathrm{t}_{87.5 \%}=3 \mathrm{t}_{1 / 2}$
(iii) $t_{90 \%}=3.33 t_{1 / 2}$
(iv) $\quad \mathrm{t}_{99 \%}=6.66 \mathrm{t}_{1 / 2}$
(v) $\quad \mathrm{t}_{99.9 \%}=10 \mathrm{t}_{1 / 2}$
(vi) $\quad t_{99 \%}=2 t_{90 \%}$
(vii) $\mathrm{t}_{99.9 \%}=3 \mathrm{t}_{90 \%}$
4. The solution of $\mathrm{H}_{2} \mathrm{O}_{2}$ of normality 0.73 is catalytically decomposed. What will be the concentration at the end of 45 minute, assuming the decomposition to follow first order rate law if half life is 15 minute?
5. The change, $\mathrm{A} \longrightarrow \mathrm{B}$ shows I order :
(a) How will the rate of reaction change when the concentration of $A$ is tripled?
(b) What will be the change in half life period in doing so ?
6. The virus prepared in a chemical bath shows inactivation process obeying I order. Calculate the rate constant for the viral inactivation if in the beginning $1.5 \%$ of the virus is inactivated per minute. Also calculate the time required for its,
(a) $50 \%$ inactivation
(b) $80 \%$ inactivation.
7. Show that for I order reaction, the time required for $99.9 \%$ decomposition of the reaction is ten folds to the time required for half of the reaction .
8. The time required for $20 \%$ completion for a reaction is 10 minute for I order reaction. Calculate:
(a) specific reaction rate.
(b) Time required for $75 \%$ completion
9. The half life for a I order reaction $\mathrm{A} \longrightarrow$ Product, is 10 minute. What $\%$ of A remains after
(i) $1 / 2$ hour
(ii) $2 / 3$ hour
(iii) 1 hour
10. The reaction $\mathrm{SO}_{2} \mathrm{Cl}_{2} \longrightarrow \mathrm{SO}_{2}+\mathrm{Cl}_{2}$ obeys I order kinetics with rate const. $3.2 \times 10^{-5} \mathrm{sec}^{-1}$ at $320^{\circ} \mathrm{C}$. What $\%$ of $\mathrm{SO}_{2} \mathrm{Cl}_{2}$ will be decomposed on heating gas for 90 minute ?
11. For the first order reaction, $\mathrm{A} \longrightarrow \mathrm{B}$, shown in the figure, what is the significance of the point at which the two curves cross each other. How is the slopes of the two curves be related at this point?

12. A first order gaseous reactions has $\mathrm{K}=1.5 \times 10^{-6} \mathrm{sec}^{-1}$ at $200^{\circ} \mathrm{C}$. If the reaction is allowed to run for 10 hour, what percentage of initial concentration would have changed into products. What is the half life period of reaction?
13. Thermal decomposition of a compound is of first order. If $50 \%$ sample of the compound is decomposed in 120 minute, how long will it take for $90 \%$ of the compound to decompose?
14. A substance is reduced to one third of its original concentration in 100 minute. Calculate the time in which it will be reduced to one ninth of its original value. Assume I order .
15. For the decomposition of $\mathrm{N}_{2} \mathrm{O}_{5}$, the rate constant is $6.2 \times 10^{-4} \mathrm{sec}^{-1}$ at $45^{\circ} \mathrm{C}$. It begins with one mole of $\mathrm{N}_{2} \mathrm{O}_{5}$ in a litre flask, how long would it take for $20 \% \mathrm{~N}_{2} \mathrm{O}_{5}$ to decompose and how long for $50 \%$ ?
16. In the decomposition of oxalic acid following data were obtained:

| Time in minute | 0 | 300 | 600 |
| :--- | :---: | :--- | :---: |
| Pressure in mm | 22.0 | 17.0 | 13.4 |

Determine the rate constant K and half life period, if reaction obeys I order kinetics.
17. Decomposition of $\mathrm{N}_{2} \mathrm{O}_{5}(\mathrm{~g})$ into $\mathrm{NO}_{2}(\mathrm{~g})$ and $\mathrm{O}_{2}(\mathrm{~g})$ is a first order reaction. If the initial concentration of $\mathrm{N}_{2} \mathrm{O}_{5}(\mathrm{~g})$, i.e., $\left[\mathrm{N}_{2} \mathrm{O}_{5}\right]_{0}$ is 0.030 mol litre ${ }^{-1}$, what will be its concentration after 30 minute? Rate constant of reaction is $1.35 \times 10^{-4} \mathrm{sec}^{-1}$.
18. For a homogeneous gaseous reaction, $A \longrightarrow B+C+D$, the initial pressure was $P_{0}$ while pressure after time $t$ was P . Derive an expression for rate constant K in terms of $\mathrm{P}_{0}, \mathrm{P}$ and $t$. assume I order reaction.
19. Acetone on heating gives CO and other hydrocarbons at $600^{\circ} \mathrm{C}$. The reaction obeys I order kinetics w.r.t. acetone concentration. The half life period is 81 sec . Calculate the time in which acetone taken in a container at $600^{\circ} \mathrm{C}$ reduces its pressure from 0.5 atm to 0.4 atm .
20. Dimethyl ether gaseous phase decomposition is :
$\mathrm{CH}_{3} \mathrm{OCH}_{3} \longrightarrow \mathrm{CH}_{4}+\mathrm{H}_{2}+\mathrm{CO}$ at 750 K having rate constant $6.72 \times 10^{-3} \mathrm{~min}^{-1}$. Calculate the time in which initial pressure of 400 mm in closed container becomes 750 mm .
21. The decomposition of $\mathrm{Cl}_{2} \mathrm{O}_{7}$ at 400 K in gaseous phase to $\mathrm{Cl}_{2}$ and $\mathrm{O}_{2}$ is of I order reaction. After 55 sec at 400 K , the pressure of reaction mixture increase from 0.62 to 1.88 atm . Calculate the rate constant of reaction. Also calculate the pressure of reaction mixture after 100 second.
22. In the vapour phase decomposition of ethylene oxide, $\mathrm{C}_{2} \mathrm{H}_{4} \mathrm{O} \longrightarrow \mathrm{CH}_{4}+\mathrm{CO}$ at $414.5^{\circ} \mathrm{C}$, the initial pressure and the pressure after 5 minute were 116.51 mm and 122.56 mm of Hg respectively. If the reaction follows I order kinetics, what must be the pressure after 12 minutes?
23. Calculate the partial pressures of reactants and products, when azomethane decomposes at an initial pressure of 200 mm for 30 minute according to $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{~N}_{2} \longrightarrow \mathrm{C}_{2} \mathrm{H}_{6}+\mathrm{N}_{2}$. The rete constant is $2.5 \times 10^{-4} \mathrm{sec}^{-1}$.
24. Rate constant of a first order reaction $A \longrightarrow B$ is $6.93 \times 10^{-2}$ minute. If initial concentration of reactant is 1 M . Then calculate :
(i) Initial rate
(ii) Rate after 600 seconds
(iii) Rate after $75 \%$ of the reaction is completed
(iv) Rate after 30 minutes.
25. In a first order reaction concentration of reactant decreases from 10 M to 2.5 M in 500 seconds. Calcualte:
(i) $t_{1 / 2}$ of the reaction
(ii) rate of reaction when concentration is 5 M .
26. Rate constant of a first order reaction is $10^{-3} \mathrm{sec}$. Calculate time in seconds when concentration is changing from:
(i)
2 M to 0.25 M
(ii) 16 M to 1 M
(iii) $\quad 6.4 \mathrm{M}$ to 1.6 M
(iv) 4 M to 0.125 M

## ANSWERS

## Daily Practice Problems 1

1. (D)
2. (C)
3. (B)
4. (B)
5. (A)
6. $\frac{\Delta[\mathrm{NO}]}{\mathrm{dt}}=3.5 \times 10^{-2} \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{~s}^{-1} \frac{\Delta\left[\mathrm{H}_{2} \mathrm{O}\right]}{\mathrm{dt}}=5.3 \times 10^{-2} \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{~s}^{-1}$
7. $6.0 \times 10^{-4} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~min}^{-1}$
8. (a) $1.6 \times 10^{-4} \mathrm{M} / \mathrm{s}$; (b) $3.2 \times 10^{-4} \mathrm{M} / \mathrm{s}$
9. (C)
10. (D)
11. (B)
12. (B)
13. (D)
14. (D)
15. (a) Rate $=\mathrm{k}\left[\mathrm{CH}_{3} \mathrm{Br}\right]\left[\mathrm{OH}^{-}\right] \quad$ (b) rate will decrease by factor of 5
(c) rate will increase by factor of 4
16. (a) $\mathrm{k}\left[\mathrm{Br}^{-}\right]\left[\mathrm{BrO}_{3}^{-}\right]\left[\mathrm{H}^{+}\right]^{2}$
(b) 4
(c) rate will increase by the factor of 9
(d) rate will decrease by factor of $1 / 4$
17. (i) $7.5 \times 10^{-7} \mathrm{M} \mathrm{min}^{-1} \quad$ (ii) rate increased by 64 times
18. order w.r.t. $[\mathrm{NO}]=2$; order w.r.t. $\left[\mathrm{Cl}_{2}\right]=1 \quad 19.8 \times 10^{-9} \mathrm{M}^{-2} \mathrm{~s}^{-1}$
19. (i) $3 / 2$ (ii) $\mathrm{atm}^{-1 / 2}$ time $^{-1} \quad$ (iii) increased by 64 times

## Daily Practice Problems 2

1. (B)
2. (C)
3. (B)
4. (C)
5. (B)
6. (A)
7. (A)
8. (B)
9. (B)
10. (B)
11. (B)
12. (a) $2 \mathrm{~N}_{2} \mathrm{O}$ (g) $\longrightarrow 2 \mathrm{~N}_{2}(\mathrm{~g})+\mathrm{O}_{2}$ (g)
(b) oxygen atom
(c) (i) unimolecular
(ii) bimolecular
(d) not defined
13. $3 / 2$
14. 

(a) Rate $=\mathrm{k}\left[\mathrm{NH}_{4}^{+}\right]\left[\mathrm{NO}_{2}^{-}\right]$
(b) $3.0 \times 10^{-4} \mathrm{M} / \mathrm{s}$
(c) $6.1 \times 10^{-6} \mathrm{M} / \mathrm{s}$
16. (i) $r=k[A]^{-1}[B]^{1 / 2}$
(ii) wrt: $\mathrm{A}=-1, \mathrm{~B}=1 / 2, \mathrm{C}=0$, overall order $=-1 / 2$
(iii) $\mathrm{k}=\frac{63}{\sqrt{3}} \times 10^{-9} \quad$ (iv) rate of reaction increases by $2 \sqrt{2}$ times
17. (i)
(i) $\mathrm{k}\left[\mathrm{A}_{2}\right]^{3}\left[\mathrm{~B}_{2}\right]$
(ii) order wrt $\mathrm{A}_{2}=3 ; \mathrm{O}$. wrt $\mathrm{B}_{2}=1$, overall order $=4$
(iii) $\mathrm{k}=7.5 \times 10^{3}(\mathrm{~mol} / \mathrm{lit})^{-3} / \mathrm{sec}$
(iv) rate of reaction decrease to $\frac{1}{16}$
18. (a) 2 and 1 (b) $\mathrm{r}=\mathrm{K}$
19. 211 torr, 13.57 min
Practice Problems 3
2. (i) $a=R_{0} K, b=\frac{R_{0} K^{2}}{2}, c=\frac{R_{0} K^{3}}{6}$
2. (i) $\mathrm{t}_{1 / 2}=66.66 \mathrm{~min}, \mathrm{k}=0.01039 \mathrm{~min}^{-1}$
(ii) $\mathrm{k}=0.06386 \mathrm{~min}^{-1} ; \mathrm{t}=36.06 \mathrm{~min}$
(iii) $0.03465 \mathrm{~min}^{-1}$
(iv) (i) 0.740 s
(ii) 2.005 s
4. 0.09
5. (a) 3
(b) No change
6. $K=2.5 \times 10^{-4} \mathrm{sec}^{-1}$,
7. (a) 46.2 minute (b) 107.3 minute
8. (a) $2.232 \times 10^{-2} \mathrm{~min}^{-1}$
(b) 62.12 minute
9. (i) $12.5 \%$,
(ii) $6.25 \%$,
(iii) $1.56 \%$
10. $15.86 \%$
11. Time at this point is $\mathrm{t}_{1 / 2}$ because $[\mathrm{A}]=[\mathrm{B}]$ : Also $\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{dt}}+\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{dt}}=0$
12. $5.25 \%, 128.33 \mathrm{hr}$
14. 200 minute
15. $3.59 \times 10^{2}, 1.1 \times 10^{3} \mathrm{sec}$
16. $8.6 \times 10^{-4} \mathrm{sec} ; 13.43$ minute
17. $0.023 \mathrm{~mol} / \mathrm{L}$
18. $\mathrm{K}=\frac{2.303}{\mathrm{t}} \log _{10} \frac{2 \mathrm{P}_{0}}{3 \mathrm{P}_{0}-\mathrm{P}}$
19. 26 sec
20. 85.64
21. $1.58 \times 10^{-2}, 233 \mathrm{~atm}$
22. 130.41
23. $\mathrm{P}_{\left(\mathrm{CH}_{3}\right)_{2} \mathrm{~N}_{2}}^{\prime}=127.55 \mathrm{~mm}, \mathrm{P}_{\mathrm{C}_{2} \mathrm{H}_{6}}^{\prime}=72.45 \mathrm{~mm}$
24. (i) $6.93 \times 10^{-2} \mathrm{M} / \mathrm{min}$.(ii) $3.465 \times 10^{-2} \mathrm{M} / \mathrm{min}$ (iii) $1.7325 \times 10^{-2} \mathrm{M} / \mathrm{min}$.(iv) $8.67 \times 10^{-3}$
25. (i) 250 seconds (ii) $0.01386 \mathrm{M} \mathrm{sec}^{-1}$
26. (i) 2079 sec (ii) 2772 sec , (iii) 1386 sec . (iv) 3465 sec .

