CHEMICAL KINETICS

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For- class B.Sc. 1

Chemical Kinetics

- The branch of chemistry, which deals with studying reaction rates and their mechanisms, is called *chemical kinetics*.

- Thermodynamics tells only about the feasibility of a reaction whereas chemical kinetics tells about the rate of a reaction.

- For example, thermodynamic data indicate that diamond shall convert to graphite but in reality the conversion rate is so slow that the change is not perceptible at all.

Chemical Kinetics

- ▶ Kinetic studies not only help us to determine the speed or rate of a chemical reaction but also describe the conditions by which the reaction rates can be altered.

- ▶ The factors such as concentration, temperature, pressure and catalyst affect the rate of a reaction.

Rate of a Chemical Reaction

▶ **The speed of a reaction or the rate of a reaction can be defined as the change in concentration of a reactant or product in unit time. It can be expressed in terms of:**

▶ (i) the rate of decrease in concentration of any one of the reactants, or

▶ (ii) the rate of increase in concentration of any one of the products.

Rate of a Chemical Reaction

Consider a hypothetical reaction, assuming that the volume of the system remains constant

$$R \rightarrow P$$

One mole of the reactant R produces one mole of the product P. If [R]1 and [P]1 are the concentrations of R and respectively at time t1 and [R]2 and [P]2 are their concentrations at time t2 then,

$$\Delta t = t_2 - t_1$$

$$\Delta[R] = [R]_2 - [R]_1 \quad \text{and} \quad \Delta[P] = [P]_2 - [P]_1$$

(The square brackets in the above expressions are used to express molar concentration.)

Rate of a Chemical Reaction

Rate of disappearance of R

= <u>Decrease in concentration of R</u> = − <u>Δ [R]</u>
Time taken   Δt

Rate of appearance of P

= <u>Increase in concentration of P</u> = + <u>Δ [P]</u>
Time taken   Δ t

(Since Δ[R] is a negative quantity (as the concentration of reactants is decreasing), it is multiplied with -1 to make the rate of the reaction a positive quantity.)

Rate of a Chemical Reaction

Consider the following chemical reaction –

$$2\ Fe^{3+}(aq) + Sn^{2+} \rightarrow 2\ Fe^{2+}(aq) \quad + Sn^{4+}(aq)$$

$t = 38.5\ s \qquad [Fe^{2+}] = 0.0010\ M$

$\Delta t = 38.5\ s \qquad \Delta[Fe^{2+}] = (0.0010 - 0)\ M$

Rate of formation of $Fe^{2+} = \dfrac{\Delta[Fe^{2+}]}{\Delta t} = \dfrac{0.0010\ M}{38.5\ s} = 2.6 \times 10^{-5}\ M\ s^{-}$

General Rate of Reaction

$$a\text{ A} + b\text{ B} \rightarrow c\text{ C} + d\text{ D}$$

Rate of reaction = rate of disappearance of reactants

$$= -\frac{1}{a}\frac{\Delta[\text{A}]}{\Delta t} = -\frac{1}{b}\frac{\Delta[\text{B}]}{\Delta t} \qquad \text{Eqn.1}$$

= rate of appearance of products

$$= \frac{1}{c}\frac{\Delta[\text{C}]}{\Delta t} = \frac{1}{d}\frac{\Delta[\text{D}]}{\Delta t} \qquad \text{Eqn.2}$$

or $\quad -\dfrac{1}{a}\dfrac{\Delta[\text{A}]}{\Delta t} = -\dfrac{1}{b}\dfrac{\Delta[\text{B}]}{\Delta t} = \dfrac{1}{c}\dfrac{\Delta[\text{C}]}{\Delta t} = \dfrac{1}{d}\dfrac{\Delta[\text{D}]}{\Delta t} \qquad$ Eqn.3

General Rate of Reaction

$$2\ Fe^{3+}(aq) + Sn^{2+} \rightarrow 2\ Fe^{2+}(aq) + Sn^{4+}(aq)$$

$$\frac{\Delta[Sn^{4+}]}{\Delta t} = \frac{1}{2}\frac{\Delta[Fe^{2+}]}{\Delta t} = -\frac{1}{2}\frac{\Delta[Fe^{3+}]}{\Delta t}$$

Average rate & Instantaneous rate

❑ **The average rate depends upon the change in conc. of reactants or products and the time taken for that change to occur.**

Equations 1-3 represent the average rate of a reaction, rav.

❑ **The rate of reaction at a particular moment of time is called the instantaneous rate, rins.**

It is obtained when we consider the average rate at the smallest time interval say dt (i.e. when Δt approaches zero).

Average rate & Instantaneous rate

▶ **Mathematically for an infinitesimally small time interval, dt, *the instantaneous rate is given by –***
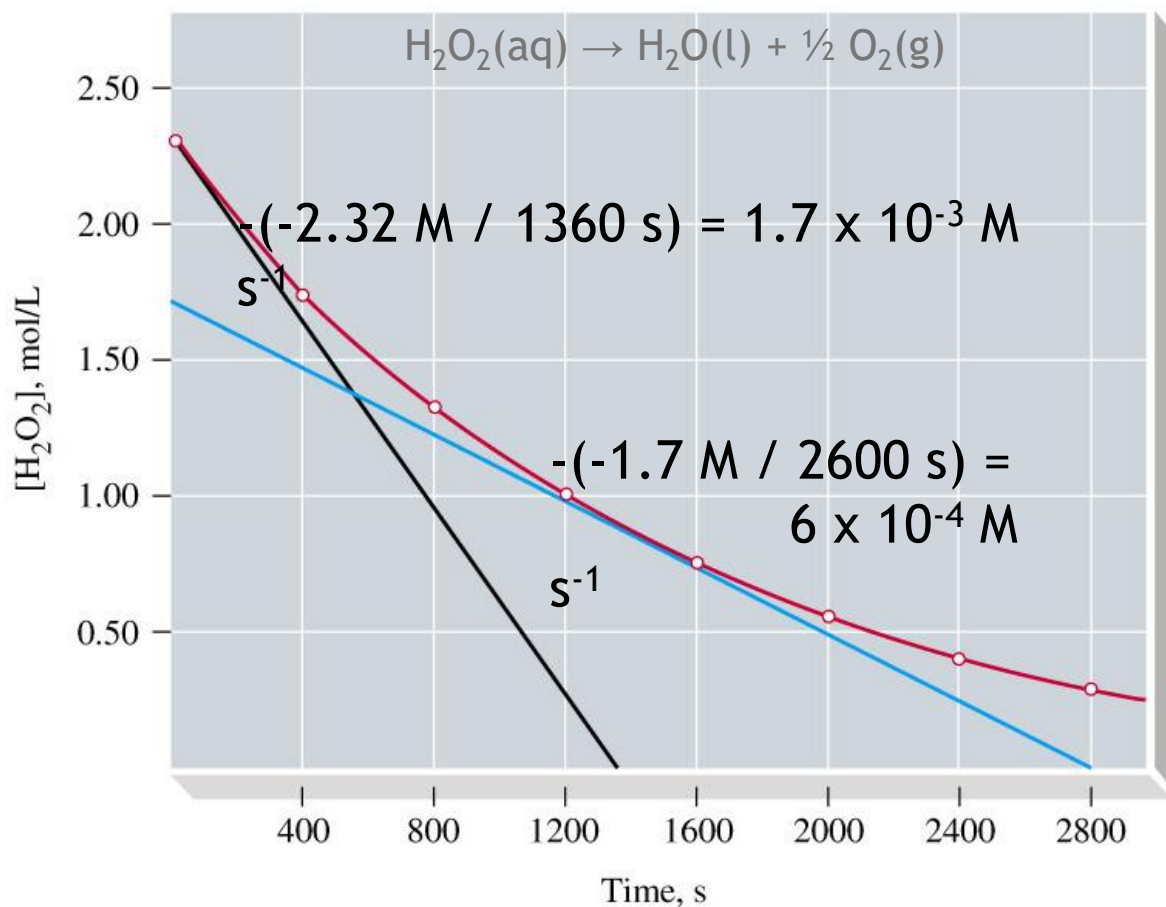
▶ *rav = −$\dfrac{\Delta[R\ ]}{\Delta t}$ = $\dfrac{\Delta[P\ ]}{\Delta t}$*

As $\Delta t \rightarrow 0$ or

$r$ins. = - $\dfrac{d[R]}{dt}$ = $\dfrac{d[P]}{dt}$

Unit of rate of reaction:- mol L^{-1} s^{-1}

Average rate & Instantaneous rate

$$H_2O_2(aq) \rightarrow H_2O(l) + \tfrac{1}{2} O_2(g)$$

$$Rate = \frac{-\Delta[H_2O_2]}{\Delta t}$$

-(-2.32 M / 1360 s) = 1.7 x 10^{-3} M s^{-1}

-(-1.7 M / 2600 s) = 6 x 10^{-4} M s^{-1}

[H$_2$O$_2$], mol/L

Time, s

Initial rate ,Average rate over a time period. Instantaneous rate – slope of tangent lin.

Factors affecting the Rate of a Chemical Reaction

1-**Nature of reactant**: Ionic substance react much faster than covalent substances.

2-**Concencentration of Reactants** : Rate of reaction is directly proportional to conc. of reactants**(partial pressure in case of gaseous - phase reactions)**.

3-**Temperature** : Rate of reaction increases with increase in temperature.

4-**Presence of Catalyst** : A catalyst alters the Rate of a reaction.

5-**Surface Area of the Reactants**: Rate of rean.$\propto$ surface area.

6- **Radiations**

Rate Law or Rate Expression and Rate Constant

▶ The expression which relates of rate of reaction to concentration of the reactants is known as *rate law*. It is also called as *rate equation* or *rate expression*.

▶ Consider a general reaction

$$aA + bB \rightarrow cC + dD$$

▶ where a, b, c and d are the stoichiometric coefficients of reactants and products.

Rate Law or Rate Expression and Rate Constant

▶ **The rate expression for this reaction is -**

Rate of reaction $\propto$ $[A]^x[B]^y$ eqn.4

or

Rate of reaction $= k [A]^x[B]^y$ eqn.5

▶ **where exponents *x* and *y* may or may not be equal to the stoichiometric coefficients (a and b) of the reactants.**

Rate Law or Rate Expression and Rate Constant

▶ **Equation 5 can also be written as-**

$$-\frac{d[R]}{dt} = k[A]^x[B]^y$$

eqn.6

▶ **This form(eq.6) of equation (5) is known as the differential rate equation, where _k is a proportionality constant called_ _rate constant_ or _velocity constant_, or _specific reaction rate_.**

Rate Law or Rate Expression and Rate Constant

▶ Thus, **rate law is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation.**

▶ Note:*Rate law for any reaction cannot be predicted by merely looking at the balanced chemical equation, i.e., theoretically but must be determined experimentally.*

Rate Law or Rate Expression and Rate Constant

▶ **Rate Constant (k) : For a general reaction**

$$aA + bB \rightarrow cC + dD$$

> **Rate of reaction = k $[A]^x[B]^y$**

Where k is known as rate constant

When [A] = [B] = 1 mol/L, than

> **Rate of reaction = k**

thus rate constant of a chemical reaction may be defined as **the reaction rate when the concentration of each reactant is unity.**

Rate Law or Rate Expression and Rate Constant

➢ **The value of the rate constant is definite and constant for a particular reaction at a given temperature.**

➢ **The rate constant is independent of the concentration of reactants it depends only upon temperature and the presence of the catalyst.**

Order of a Reaction

▶ **The sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction.**

▶ **For a general reaction**

$$aA + bB \rightarrow cC + dD$$
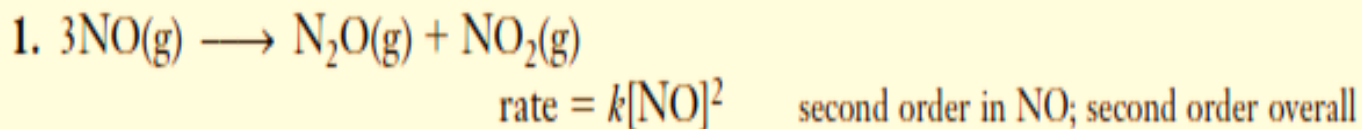
Let   Rate of reaction = k $[A]^x[B]^y$

Here ,

x = order of reaction w.r.t. A

y = order of reaction w.r.t. B

Overall order of reaction(n) = x + y

Order of a Reaction

Examples of observed rate laws for some reactions follow.

1. $3NO(g) \longrightarrow N_2O(g) + NO_2(g)$

   $rate = k[NO]^2$ second order in NO; second order overall

2. $2NO_2(g) + F_2(g) \longrightarrow 2NO_2F(g)$

   $rate = k[NO_2][F_2]$ first order in NO_2 and first order in F_2; second order overall

3. $2NO_2(g) \longrightarrow 2NO(g) + O_2(g)$ $rate = k[NO_2]^2$ second order in NO_2; second order overall

4. $H_2O_2(aq) + 3I^-(aq) + 2H^+(aq) \longrightarrow 2H_2O(\ell) + I_3^-(aq)$

   $rate = k[H_2O_2][I^-]$ first order in H_2O_2 and first order in I^-; zero order in H^+; second order overall
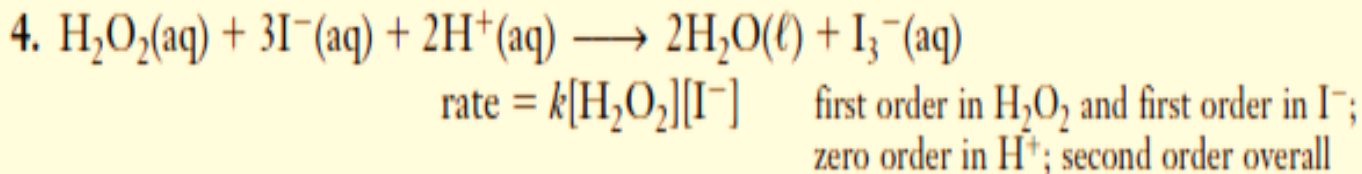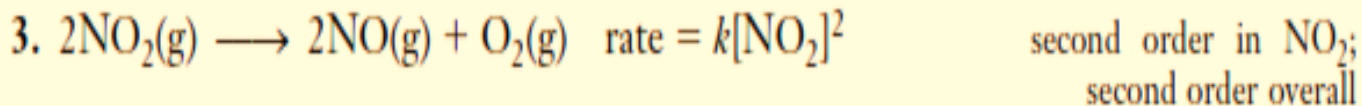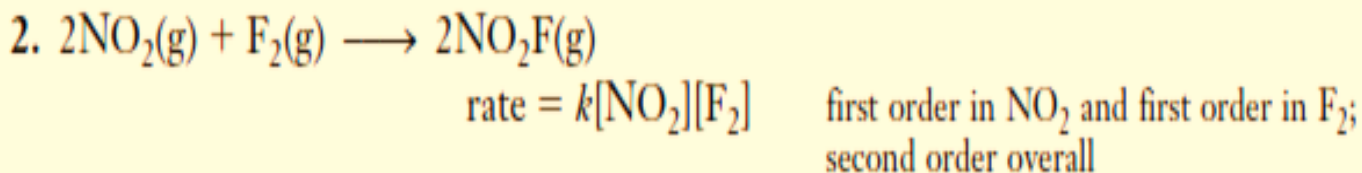
Order of a Reaction

➢ **Order of a reaction can be 0, 1, 2, 3 and even a fraction.**

➢ Depending upon order of reaction, reactions are termed as zero, first or second order reactions.

➢ **A zero order reaction means that the rate of reaction is independent of the concentration of reactants.**

➢ Order of reaction cannot be predicted by merely looking at the balanced chemical equation, i.e., theoretically but must be determined experimentally.

Order of a Reaction& Units of Rate Constant

For a nth order reaction-   A → Product

$$Rate = k [A]^n$$

$$k = \frac{Rate}{[A]^n} = \frac{concentration}{time} \times \frac{1}{(concentration)^n}$$

$$k = (concentration)^{1-n} \, time^{-1}$$

Reaction	Order	Units of rate constant
Zero order reaction	0	$\dfrac{\text{mol L}^{-1}}{\text{s}} \times \dfrac{1}{\left(\text{mol L}^{-1}\right)^0} = \text{mol L}^{-1}\text{s}^{-1}$
First order reaction	1	$\dfrac{\text{mol L}^{-1}}{\text{s}} \times \dfrac{1}{\left(\text{mol L}^{-1}\right)^1} = \text{s}^{-1}$
Second order reaction	2	$\dfrac{\text{mol L}^{-1}}{\text{s}} \times \dfrac{1}{\left(\text{mol L}^{-1}\right)^2} = \text{mol}^{-1}\text{L s}^{-1}$

Practice Problems

1. For a reaction, $A + B \rightarrow$ Product; the rate law is given by, $r = k[A]^{1/2}[B]^2$. What is the order of the reaction?

2. 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 ?

3. For the reaction

   A + B $\longrightarrow$ Products

   The following initial rates were obtained at various given initial concentrations

S. No	[A]	[B]	Rate (mol lt^{-1} sec^{-1})
1.	0.1	0.1	0.05
2.	0.2	0.1	0.10
3.	0.1	0.2	0.05

   Write rate law and find the rate constant of the above reaction.

Molecularity of a Reaction

The molecularity of a reaction is simply the number of reacting species (atoms, ions or molecules) involving is an elementary reaction that must collide simultaneously.

Let us consider the following reactions,

Reaction	Molecularity
(i) $NH_4 NO_2 \longrightarrow N_2 + 2H_2O$	1. (Unimolecular)
(ii) $2HI \longrightarrow H_2 + I_2$	2. (Bimolecular)
(iii) $2NO + O_2 \longrightarrow 2NO_2$	3. (Trimolecular)

Molecularity of a Reaction

Q.Why the reactions having molecularity greater than three is rare ?

Ans:- Since the chances of collision and reaction of more than three molecules at a time are very less, molecularity greater than three is rare.

Molecularity of a Reaction

Molecularity in case of complex reactions?

Molecularity of a complex reaction has no meaning. Actually a complex reaction is the series of two or more elementary reactions and thus, it completes in several steps. The slowest step or slowest reaction determines the rate of the reaction. Hence we find out the molecularity of the slowest elementary reaction of a complex reaction which is, in general, similar to the overall order of the complex reaction.

Molecularity vs. Order

Molecularity of Reaction	Order of Reaction
It is the number of atoms, ions or molecules that must collide with one another simultaneously so as to result into a chemical reaction.	It is the sum of the power of concentration terms on which the rate of reaction actually depends or it is the sum of powers of the concentration terms in the rate law equation.
Molecularity of reaction Cannot be zero.	Order of reaction can be zero.
It is a theoretical concept.	It is determined experimentally.
It is always a whole number.	It can even have fractional values.
The overall molecularity of complex reaction has no significance. Individual step has its own molecularity.	Order of reaction is for overall reaction.

Zero Order Reactions

Zero order reaction means that the rate of the reaction is proportional to zero power of the concentration of reactants. Consider the reaction,

$$R \rightarrow P$$
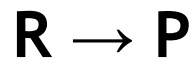
$$\text{Rate} = -\frac{d[R]}{dt} = k[R]^0$$

As any quantity raised to power zero is unity

$$\text{Rate} = -\frac{d[R]}{dt} = k \times 1$$

$$d[R] = -k \, dt$$

Integrated Rate Equations

Integrating both sides between proper limits

$$\int_{R_0}^{R} d[R] = -k \int_{0}^{t} dt$$

$$[R] - [R_o] = -kt$$

Or

$$[R_o] - [R] = kt$$

Or

$$k = \frac{[R_o] - [R]}{t}$$

Integrated Rate Equations
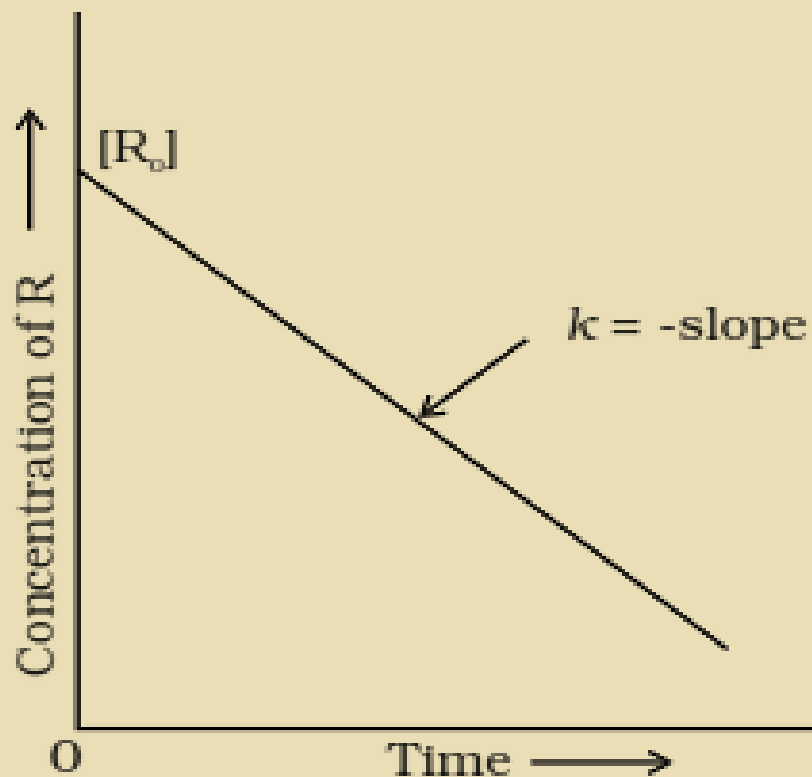
Fig. ' .: *Variation in the concentration vs time plot for a zero order reaction*

Integrated Rate Equations

First Order Reactions

First order reaction means that the rate of the reaction is proportional to first power of the concentration of reactants. Consider the reaction,

$$R \rightarrow P$$
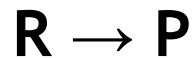
$$\text{Rate} = -\frac{d[R]}{dt} = k[R]$$

or $\quad \dfrac{d[R]}{[R]} = -kdt$

Integrated Rate Equations

Integrating both sides between proper limits

$$\int_{R_0}^{R} \frac{d[R]}{R} = -k \int_{0}^{t} dt$$

$$\ln[R] - \ln[R_o] = -kt$$

Or

$$\ln[R_o] - \ln[R] = kt$$

Or

$$kt = \ln \frac{[Ro]}{[R]}$$

$$k = \frac{1}{t} \ln \frac{[Ro]}{[R]}$$

Or

$$k = \frac{2.303}{t} \log_{10} \frac{[Ro]}{[R]}$$

Integrated Rate Equations

$$k = \frac{2.303}{t} \log_{10} \frac{[Ro]}{[R]}$$

$$\log \frac{[R]_0}{[R]} = \frac{kt}{2.303}$$
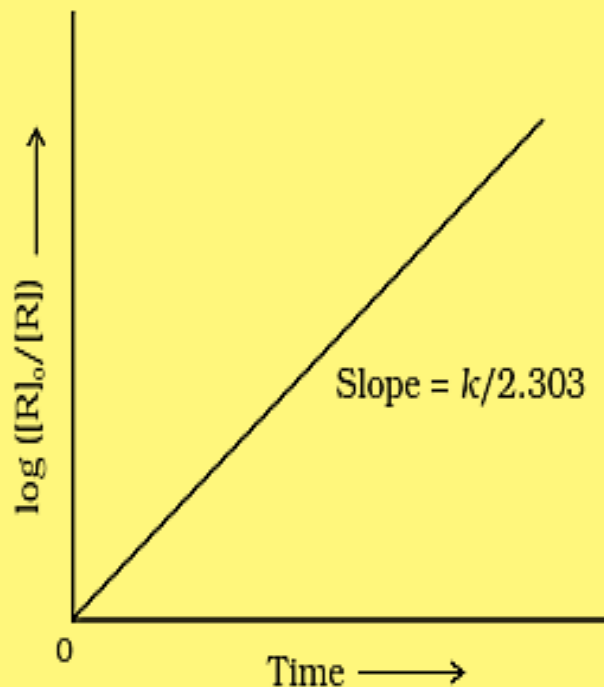
Fig. 4.5: Plot of log [R]₀/[R] vs time for a first order reaction

Integrated Rate Equations

Practice Problems

1. The thermal decomposition of HCOOH is a first order reaction with a rate constant of 2.4 x 10^{-3} s $^{-1}$ at a certain temperature. Calculate how long will it take for three-fourth (3/4) of initial quantity of HCOOH to decompose ? (log 0.25 = − 0.6021) [2011]

2.A first order reaction has a rate constant of 0.0051 min^{-1} . If we begin with 0.10 M conc. of the reactant, how much conc. of the reactant will remain is solution after 3 hrs? [2011,09]

3. The rate constant for a reaction of Zero order in A is 0.0030 mol L^{-1} s^{-1} . How long will it take for the initial conc. of A to fall from 0.10 M to .075 M ? [2010]

Half-Life of a Reaction

The half-life of a reaction is the time in which the concentration of a reactant is reduced to one-half of its initial concentration. It is represented as $t_{1/2}$

$t_{1/2}$ for a Zero Order Reactions

For a zero order reaction, rate constant is given by equation

$$k = \frac{[R]_0 - [R]}{t}$$

At $t = t_{1/2}$, $[R] = \frac{1}{2}[R]_0$

The rate constant at $t_{1/2}$ becomes

$$k = \frac{[R]_0 - 1/2[R]_0}{t_{1/2}}$$

$$t_{1/2} = \frac{[R]_0}{2k}$$

It is clear that $t_{1/2}$ for a zero order reaction is directly proportional to the initial concentration of the reactants and inversely proportional to the rate constant.

Half-Life of a Reaction

$t_{1/2}$ for a First Order Reactions

For the first order reaction,

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

at $t_{1/2}$ $[R] = \frac{[R]_0}{2}$

So, the above equation becomes

$$k = \frac{2.303}{t_{1/2}} \log \frac{[R]_0}{[R]/2}$$

or $t_{1/2} = \frac{2.303}{k} \log 2$

$$t_{1/2} = \frac{2.303}{k} \times 0.301$$

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

Thus for a first-order reaction, the half-life period is constant, i.e., it is independent of the initial concentration of the reacting species.

Practice Problems

1. A first order reaction takes 40 minutes for 30 % completion . calculate its $t_{1/2}$ value.
(2008,13)

2. The decomposition of phosphine PH_3 . Proceeds acc. to following eqn:

$$4\ PH_3\ (g)\quad ---> P_4(g)\ + 6H_2\ \ (g)\ \ ;$$

It is found that he reaction follows the following rate equation:

$$Rate\ \ = K\ [PH_3]\ \ ;$$

The half lite of PH_3 is 37.9 S at 120^0C
(a) How much time is required of $3/4^{th}$ of PH_3 to decompose ?
(2) What fraction of original sample of PH_3 remains behind after 1 minute ?
(2010,09)

Pseudo - first order reaction

Reactions which are not truly of the first order but under certain conditions reactions become that of first order are called pseudo unimolecular reaction.

For example: Hydrolysis of ester in presence of acid

$$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$$

From this reaction, the rate expression should be

$$r = k\ [ester]\ [H_2O]$$

Since, hydrolysis takes place in the excess of H_2O and concentration change of H_2O is negligible practically.

therefore, $r = k'\ [ester]$

Where $k' = k[H_2O].$

Methods of determining the order of a reaction

Integrated method

The equation which gives a constant value of k decides the order of reaction

Graphical method

The data are plotted acc to different integrated rate equations so as to yield a straight line .Slope gives the value of rate constant

Initial rate method

Concentration of one of the reactant is varied

Half life method

In this method we plot half life of the reactant versus conc. of the reactant.

Methods of determining the order of a reaction

Reaction Order	Differential rate law	Integrated rate law	Characteristic kinetics Plot	Slope of kinetics plot	Units of rate constant
Zero	$\dfrac{-d[A]}{dt} = k$	$[A]=[Ao]-kt$	$[A]$ vs t	$-k$	Mole l^{-1} sec^{-1}
First	$\dfrac{-d[A]}{dt} = k[A]$	$[A]=[Ao]e^{-kt}$	$ln[A]$ vs t	$-k$	sec^{-1}
Second	$\dfrac{-d[A]}{dt} = k[A]^2$	$A = \dfrac{[Ao]}{1+k+[A]}$	$1/[A]$ vs t	k	L mole^{-1} sec^{-1}

Graphical Representation
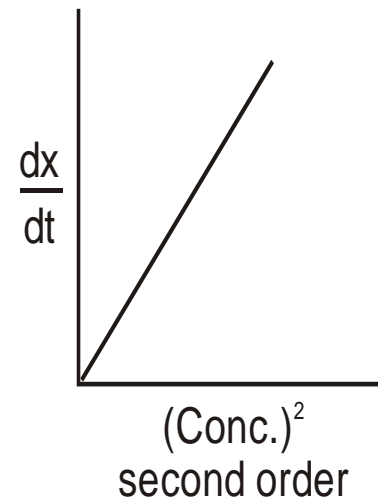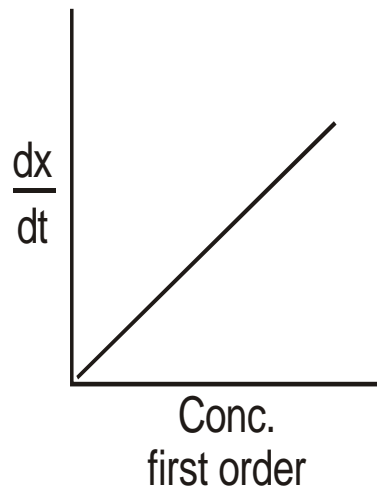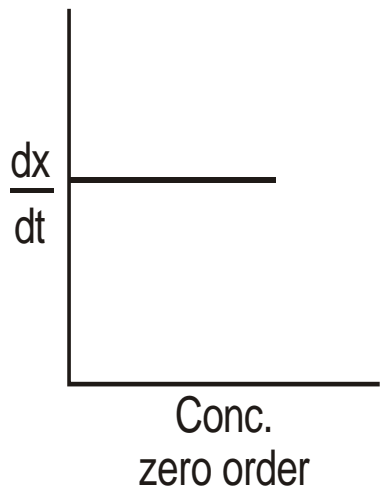
Graphical representation of rate versus concentrations

Graphical Representation

Conc. [A] — zero order

log [A] — first order

1/ [A] — second order
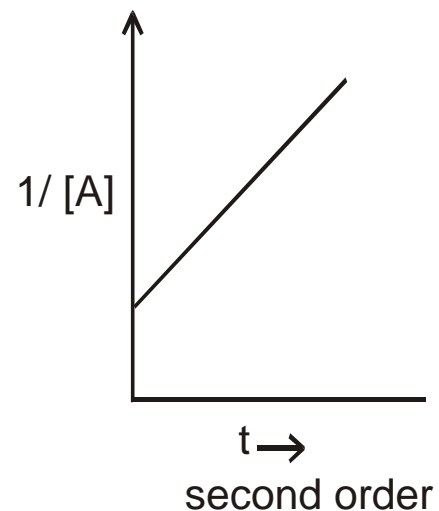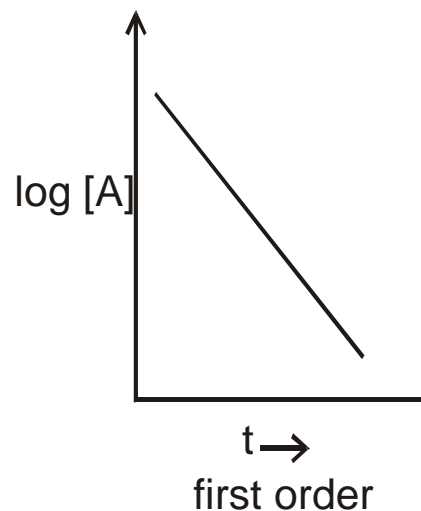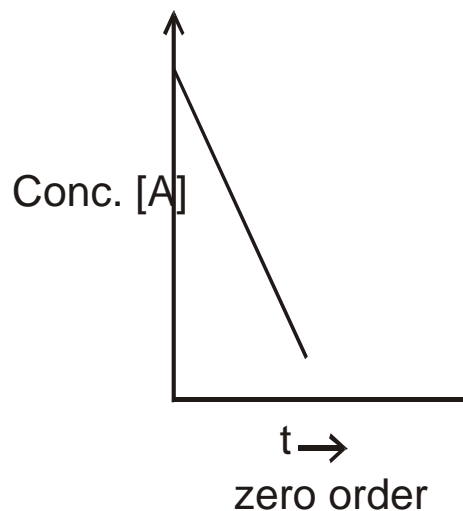
Graphical representation for concentration of integrated rate equation versus time
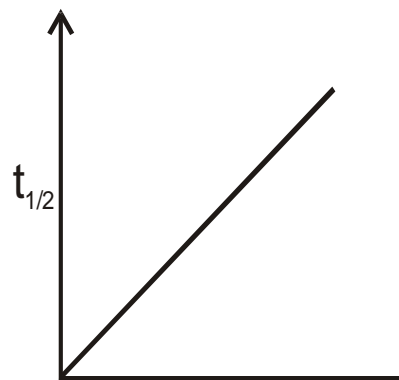
Initial rate method

- **This method involves the determination of the order of each reactant separately.**

- **To determine the order of a particular reactant, its concentration is varied keeping the concentrations of other reactants constant.**

- **In every experiment, we determine the initial rate of the reaction and observe the dependence of rate on that particular reactant.**

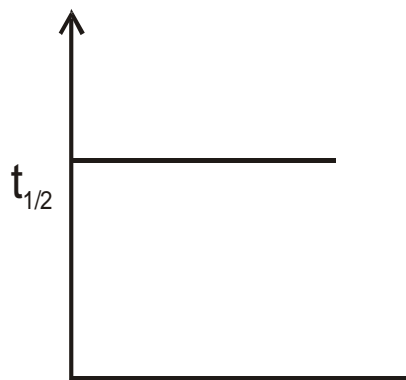$$r \propto [A]^m [B]^n \qquad \text{Keeping [B] constant}$$

$$\frac{r_1}{r_2} = \frac{[A_1]^m [B]^n}{[A_2]^m [B]^n}, \quad \frac{r_1}{r_2} = \left[\frac{[A_1]}{[A_2]}\right]^m$$
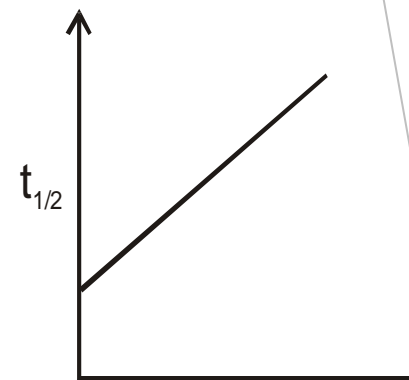
Half life method

$$t_{1/2} \; \alpha \; \frac{1}{[A]_0^{\,n-1}}$$

zero order   first order   second order

Graphical representation for half lives versus concentration

Illustrative Example

The half-life of a particular chemical reaction at two different initial concentrations 5×10^{-4} and 25×10^{-5} M are 2 and 16 hours. Calculate the order of reaction.

Solution:

$$\frac{(t_{1/2})_2}{(t_{1/2})_1} = \left\{ \frac{\left([A]_0\right)_1}{\left([A]_0\right)_2} \right\}^{n-1}$$

$$\Rightarrow \frac{16}{2} = \left(\frac{5 \times 10^{-4}}{25 \times 10^{-5}} \right)^{n-1} = (2)^{n-1}$$

$$\Rightarrow 8 = (2)^{n-1}$$

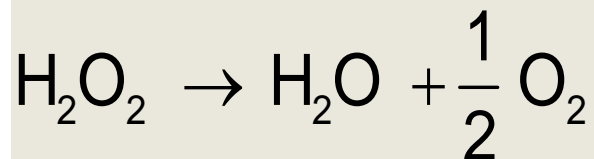$$\Rightarrow n - 1 = 3$$

$$\Rightarrow n = 4$$

Integrated method

In this method, we put the data into the integrated form of the rate laws and calculate the values of the rate constants for different kinetics of the reaction.

The order of the reaction is that one for which the value of rate constant is constant.

Some first order reactions

Decomposition of H$_2$O$_2$

$$H_2O_2 \rightarrow H_2O + \frac{1}{2} O_2$$

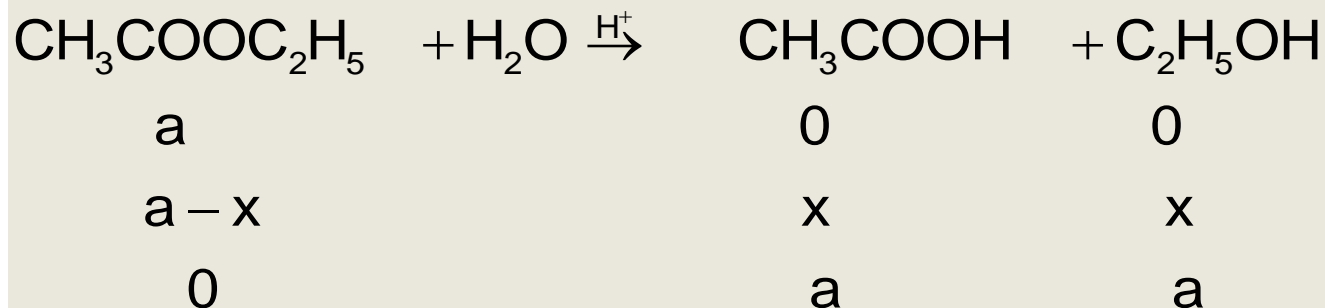**Let V$_o$ & V$_t$ be volume of KMnO$_4$ used during zero & time t respectively**

$$V \; \alpha \; a$$

$$V_t \; \alpha \; a - x$$

$$k = \frac{2.303}{t} \log \frac{V_o}{V_t}$$

Some first order reactions

Hydrolysis of ester

$$CH_3COOC_2H_5 \; + H_2O \xrightarrow{H^+} \; CH_3COOH \; + C_2H_5OH$$

a	0	0
a − x	x	x
0	a	a

Let V_0 , V_t be the volume of alkali required for titration during 0 ,t & infinite time

$V_O \quad \alpha \quad HCl$

$V_t \quad \alpha \quad HCl \; + x$

$V_\infty \quad \alpha \quad HCl \; + a$

$V_\infty - V_t \quad \alpha \quad a \; - x$

$\quad V_\infty \quad \alpha \quad a$

$$k \quad = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$$

Theories of chemical kinetics

1. Collision theory

2. Transition state theory

Collision theory

Reaction occurs when reacting species have sufficient energy to collide and proper orientation in space.

Energy barrier:
 The minimum energy which the colliding particles possess in order to bring about the chemical reaction is called threshold energy
The energy difference between threshold energy & average energy of reacting molecules is called activation energy

Orientation barrier:
Colliding molecules should be in their proper orientation at the time of collision.

Transition State Theory

In the **activated complex theory**, we consider two reactants approaching and their potential energy rising and reaching a maximum.
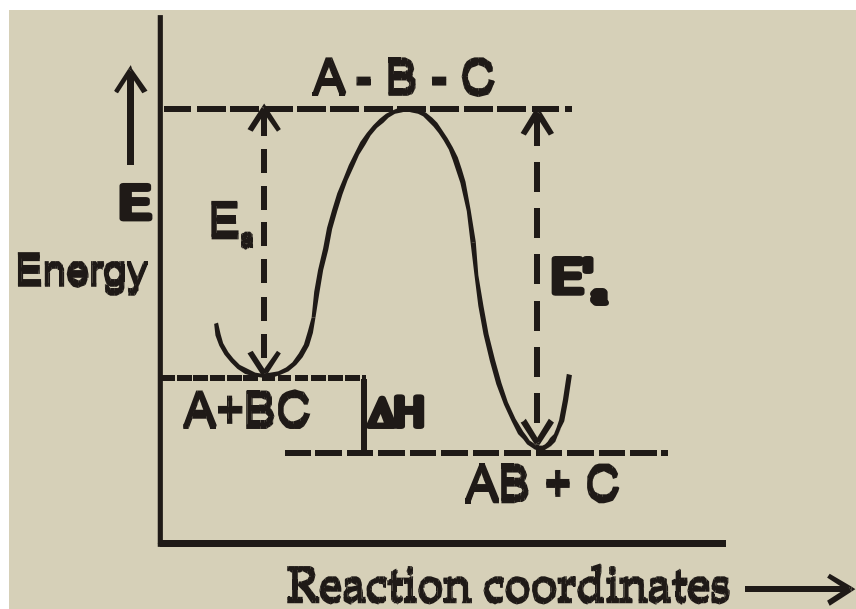
$$\Delta H = E_a - E_a{}^\grave{}$$

Activation energy - the energy needed to form activated complex is called energy of activation. It is very low for some reactions and very high for others.

Some Points about E_a

1. E_a is always positive.

2. The larger the value of E_a, the slower the rate of a reaction at a given temperature.

3. The larger the value of E_a, the steeper the slope of ($\ln k$) vs ($1/T$). A high activation energy corresponds to a reaction rate that is very sensitive to temperature.

Effect of temperature on rate of chemical reaction

Arrhenius equation

The temperature dependence of the rate of a chemical reaction can be accurately explained by Arrhenius equation
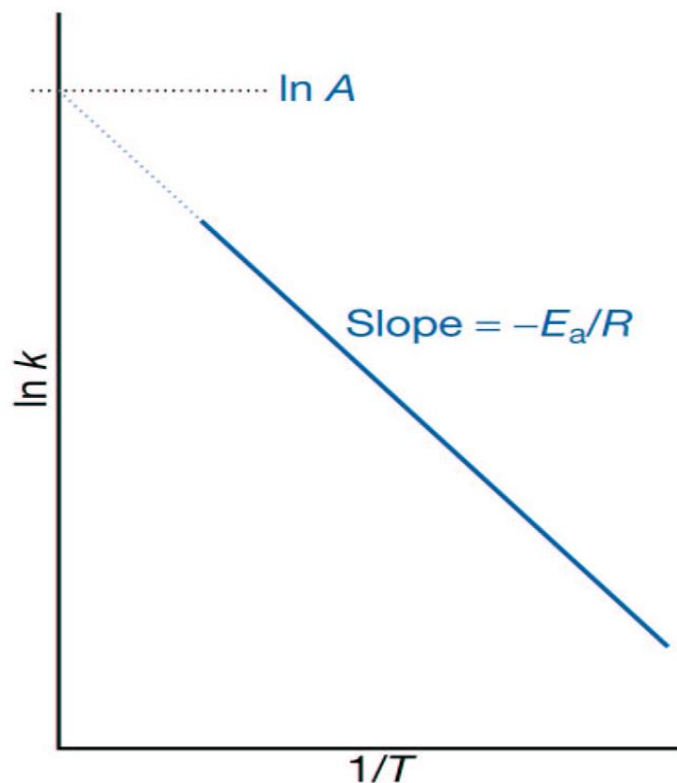
$$k = A.e^{-Ea/RT}$$

A is frequency factor or Arhenius constant, E_a is activation energy

or

$$\ln k = -\frac{E_a}{RT} + \ln A$$

Plot of log k vs 1/T is a straight line
& slope = $-E_a/2.303R$

Effect of temperature on rate of chemical reaction

Plot of ln k vs 1/T is a straight line & slope $=-E_a/R$

Effect of temperature on rate of chemical reaction

At temperature T_1

$$\ln\ k_1 = -\frac{E_a}{RT_1} + \ln A$$ Eqn.1

At temperature T_2

$$\ln\ k_2 = -\frac{E_a}{RT_2} + \ln A$$ Eqn.2

k_1 and k_2 are the values of rate constants at temperatures T_1 and T_2 respectively. Subtracting equation (2) from (1), we obtain
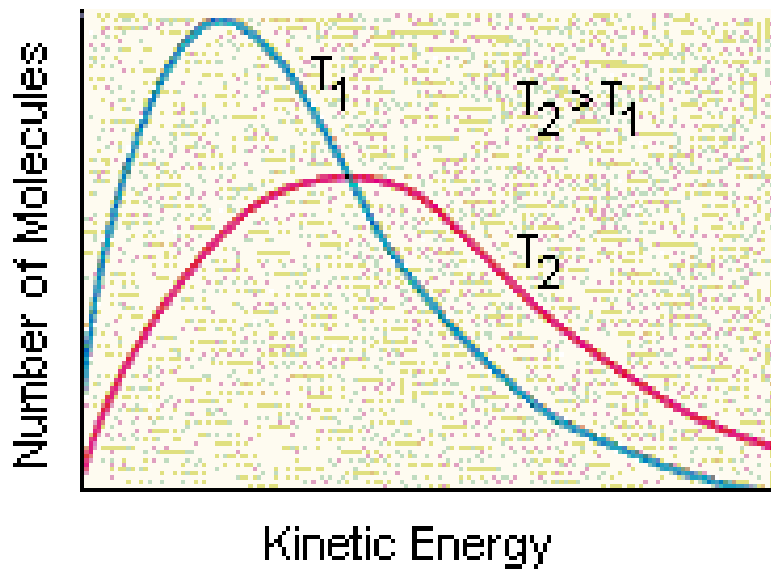
$$\ln\ k_2 - \ln\ k_1 = \frac{E_a}{RT_1} - \frac{E_a}{RT_2}$$

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Effect of temperature on rate of chemical reaction

$$k = A.e^{-Ea/RT}$$

$$\text{or } \log \frac{k_2}{k_1} = \frac{E_a}{2.303 \ R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

Illustrative Example

The specific reaction rate for a reaction increases by a factor 4 if the temperature is changed from 27º C to 47º C. Find the activation energy for the reaction.

Solution:

$$\log_{10}\left(\frac{K_2}{K_1}\right) = \frac{E_a}{2.303\,R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\log 4 = \frac{E_a}{2.303 \times 1.987}\left(\frac{320 - 300}{300 \times 320}\right)$$

$$E_a = \frac{0.60205 \times 2.303 \times 1.987 \times 300 \times 320}{20}$$

$$= 13222.98 \text{ cals}$$
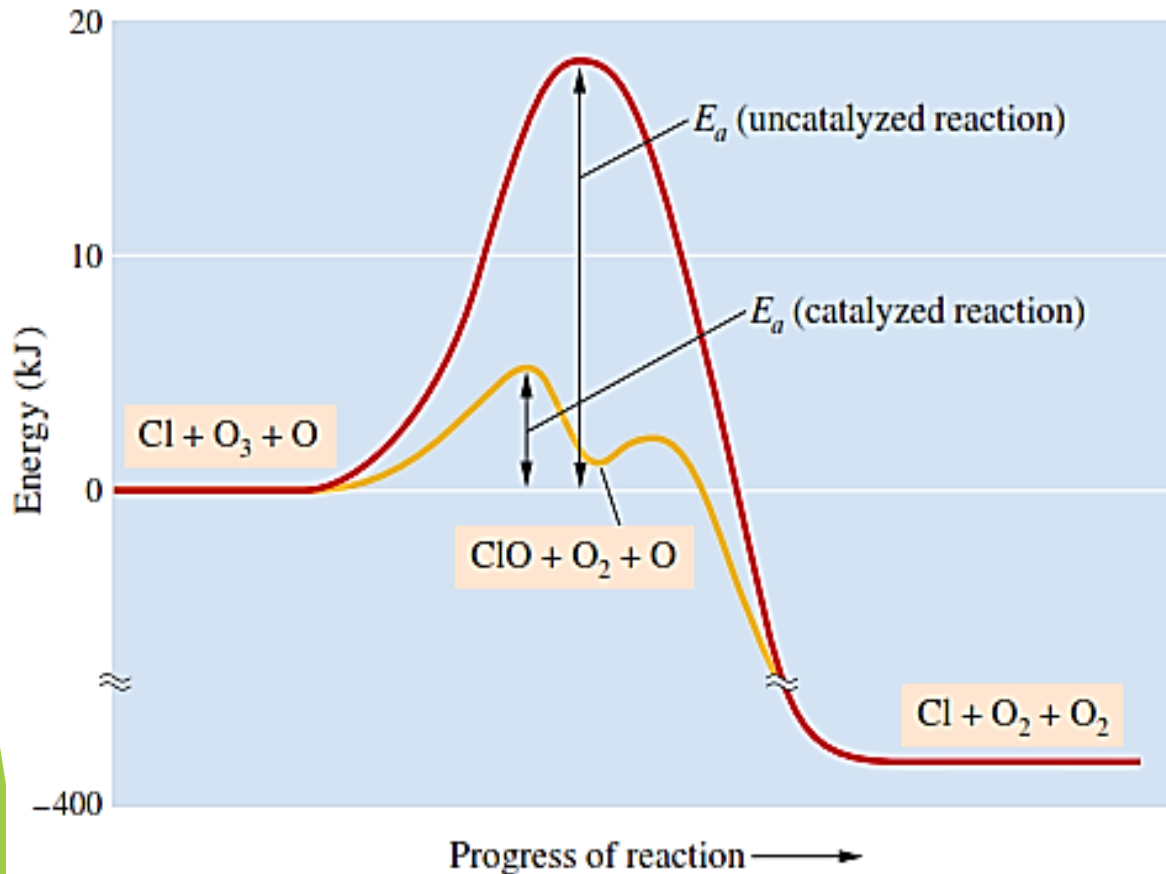
$$E_a = 13.311 \text{ K cals}$$

Catalysis

Catalyst: A substance that changes the rate of a reaction without being consumed in the reaction.

- Provides an easier way to react.
- Lower activation energy.
- Still make the same products.
- Enzymes are biological catalysts.

Inhibitor: A substance that **<u>de</u>creases the rate** of reaction (a negative catalyst).

How catalyst change reaction rate

Catalysts are the one way to lower the energy of activation for a particular reaction by altering the path of the reaction.

The lower activation energy allows the reaction to proceed faster.

Rate Law and Mechanism

A mechanism is a collection of elementary steps devised to explain the reaction in view of the observed rate law.

For the reaction, $2\ NO_2\ (g) + F_2\ (g) \rightarrow 2\ NO_2F\ (g)$, the rate law is,

$$rate = k\ [NO_2]\ [F_2]\ .$$

Can the elementary reaction be the same as the overall reaction?

If they were the same the rate law would have been

$$rate = k\ [NO_2]^2\ [F_2],$$

Therefore, the overall reaction is not an elementary reaction.

Rate-determining Step in a Mechanism

Slowest step:

The rate determining step is the slowest elementary step in a mechanism, and the rate law for this step is the rate law for the overall reaction.

Steady-state approximation:

The steady-state approximation is a general method for deriving rate laws when the relative speed cannot be identified. It is based on the assumption that the concentration of the intermediate is constant.

The hypothetical reaction $A_2 + B_2 \rightarrow$ follows the following mechanism

$A_2 \rightarrow A + A$ (fast)
$A + B_2 \rightarrow AB + B$ (slow)

$A + B \rightarrow AB$ (fast)

The order of the overall reaction is

(a) 0   (b) 1

(c) 2   (d) 3/2

Solution

The order depends on slowest step

$$\therefore \text{Rate(slow step)} = k[A][B_2]$$

$$= k[B_2].k`[A_2]^{1/2}$$

$$= k"[A_2]^{1/2}[B_2]$$

$$\text{Overall order} = \frac{1}{2} + 1 = \frac{3}{2}$$

Hence, the answer is (d).

At 380° C, the half-life period for the first order decomposition of H_2O_2 is 360 min. The energy of activation of the reaction is 200 kJ mole^{-1}. Calculate the time required for 75% decomposition at 450° C.

Solution

$$k_{380} = \frac{0.693}{360} = 1.925 \times 10^{-3} \text{ min}^{-1}$$

$$\therefore \log\frac{k_{450}}{k_{380}} = \frac{200 \times 103}{2.303 \times 8.314}\left(\frac{1}{653} - \frac{1}{723}\right)$$

$$\log\frac{k_{450}}{1.925 \times 10^{-3}} = 1.55 \quad \therefore k_{450} = 6.83 \times 10^{-2}$$

$$\therefore t_{\frac{1}{2}} \text{ at } 450°C = \frac{0.693}{6.83 \times 10^{-2}} = 10.15 \text{ min}$$

$$\therefore t_{75\%} = 2t_{\frac{1}{2}} = 20.29 \text{ min.}$$