CHEMICAL KINETICS

Chemical kinetics:

Rates of chemical reactions; Order of reactions; Rate constant; First order reactions; Temperature dependence of rate constant (Arrhenius equation).

INTRODUCTION:

In thermodynamics, we have studied whether a reaction will take place or not and if it does then up to what extent(chemical equilibrium).In this chapter we will look into how fast a reaction will take place and what are the different factors affecting this rate of chemical reaction.

RATE OF CHEMICAL REACTION:

The rate of change of concentration with time of different chemical species taking part in a chemical reaction is known as rate of reaction of that species.

Expression of Rate:

Consider the following reaction between CO and NO_2

$CO + NO_2 \rightarrow CO_2 + NO$

The equation shows that when one mole of CO reacts with one mole of NO_2, one mole each of CO_2 and NO are formed. The average rate of reaction can be expressed either by decrease of concentration of any one of the reactants (CO or NO_2) or by the increase in concentration of any one of the products (CO_2 or NO).

Thus, $-\Delta[CO]/\Delta t = -\Delta[NO_2]/\Delta t = \Delta[CO_2]/\Delta t = \Delta[NO]/\Delta t$

However, for the reaction, $2H_2O_2 \rightarrow 2H_2O + O_2$

It is observed that when 2 moles of H_2O_2 decompose, one mole of O_2 is formed in the same time interval. The rate of increase in the concentration of O_2, therefore, is half that of the disappearance of the concentration of H_2O_2 in the same time interval;

So $\Delta[O_2]/\Delta t = -1/2\Delta[H_2O_2]/\Delta t$

In general, for a reaction,

$n_1A + n_2B \rightarrow m_1C + m_2D$

The rate expression may be expressed as

$-1/n_1\Delta[A]\Delta t = -1/n2\Delta[B]/\Delta t = 1/m_1\Delta[C]/\Delta t = 1/m_2\Delta[D]/\Delta t$

Thus, for the reaction,

$H_2 + I_2 \leftrightarrow 2HI$

The rate may be expressed as

$-\Delta[H_2]/\Delta t = \Delta[I_2]/\Delta t = 1/2\Delta[HI]/\Delta t$

Similarly, for the decomposition of N_2O_5 in CCl_4 medium, the rate may be expressed as

$2N_2O_5 \rightarrow 4NO_2 + O_2$

$-1/2\Delta[N_2O_5]/\Delta t = 1/4\Delta[NO_2]/\Delta t = \Delta[O_2]/\Delta t$

Example: Decomposition of N_2O_5 is expressed by the equilibrium $2N_2O_5 \rightarrow 4NO_2 + O_2$

If during a certain time interval the rate of decomposition of N_2O_5 is 1.8×10^{-3} mol litre^{-1} min^{-1}, what will be the rates of formation of NO_2 and O_2 during the same interval?

Solution: The rate expression for the decomposition of N_2O_5 is

$-\Delta[N_2O_5]/\Delta t = 1/2\,\Delta[NO_2]/\Delta t = 2.\Delta[O_2]/\Delta t$

So $\Delta[NO_2]/\Delta t = 2\,\Delta[N_2O_5]/\Delta t = 2\times 1.8\times 10^{-5}$

$= 3.6\times 10^{-3}$ mol litre^{-1} min^{-1}

And $\Delta[O_2]/\Delta t = 1/2\,\Delta[N_2O_5]/\Delta t = 1/2\times 1.8\times 10^{-3}$

$= 0.9\times 10^{-3}$ mol litre^{-1} min^{-1}

[Rate is always positive and hence -$\Delta[N_2O_5]/\Delta t$ is taken positive.]

Instantaneous Rate

In chemical kinetic, the rate at any particular instant, i.e., instantaneous rate rather than the average rate over a time interval has much more practical application and importance. It is defined as the rate of change of concentration of any one of the reactants or products over a very small interval of time.

If we take infinitesimal small interval of time dt, it may be assumed that the rate is uniform through this interval; then if dx is amount of substance A transformed to B bring this interval, the rate of reaction at that instant is given as $-dx/dt$.

[In differential calculus, when Δt becomes very small and approaches zero, the ratio $\Delta[A]/\Delta t$ may be replaced by the derivative, $d[A]/dt$. that is

$r_{inst} = \lim_{\Delta t \to 0} -\Delta[A]/\Delta t = -d[A]/dt$]

On the other hand, if the rate of reaction is expressed in terms of the concentration of any of the products which goes on increasing, then rate of reaction at particular instant $= dx/dt$.

In general, for a reaction,

$n_1A + n_2B \rightarrow m_1C + m_2D$

The instantaneous rate may be expressed as

$r_{inst} = 1/n_1 \ d\{A)/dt = -1/n_2 = d(B)/dt = 1/m_1 \ d(C)/dt=1/m_2 \ d(D)/dt$

Experimental determination of instantaneous rate of reaction

In order to determine changes in concentration of reactants or products, it is customary to take small portions of the reaction mixture at suitable intervals of time and freeze them rapidly to about 0°C as to stop the reaction. The concentration is then measured with the help of a suitable method. In several cases concentration changes are measured by observing changes in certain physical propertied which are proportional to it such as optical densities, electrical conductivity, optical rotation, etc. A curve is plotted between concentration and time. A tangent is drawn to the curve at the point corresponding to time interval 't'. The slope of this tangent gives the instantaneous rate of reaction. This is shown in fig.8.2 (a)

Instantaneous rate of reaction = Slope of curve

(Intercept along ordinate)/(Intercept along abscissa) = $\Delta x/\Delta t$

Expression of Rate

Since the concentrations of the reactants keep on decreasing with time, the rate of reaction correspondingly decreases with time. Thus, the rate of reaction will depend on the stage considered during progress of the reaction. The rate of reaction is maximum at the initial stage and decreases with time. Theoretically, infinite time would be required for a reaction to complete. But the reaction rate becomes so slow after a certain time that for all practical purposes, the reaction can be considered to be completed. It is evident from fig 8.2 (b) that the rate of reaction is varying from moment to moment.

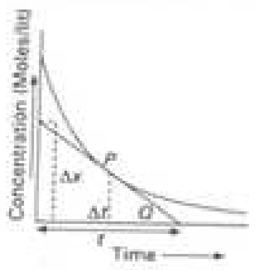


Fig. 8.2(a) Determination of rate of reaction

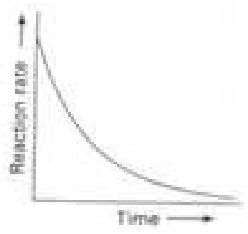


Fig. 3.2(b) Variation of rate

Reaction life time

It is defined as the time taken by a reaction to proceed to 98% of completion. The shorter the life time, the faster the reaction. Reaction life times are used to compare the various reaction. Reactions are also compared with half life periods. The half life period is defined as the time during which the concentration of a reactant is reduced to one half of its initial value or the time in which half of the reaction is completed. It is generally denoted by $t_{1/2}$. The shorter the half life period, the faster is the reaction.

Example: For each of the following reactions express the given rate of change of concentration of the reactant or product in terms of the rate of change of concentration of other reactants or products in that reaction.

(a) $H_2O_2 + 2H^+ + 2I^- \rightarrow I_3^- + 2H_2O; -\frac{d[I^-]}{dt} = ?; -\frac{d[H^+]}{dt} = ?$

(b) $16H^+ + 2mnO_4^- + 10I^- \rightarrow 2Mn^{2+} + 8H_2O + 5I_2; -\frac{d(MnO_4^-)}{dt} = ?$

(c) $4NH_3 + 5O_2 \rightarrow 4NO_2 + 6H_2O; -\frac{d(NH_3)}{dt} = ?$

Solution: We have

(a) $H_2O_2 + 2H^+ + 2I^- \rightarrow I_3^- + 2H_2O;$

The equality in this case is

$-d[H_2O_2]/dt = -1/2\ d[H^+]/dt = -1/2\ d[I_3^-]/dt = 1/2\ d[H_2O]/dt$

So, $-d[I^-]/dt = -3d[H_2O_2]/dt = -3/2\ d[H^+]/dt = 3d[I_3^-]/dt = 3/2\ d[H_2O]/dt$

and $-d[H^+]/dt = -2d[H_2O_2]/dt = -2/3\ d[I^-]/dt = 2d[I_3^-]/dt = d[H_2O]/dt$

(b) $16H^+ + 2mnO_4^- + 10I^- \rightarrow 2Mn^{2+} + 8H_2O + 5I_2;$

The equality in this case is

$-1/16\ d[H^+]/dt = -1/2\ d[MnO_4^-]/dt = -1/10\ d[I^-]/dt$

$= 1/2\ d[Mn^{2+}]/dt = 1/8\ d[H_2O]/(dt\ ) = 1/5\ d[I_2]/dt$

So $-d[MnO_4^-]/dt = -1/8\ d[H^+]/dt = -1/5\ d[I^-]/dt$

$-(d[Mn^{2+}])/dt = 1/4(d[H_2O])/dt = 2/5\ d[I_2]/dt$

(c) $4NH_3 + SO_2 \rightarrow 4NO_2 + 6H_2O$

The equality in this case is

$-1/4\ d[NH_3]/dt = -1/5\ d[O_2]/dt = 1/4\ d[NO_2]/dt = 1/6\ d[H_2O]/dt$

So $-d[NH_3]/dt = -4/3\ d[O_2]/dt = d[NO_2]/dt = d[H_2O]/dt$

Example: The following reaction was carried out in water: $Cl_2 + 2I^- \rightarrow I_2 + 2Cl^-$ the initial concentration of I^- was 0.25 mol L^{-1} and the concentration after 10 minutes 0.23 mol L^{-1}. Calculate the rate of disappearance of I^- and appearance of I_2.

Solution: $\Delta[I^-] = [I^-]_{final} - [I^-]_{initial}$

$= 0.23 - 0.25 = -0.02$ mol L^{-1}

$\Delta t = 10 - 0 = 10$ min

$-\Delta[I^-]/\Delta t = -((-0.02))/10 = 0.002$ mol L^{-1} min^{-1}

Rate of appearance of $I_2 = 1/2\ \Delta[I^-]/\Delta t = 0.002/2$

$= 0.001$ mol L^{-1} min^{-1}

$= 1 \times 10^{-3}$ mol L^{-1} min^{-1}

Factors Affecting Rate Of Reaction

1. Concentration
2. Temperature
3. Nature of reactants & products
4. Catalyst

5. pH of the solution
6. Dielectric constant of the medium
7. Radiation
8. Pressure
9. Electric and Magnetic field

ORDER OF REACTION

Let us consider a good reaction:

$m_1A + m_2B + m_3C \rightarrow$ product

Let active moles of 'A', 'B' and 'C' be 'α', 'β' and 'γ' respectively. Then, rate of reaction may be given as:

Rate $= k[A]^{\alpha} [B]^{\beta} [C]^{\gamma}$

Sum of powers of concentration terms involved in rate law expression is called order of reaction.

$\alpha + \beta + \gamma$ order.

When $\alpha + \beta + \gamma = m_1 + m_2 + m_3$, then

Order of reaction = molecularity of reaction

Order is an experimentally determined quantity. It may be equal to zero, positive, negative, fractional and greater than three. Infinite and imaginary values are not possible.

Examples: (i) $2H_2O_2 \rightarrow 2H_2O + O_2$ (observed from law of mass action)

Step 1: $H_2O_2 \rightarrow H_2O + [O]$ [slow]

Step 2: $[O] + [O] \rightarrow O_2$ (fast)

Actual rate $-dx/dt = k[H_2O_2]$

Thus, order of reactions in unity

(ii) $2NO_2 + F_2 \rightarrow 2NO_2F$

Rate law from law of mass action:

$-dx/dt = k[NO_2][F_2]$

Experimentally observed rate law:

$-dx/dt = k[NO_2][F_2]$

Slowest step is $NO_2 + F_2 \rightarrow NO_2F + [F]$

Thus, order of reaction $= 1 + 1 = 2$

(iii) $CH_3CHO \rightarrow CH_4 + CO$

The rate equation derived from experimental data is found to be

$-dx/dt = k[CH_3CHO]^{1.5}$

The order of reaction is 1.5

MOLECULARITY OF REACTION

In general, molecularity of simple reactions is equal to the sum of the number of molecules of reactants involved in the balanced stoichiometric equation.

OR

The molecularity of a reaction is the number of reactant molecules taking part in a single step of the reaction.

e.g, $PCl_5 \rightarrow PCl_3 + Cl_2$ (Unimolecular)

$2HI \rightarrow H_2 + I_2$ (Bimolecular)

$2SO_2 + O_2 \rightarrow 2SO_3$ (Trimolecular)

$NO + O_3 \rightarrow NO_2 + O_2$ (Bimolecular)

$2CO + O_2 \rightarrow 2CO_2$ (Trimolecular)

Note:

- Molecularity is a theoretical concept.
- Molecularity cannot be zero, -ve, fractional, infinite and imaginary.
- Molecularity cannot be greater than three because more than three molecules may not mutually collide with each other.
- For complex reaction molecularity has no meaning.

INTEGRATED RATE LAWS:

Zero Order Reactions:

For a zero order reaction,

General rate law is,

Rate $=k[\text{conc}]^0$=conctant

If C_0 is the initial concentration of a reactant and C_t is the concentration at time 't' then

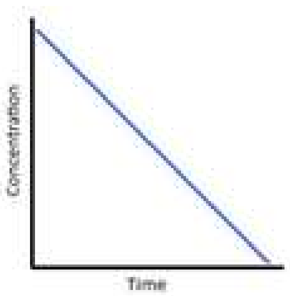
Rate=$k=(C_0 - C_t)/t$

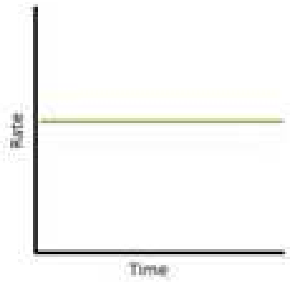
Or $C_t = C_0 - kt$

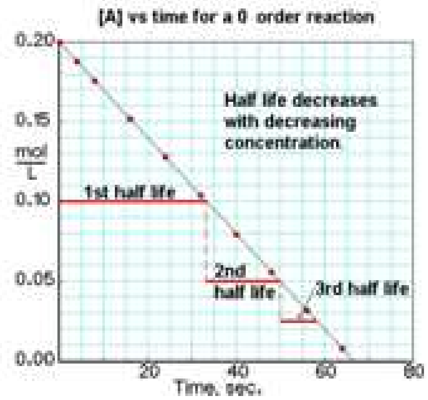
Units Of k=mole lit^{-1} sec^{-1}.

$T_{1/2}$(half life period)=$C_0/2k$ (Remember)

Examples: Photochemical Reaction: Hydrogen gas and chlorine gas forms hydrogen chloride gas with light. Catalytic Reaction: Ammonia gas decomposes into nitrogen gas and hydrogen gas with a platinum catalyst:







Practice Questions:

1. Using the integrated form of the rate law, determine the rate constant k of a zero-order reaction if the initial concentration of substance A is 1.5 M and after 120 seconds the concentration of substance A is 0.75 M.

2. Using the substance from the previous problem, what is the half-life of substance A if its original concentration is 1.2 M?

3. If the original concentration is reduced to 1.0 M in the previous problem, does the half-life decrease, increase, or stay the same? If the half-life changes what is the new half-life?

4. Given are the rate constants k of three different reactions:

Reaction A: k = 2.3 M-1s-1

Reaction B: k = 1.8 Ms-1

Reaction C: k = 0.75 s-1

Which reaction represents a zero-order reaction?

5. True/False: If the rate of a zero-order reaction is plotted as a function of time, the graph is a strait line where rate = k.

Answers:

1. The rate constant k is 0.00624 M/s

2. The half-life is 96 seconds.

3. Since this is a zero-order reaction, the half-life is dependent on the concentration. In this instance, the half-life is decreased when the original concentration is reduced to 1.0 M. The new half-life is 80 seconds.

4. Reaction B represents a zero-order reaction because the units are in M/s. Zero-order reactions always have rate constants that are represented by molars per unit of time. Higher order reactions, however, require the rate constant to be represented in different units.

5. True. When using the rate function $rate = k[A]^n$, n is equal to zero in zero-order reactions. Therefore, rate is equal to the rate constant k.

First Order Reaction:

Let a 1st order reaction is

A -------> Products

Conc. a 0 t=0

a-x x t='t'

Let dx/dt be the rate of reaction at time 't':

$dx/dt=k(a-x)^1$

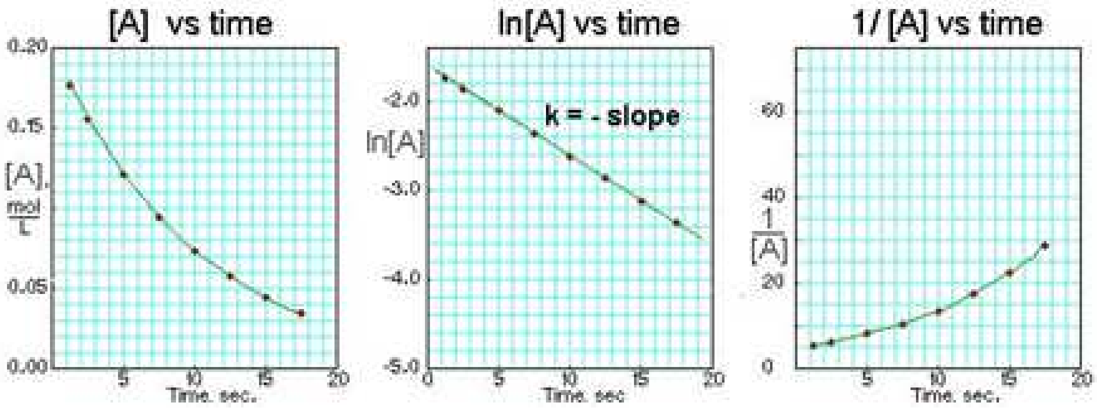
or $dx/(a-x)=k\,dt$

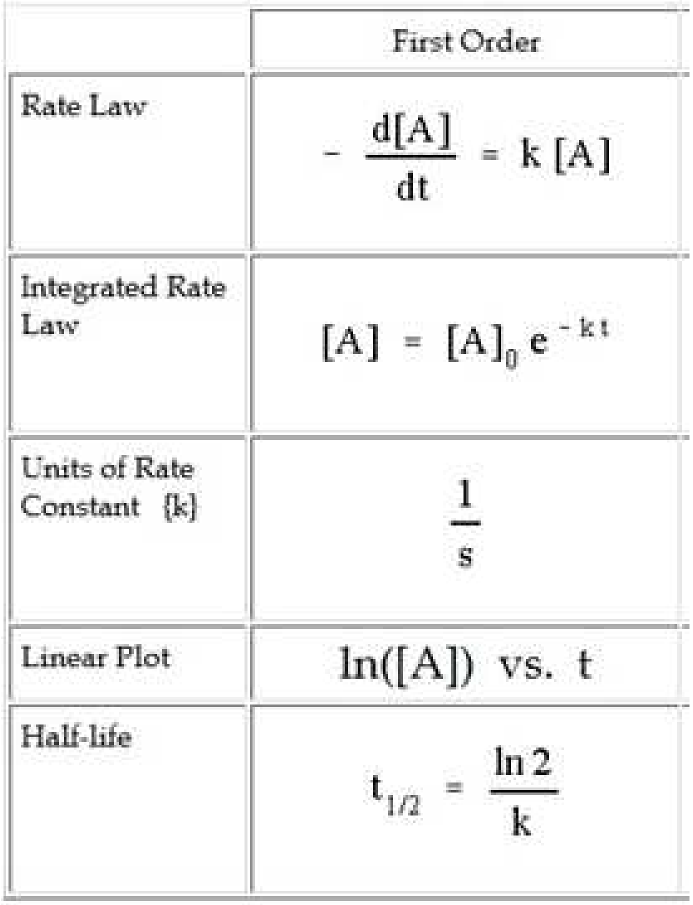
On solving $t=\frac{2.303}{k}\log\left(\frac{a}{a-x}\right)$

$$k = \frac{2.303}{k}\log\left(\frac{C_0}{C_t}\right)$$

Half Life Time ($t_{1/2}$):

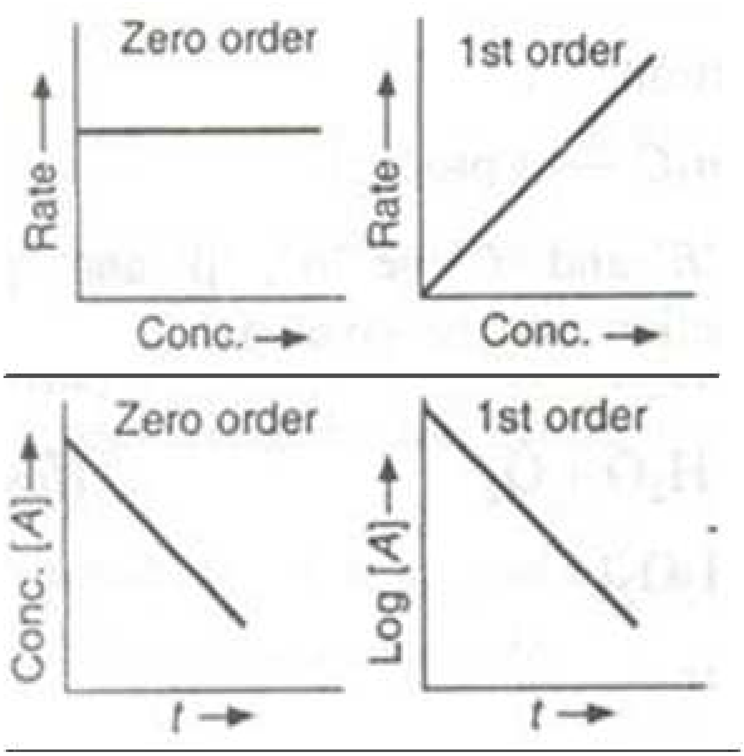
$$k = \frac{2.303}{t_{1/2}}\log\left(\frac{2C_0}{C_0}\right) = \frac{\ln 2}{k} = \frac{0.693}{k} \quad \text{(Remember)}$$





	First Order
Rate Law	$-\frac{d[A]}{dt} = k[A]$
Integrated Rate Law	$[A] = [A]_0 e^{-kt}$
Units of Rate Constant (k)	$\frac{1}{s}$
Linear Plot	$\ln([A])$ vs. t
Half-life	$t_{1/2} = \frac{\ln 2}{k}$

GRAPHICAL COMPARISION OF DIFFERENT ORDERS:



Examples: Calculate the average rate of decomposition of N_2O_5 of the reaction

$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

During the time interval $t = 600s$ to $t = 1200s$. Use the following data:

Time	$[N_2O_5]$
600s	1.24×10^{-2} M
1200s	0.93×10^{-2} M

Assume it as first order reaction.

Solution: We know that the decomposition of N_2O_5 is a first order reaction. Therefore,

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$\text{or } k = \frac{2.303}{(1200-600)} \log \frac{1.24 \times 10^{-2}}{0.93 \times 10^{-2}}$$

Now rate of decomposition at 600s

$$-\frac{dC}{dt} = kC_1 = (4.8 \times 10^{-4} s^{-1})\ (1.24 \times 10^{-2} M)$$

$$= 5.95 \times 10^{-6}\ M\ s^{-1}$$

Similarly rate of decomposition at 1200s

$= (4.8 \times 10^{-4}\ s^{-1})\ (0.93 \times 10^{-2}\ M) = 4.46 \times 10^{-6}\ M\ s^{-1}$

Average rate of decomposition $= \dfrac{5.95\times10^{-6} + 4.46\times10^{-6}}{2}\ Ms^{-1}$

$= 5.205 \times 10^{-6}\ Ms^{-1}$

Example: Find out the order of reaction under following conditions:

a) When $t_{1/2}$ of the reaction is halved as initial concentration of reactant is doubled.

b) When $t_{1/2}$ of the reaction is doubled as the initial concentration of reactant is doubled.

c) When $t_{1/2}$ of the reaction remains unchanged as initial concentration of reactant is doubled.

Solution: a) In present case

$t_{1/2}\ \alpha\ \dfrac{1}{a_o^{n-1}}$ [a_0 = initial concentration] ...(1)

$\dfrac{1}{2}\times t_{1/2}\ \alpha\ \dfrac{1}{(2a_0)^{n-1}}$ ...(2)

∴ On dividing equation (1) by equation (2)

$2 = 2^{n-1}$

$n - 1 = 1$

or $n = 2$

b) In this case

$2 \times t_{1/2}\ \alpha\ \dfrac{1}{(2a_0)^{n-1}}$ ...(3)

On dividing equation (1) by equation (2)

$\dfrac{1}{2} = 2^{n-1}$

$0.5 = 2^{n-1}$

$\log 0.5 = (n - 1) \log 2$

$\therefore n - 1 = \dfrac{\log 0.5}{\log 2}$

$n - 1 = -1$

$\therefore n = 0$

c) In this case

$$t_{1/2} \propto \frac{1}{(2a_0)^{n-1}} \qquad ...(4)$$

On dividing equation (1) by equation (4)

$1 = 2^{n-1}$

$\log 1 = (n-1)\log 2$

$$\therefore n-1 = \frac{\log 1}{\log 2} = 0$$

or n = 1

Example: We are given a first order reaction

A → B+C where we assume that A,B and C are gases.The data given to us is

Time	0	t
Partial pressure of A	P_1	P_2

And we have to find the rate constant of the reaction.

Solution: Since A is a gas and assuming it to be ideal, we can state that P_A = [A]RT [From PV = nRT]. ∴ at t = 0, $P_1 = [A]_o RT$ and at t = t, $P_2 = [A]_t RT$. Thus the ratio of the concentration of A at two different time intervals is equal to the ratio of its partial pressure at those same time intervals.

$$\therefore \frac{[A]_o}{[A]_t} = \frac{P_1}{P_2}$$

$$\therefore \mathbf{k} = \frac{1}{t}\ln\frac{P_1}{P_2}$$

Example: Now we consider the same reaction with different set of data

$$A \longrightarrow B + C$$

Time	0	t
Total pressure of A +B+C	P_1	P_2

Find k.

Solution: In this we are given total pressure of the system at these time intervals. The total pressure obviously includes the pressure of A, B and C. At t = 0, the system would only have A. Therefore the total pressure at t = 0 would be the initial pressure of A $\therefore$ P_1 is the initial pressure of A. At time t let us assume that same moles of A decomposed to give B and C because of which its pressure is reduced by an amount x while that of B and C is increased by x each. That is

	A $\longrightarrow$	B +	C
Initial	P_1	0	0
At time t	$P_1 - x$	x	x

$\therefore$ total pressure at time t = $P_1 + x = P_2$ $\Rightarrow x = P_2 - P_1$

Now the pressure of A at time t would be $P_1 - x = P_1 - (P_2 - P_1) = 2P_1 - P_2$

$$\therefore k = \frac{1}{t}\ln\frac{[A]_0}{[A]_t} = \frac{1}{t}\ln\frac{P_1}{(2P_1 - P_2)}$$

Example: In this case we have

$A \longrightarrow B + C$

Time	t	∞
Total pressure of A+B+C	P_2	P_3

Find k.

Solution: Here ∞ means that the reaction is complete. Now we have

	A $\longrightarrow$	B +	C
At t=0	P_1	0	0
At t =t	$(P_1 - x)$	x	x
At t =∞	0	P_1	P_1

$\therefore 2P_1 = P_3$

$$\Rightarrow P_1 = \frac{P_3}{2}$$

At time t,

$P_1 + x = P_2$

$$\Rightarrow \frac{P_3}{2} + x = P_2$$

$$\Rightarrow x = P_2 - \frac{P_3}{2}$$

$$\Rightarrow P_1 - x = \frac{P_3}{2} - (P_2 - \frac{P_3}{2}) = P_3 - P_2$$

$$\therefore \ k = \frac{1}{t}\ln\frac{[A]_0}{[A]_t} = \frac{1}{t}\ln\frac{P_3/2}{(P_3 - P_2)} = \mathbf{\frac{1}{t}\ln\frac{P_3}{2(P_3 - P_2)}}$$

Example: $A \longrightarrow B + C$

Time	T	∞
Total pressure of (B+C)	P_2	P_3

Find k.

Solution: $A \longrightarrow B + C$

At t=0 P_1 0

0

At t =t $P_1 -$ x x

x

At t = ∞ 0 P_1 P_1

$\therefore 2P_1 = P_3$

$$\Rightarrow P_1 = \frac{P_3}{2}$$

$2x = P_2$

$$\Rightarrow x = \frac{P_2}{2}$$

$$\therefore P_1 - x = \frac{P_3}{2} - \frac{P_2}{2} = \frac{P_3 - P_2}{2}$$

$$\therefore k = \frac{1}{t}\ln\frac{[A]_0}{[A]_t} = \mathbf{\frac{1}{t}\ln\frac{P_3}{(P_3 - P_2)}}$$

METHODS TO DETERMINE ORDER OF REACTION:

1. Method Of Half Lives:

The half lives of each order is unique so by comparing half lives we can determine order for n^{th} order reaction:

$$T_{1/2} \propto \frac{1}{[R_0]^{n-1}}$$

2. Ostwald's isolation method:

This method is useful for reaction which involve a large number of reactants. In this method, the concentration of all the reactants are taken in large excess exception that of one, so if

$Rate=k[A]^a[B]^b[C]^c \;=k_0[A]^a$

COLLISION THEORY OF REACTION RATE (ARRHENIUS THEORY OF REACTION RATE)

(1) A chemical reaction takes place due to collision among reactant molecules. The number of collisions taking place per second per unit volume of the reaction mixture is known as collision frequency (Z). The value of collision frequency is very high, of the order of 10^{25} to 10^{28} in case of binary collisions.

(2) Every collision does not bring a chemical change. The collisions that actually produce the products are effective collisions. The effective collisions which bring chemical change are few in comparison to the form a product are ineffective elastic collisions, i.e., molecules just collide and disperse in different directions with different velocities. For a collision to be effective, the following two barriers are to be cleared.

Energy barrier

The minimum amount of energy which the colliding molecules must possess as to make the chemical reaction to occur, is known as threshold energy.

Thus, every chemical reaction whether exothermic or endothermic has an energy barrier which has to be overcome before reactants can be transformed into products. If the reactant molecules have sufficient energy, they can reach the peak of the energy barrier after collision and then they can go to the right side of the slope and consequently change into products. If the activation energy for a reaction is low, the fraction of effective collisions will be large and the reaction will be fast. On the other hand, if the activation energy is high, then fraction of effective collisions will be small and the reaction will be slow. When temperature is increased, the number of active molecules increases, i.e., the number of effective collisions will increase and the rate of reaction will increase.

Activation energy $E_a = E_{(activated\ complex)} - E_{(ground\ state)}$

ΔH = activation energy of forward reaction - activation energy of background reactions

Orientation barrier: Energy alone does not determine the effectiveness of the collision. The reacting molecules must collide in proper manner if the reaction is to occur. This has been shown in Fig8.5.

Rate of reaction is directly proportional to the number of effective collisions.

Rate = dx/dt = collision frequency × factor of effective collisions

$= z \times f$

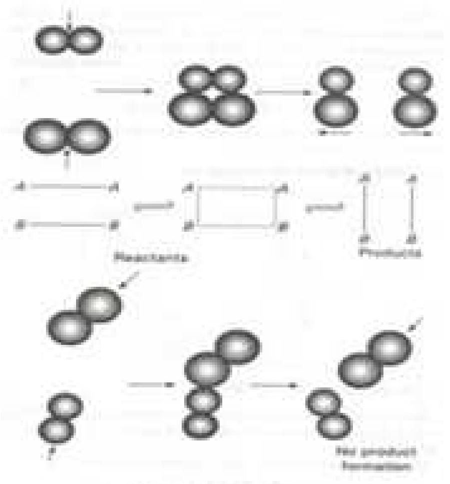


Fig. 8.5 Orientation of collisions

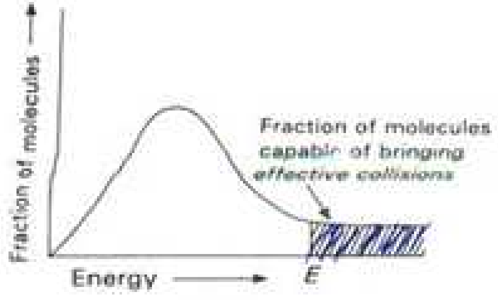


Fig. 8.3

In the graph 'E' corresponds to minimum or threshold energy for effective collision in a hypothetical reaction.

There is an energy barrier for each reaction. The reacting species must be provided with sufficient energy as to cross the energy barrier.

The minimum amount of energy required by reactant molecules to participate in a reaction is called activation energy.

Activation energy = threshold energy - average kinetic energy of reacting molecules

Threshold energy = initial potential energy of reactant molecules + activation energy.

A collision between high energy molecules overcomes the forces of repulsion and brings the formation of an unstable molecule cluster, called the activated complex. The life span of an activated complex is very small. Thus, the activated complex breaks either into reactants again or new substances, i.e., products. The activation energy (E_a) depends upon the nature of chemical bonds undergoing rupture and is independent of enthalpies of reactants and products. The energy changes during exothermic and endothermic reactions versus the progress of the reaction.

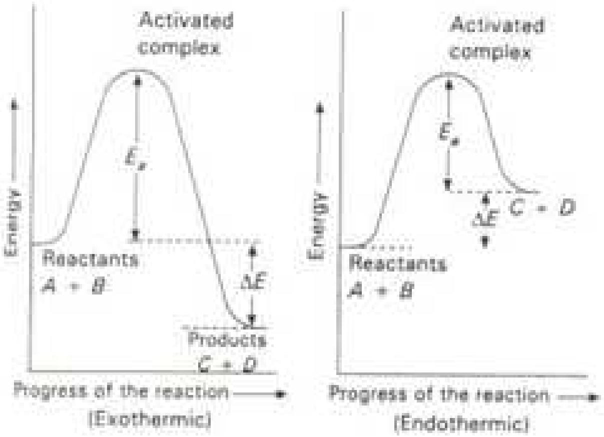


Fig. 8.4 Activation energy of exothermic and endothermic reaction

Assignments

1. The half – life period of a first order reaction is 30 minutes. Calculate the specific reaction rate of the reaction. What fraction of the reactant remains after 70 minutes?
2. A first – order reaction is 20% complete in 10 minutes. Calculate (i) specific rate constant of the reaction, and (ii) the time taken for the reaction to go to 75% completion.
3. The specific reaction rate of a first – order reaction is $0.02 s^{-1}$. The initial concentration of the reactant is 2 moles / litre. Calculate (a) initial rate, and (b) rate after 60 seconds.

4. The rate law for the reaction $A + B \rightarrow$ product is rate $= -\frac{d[A]}{dt} = +\frac{d[Product]}{dt} = k[A]^{\frac{3}{2}}$. Find the order.
5. Radioactive decay is a first order process. Radioactive carbon in wood sample decays with a half – life of 5770 years. What is the rate constant (in year – ^{1}) for the decay? What fraction would remain after 11540 years?
6. While studying the decomposition of N_2O_5 it is observed that a plot of logarithm of its partial pressure versus time is linear. What kinetic parameters can be obtained from this observation?
7. The rate of a reaction, $A + B \rightarrow$ Product, is given below as a function of different initial concentrations of A and B.

	[A] (moles/litre)	[B] (moles/litre)	Initial rate (moles/litre/min)
(i)	0.01	0.01	0.005
(ii)	0.02	0.01	0.010
(iii)	0.01	0.02	0.005

Determine the order of the reaction with respect to A and with respect to B. What is the half – life of A in the reaction?

8. For the reaction $2NO + Cl_2 \rightarrow 2NOCl$, it is found that doubling the concentration of both reactants increases the rate by a factor of 8, but doubling the Cl_2 concentration alone, only doubles the rate. What is the order of the reaction with respect to NO and Cl_2?
9. In a reaction $2N_2O_5 \rightarrow 4NO_2 + O_2$, the rate can be expressed as

   (i) $-\frac{d[N_2O_5]}{dt} = k_1[N_2O_5]$ (ii) $\frac{d[NO_2]}{dt} = k_2[N_2O_5]$ (iii) $\frac{d[O_2]}{dt} = k_3[N_2O_5]$

   (ii) How are k_1, k_2 and k_3 related?
10. The reaction, $2N_2O_5 \rightarrow 4NO_2 + O_2$, is forming NO_2 at the rate of 0.0072 mole/L/s at some time

    (a) What is the rate of change of $[O_2]$ at this time?
    (b) What is the rate of change of $[N_2O_5]$ at this time?
    (c) What is the rate of reaction at this time?
11. At some temperature, the rate constant for the decomposition of HI on a gold surface is 0.08 $M.s^{-1}$

    $$2HI(g) \rightarrow H_2(g) + I_2(g)$$

    What is the order of the reaction? How long will it take for the concentration of HI to drop from 1.50 M to 0.30 M?

12. The rate law of a chemical reaction $2NO(g) + O_2(g) = 2NO_2(g)$ is given as rate $= k[NO]^2[O_2]$. How will the rate of the reaction change if the volume of the reaction vessel is reduced to one – fourth of its initial volume?
13. The following data were obtained for a gaseous reaction: $A_2 + 2B \rightarrow 2AB$

$[A_2]$ mole L^{-1}	$[B]$ mole L^{-1}	$-\frac{d[A_2]}{dt}$ mole/lit/min
(i) 0.10	0.01	0.072
(ii) 0.10	0.04	0.0288
(iii) 0.20	0.01	

14. In the decomposition of H_2O_2 at 300 K, the energy of activation was found to be 18 kcal/ mole, while it decreased to 6 kcal/mole when the cecomposition was carried out in the presence of a catalyst at 300 K. how many times is the catalyzed reaction faster than the uncatalysed one?
15. The energy of activation and specific rate constant for a first order reaction at 25^0 C

$$2N_2O_5 \rightarrow 2N_2O_4 + O_2$$

$$(in\ CCl4) \qquad (in\ CCl4)$$

Are 100 kJ/mole and $3.46 \times 10^{-5} s^{-1}$ respectively. Determine the temperature at which the half – life of the reaction is 2 hours.

16. In Arrhenius's equation for a certain reaction, the value of A and E (activation energy) are $4 \times 10^{13} s^{-1}$ and $98.6\ kJ\ mol^{-1}$ respectively. If the reaction is of first order, at what temperature will its half – life period be ten minutes?
17. What is the energy of activation of a reaction if its rate doubles when the temperature is raised from 290 K to 300 K?
18. For the reaction $A + B \rightarrow C + D; \Delta H = 20\ kJ/mole$, the activation energy of the forward reaction is 85 kJ/mole. Calculate the activation energy of the reverse reaction.
19. 1 mL of methyl acetate was added to 20 mL of 0.5 N HCl and 2mL of the mixture was withdrawn from time tc time during the progress of hydrolysis of the ester and titrated with a solution of alkali. The amount of alkali needed for titration at various intervals is given below:

Time: (min)	0	20	119	∞
Alkali used: (mL)	19.24	20.73	26.6	42.03

Establish that the reaction is of first order.

20. The following data were obtained for the saponification of ethyl acetate using equal concentration of ester and alkali.

Time: (min)	0	4	10	20

Vol. of acid used: (mL)	8.04	5.30	3.50	2.22

21. The decomposition of N_2O_5 according to the equation $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ is a first – order reaction. After 30 minutes from the start of the decomposition in a closed vessel , the total pressure developed is found to be 284.5 mm of Hg and on complete decomposition the total pressure is 584.5 mm of Hg. Calculate the rate constant of the reaction.
22. For the displacement reaction $[Co(NH3)5Cl]^{2+} + H2O \rightarrow [Co(NH3)5(H2O)]^{3+} + Cl^-$ the rate constant is given by In $[k/(\text{min}^{-1})] = -\frac{11067K}{T} + 31.33$ Evaluate k, E and A for the chemical reaction at 25^0C.
23. The approach to the following equilibrium was observed kinetically from both directions. $PtCl_4^{2-} + H_2O \rightleftharpoons Pt(H_2O)Cl_3^- + Cl^-$ at $25^0 C$. It was found that $-\frac{d[PtCl_4^{2-}]}{dt} = (3.9 \times 10^{-5})[PtCl_4^{2-}] - (2.1 \times 10^{-3})[Pt(H_2O)Cl_3^-][Cl^-]$. Calculate the equilibrium constant for the complexation of the fourth Cl^- by Pt (II)
24. For the reaction $2H_2 + 2NO \rightarrow N_2 + 2H_2O$, the following mechanism has been suggested:

    $2NO \rightleftharpoons N_2O_2$ .... Eqb. Constant $= K_1$

    $N_2O_2 + H_2 \xrightarrow{k_2} N_2O + H_2O$ .... Rate determining step

    $N_2O + H_2 \rightarrow N_2 + H_2O$ .... Fast

    Establish the rate law for this reaction.

25. The possible mechanism for the reaction $2NO + Br_2 \rightarrow 2NOBr$ is $NO + Br_2 \rightarrow NOBr_2(fast)$; $NOBr_2 + NO \rightarrow 2NOBr\ (slow)$ Establish the rate law.
26. Some $PH_3(g)$ is introduced into a flask at $600^0 C$ containing an inert gas. PH_3 prodeeds to decompose into $P_4(g)$ and $H_2(g)$ and the reaction goes to completion. The total pressure is given below as function of time. Find the order of the reaction and calculate the rate constant for the reaction:

    $$4PH_3 \rightarrow P_4 + 6H_2$$

Time (s):	0	60	120	∞
p mm (Hg):	262.40	272.90	275.51	276.40

Answers

1. $0.0231\ \text{min}^{-1}$; 0.2
2. (i) $0.0223\ \text{min}^{-1}$ (ii) 62.18 *mins*
3. (a) 0.04 mol/l/sec (b) 0.012 mol /l/sec
4. 3/2
5. $0.00012 yr^{-1}$, 1/4

6. The reaction is of 1st order.
7. W.r.t. A = 1, w.r.t B = 0, $t_{1/2} = 1.39\ min$
8. W.r.t No = 2, w.r.t $Cl_2 = 1$
9. $2k_1 = k_2 = 4k_3$
10. (a) 0.0018 mol/l/s (b) – 0.0036 mol/l/s (c) 0.0018 mol/l/s
11. Order = 2, t = 7.55
12. Rate grous 64 times
13. Rate constant – 72 L mol^{-1} min^{-1}
14. 4.8×10^{8} times
15. $T = 310K$
16. 311.2K
17. 12 kol
18. 65 Kj
19.
20. 2 nd order reaction
21. 2.625×10^{-3} min^{-1}
22. $K = 5.10 \times 10^{-5} s^{-1}$, $A = 6.73 \times 10^{11} s^{-1}$, $E = 92.011\ Kj/mol$
23. 53.85
24. $K[NO]^2[H_2]$
25. $K[NO]^2[Br_2]$
26. Order = 1, $5.8 \times 10^{-3} s^{-1}$