CHEMICAL KINETICS

Rate of chemical reactions

The rate of a reaction tells us how fast the reaction occurs. Let us consider a simple reaction.

$A + B \rightarrow C + D$

As the reaction proceeds, the concentration of the reactant A and B decreases with time and the concentration of the products C + D increase with time simultaneously. The rate of the reaction is defined as the change in the concentration of any reactant or product in the reaction per unit time. For the above reaction,

Rate of the reaction
= Rate of disappearance of A
= Rate of disappearance of B
= Rate of appearance of C
= Rate of appearance of D

During the reaction, changes in the concentration is infinitesimally small even for small changes in time when considered in seconds.

Therefore differential form of rate expression is adopted. The negative sign shows the concentration decrease trend and the positive sign shows the concentration increase trend.

$$\therefore Rate = \frac{concentration\ change}{time\ taken}$$

$$Rate = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = \frac{d[D]}{dt}$$

For a general balanced reaction,

$aA + bB \rightarrow cC + dD$

$$Rate = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

Example Consider the reaction, $2NO + 2H_2 \rightarrow N_2 + 2H_2O$

$$Rate = -\frac{1}{2}\frac{d[NO]}{dt} = -\frac{1}{2}\frac{d[H_2]}{dt} = \frac{d[N_2]}{dt} = \frac{1}{2}\frac{d[H_2O]}{dt}$$

Units of Rate

Reaction rate has units of concentration divided by time. Since concentration is expressed in mol lit^{-1} or mol dm^{-3} the unit of the reaction rate is mol lit^{-1} s^{-1} or mol dm^{-3} s^{-1}.

Factors influencing reaction rates

There are number of factors which influence the rate of the reaction. These are :
(i) Nature of the reactants and products
(ii) Concentration of the reacting species
(iii) Temperature of the system
(iv) Presence of catalyst
(v) Surface area of reactants
(vi) Exposure to radiation

(i) Effect of nature of the reactant and product

Each reactant reacts with its own rate. Changing the chemical nature of any reacting species will change the rate of the reaction. For example, in halogenation reaction, the reactions involving iodine is found to be slower than those involving chlorine.

In case of products, some of them are capable of reacting back to form reactants or some other kind of products. In such cases, the overall rate will be altered depending on the reactivity of the products.

(ii) Effect of reacting species

As the initial concentration of the reactants increase in the reaction mixture, the number of reacting molecules will increase. Since the chemical reaction occurs when the reacting species come close together and collide, the collisions are more frequent when the concentrations are higher. This effect increases the reaction rate.

(iii) Effect of temperature

Increase in temperature of the system increases the rate of the reaction. This is because, as the temperature increases the kinetic energy of the molecules increases, which increases the number of collisions between the molecules. Therefore the overall rate of the reaction increases. This condition is valid only for endothermic reaction. For exothermic reaction the overall rate decreases with increasing temperature.

(iv) Effect of presence of catalyst

A catalyst is a substance that alters the rate of a chemical reaction, while concentration of catalyst remaining the same before and after the reaction. The addition of catalyst generally increases the rate of the reaction at a given temperature. Also, catalyst is specific for a given reaction.

(v) Effect of surface area of reactants

In case of reactions involving solid reactants and in case of heterogeneous reactions, surface area of the reactant has an important role. As the particle size decreases surface area increases for the same mass.

More number of molecules at the surface will be exposed to the reaction conditions such that the rate of the reaction increases. Thus the reactants in the powdered form (or) in smaller particles react rapidly than when present in larger particles.

(vi) Effect of radiation

Rates of certain reactions are increased by absorption of photons of energy. Such reactions are known as photochemical reactions. For example, H_2 and Cl_2 react only in the presence of light. With increase in the intensity of the light (or) radiation, the product yield increases. For photosynthesis light radiation is essential and the process does not proceed in the absence of light.

Solved numerical

Q) In the reaction $2N_2O_5 \rightarrow 4NO_2 + O_2$, NO_2 is being formed at the rate of 0.0072 $molL^{-1}$. What is the rate of reaction at this time?

Solution

Rate of reaction can be given in terms of any reactant or product

$$Rate = \frac{1}{4}\frac{d[NO_2]}{dt}$$

$$Rate = \frac{1}{4} \times 0.0072 = 0.0018\, moleL^{-1}s^{-1}$$

Q) The concentration of a reactant changes from 0.06 mol L^{-1} to 0.05 mol L^{-1} in 25 minutes. Calculate the average rate of reaction

Solution

$$rate_{av} = \frac{change\ in\ concnetration}{time}$$

$$rate_{av} = \frac{0.06 - 0.05}{25} = 4 \times 10^{-4} molL^{-1}min^{-1}$$

Q) For reaction ; $4NH_3 + 5O_2 \rightarrow NO + 6H_2O$ if the rate of disappearance of NH_3 is 3.6×10^{-3} mol $L^{-1}sec^{-1}$. Then what is the rate of formation of H_2O

Solution

(1/4) [rate of disappearance of NH_3] = (1/6) [Rate of formation of H_2O]

$$\frac{d[H_2O]}{dt} = \frac{6}{4} \times 3.6 \times 10^{-3} molL^{-1}sec^{-1}$$

Rate law

The rate of a chemical reaction is proportional to the product of effective concentration (active mass) of the reacting species, each raised to a power that is equal to the corresponding stoichiometric number of the substance appearing in the chemical reaction

Consider a general reaction

$aA + bB \rightarrow cC + dD$.

The rate law is given by the expression,

Rate $\propto [A]^a [B]^b$

Rate = $k[A]^a [B]^b$ ---------eq(1)

where k is proportionality constant also known as the rate constant or velocity constant of the reactions.

If the rate of a reaction is determined experimentally, it is found that equation (1) is not applicable always. However, the experimental results can benefitted to satisfy a relation of the type equation(1) where the exponents may or may not be equal to the respective stoichiometric coefficients. In general, we may write the rate as

Rate = $k[A]^p [B]^q$ ---------eq(2)

Here p and q may or may not be equal to a and b , they may be negative or fraction or hole numbers

Equation (2) , which relates the rate of reaction, with the concentrations of reacting species is known as **differential rate law**

Rate constant

In the above general equation k represents the rate constant. Rate constant or velocity constant (or) specific reaction rate is defined as the rate of the reaction when the concentration of each of the reactants is unity in the reaction.

When concentration of A and B is unity then, the rate constant is equal to the rate of the reaction. When the temperature of the reaction mixture changes, the value of rate constant changes.

Characteristics of rate constant

1. Rate of reaction is proportional to rate constant. Greater the value of rate constant, faster is the reaction
2. Value of rate constant is definite for a reaction at a particular temperature. With the change of temperature, rate constant also changes
3. The value of rate constant is independent of concentration of reactant
4. Units of rate constant depend upon the order of reaction
5. Presence of catalyst changes the rate of reaction and thus rate constant as well, by lowering the activation energy

Order of the reaction

Order of a reaction is defined as the sum of the exponential powers to which each concentration is raised in the rate expression. For example, if the overall rate is given by the expression Rate = $k[A]^p [B]^q$

Then, the overall order of the reaction is (p+q). The order with respect to A is p. The order with respect to B is q. If p+ q=1 the order of the reaction is 1, and the reaction is called first order. If p+q=2 the order of the reaction is 2 and the reaction is called second order and so on.

A zero order reaction is one where the reaction rate does not depend upon the concentration of the reactant. In this type of reaction, the rate constant is equal to the rate of the reaction.

Unit of rate constant

In general, rate expression for the reaction, Rate = $k[A]^p [B]^q$

$$k = \frac{Rate}{[A]^p[B]^q}$$

$$k = \frac{\frac{mol\ lit^{-1}}{time}}{\left[\frac{mol}{lit}\right]^p \left[\frac{mol}{lit}\right]^q} = \frac{(mol\ lit^{-1})^{p+q-1}}{time} = \frac{(mol\ lit^{-1})^{1-n}}{time}$$

Here n is order of reaction

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

Order	Units
Zero	mol L^{-1} sec^{-1}
First	Sec^{-1}
Third	mol^{-2} L^{2} sec^{-1}

In case of gaseous reaction, concentration is expressed in terms of pressure with the unit of atmosphere

Following are the important differences between rate and rate constant of a reaction

Sr.No.	Rate of reaction	Rate constant of reaction
1	It represents the speed at which the reactants are converted into products at any instant	It is the constant of proportionality in the rate law expression.
2	At any instant of time, the rate depends upon the concentration of reactants at that instant	It refers to the rate of a reaction at the specific point when concentration of every reacting species is unity
3	It decreases as the reaction proceeds	It is constant and does not depend on the progress of the reaction.
4	Rate of rate determining step determines overall rate value.	It is an experimental value. It does not depend on the rate determining step.

Zero order reaction

In zero order reaction, the rate does not depend on concentration of reactants. Thus, rate of reaction remains constant throughout the course of time

For example $H_2+Cl_2 \rightarrow 2HCl$ (in presence of infra red radiation)

Rate = $k[H_2]^0+[Cl_2]^0 = k$

i.e k = dx/dt unit of k = mol L^{-1} $time^{-1}$

Integrated rate expression

For a general reaction A → product

Integrated rate equation for zero order reaction is given by

$$\text{Rate } = \frac{\mathrm{d[A]}}{\mathrm{dt}} = [\mathrm{A}]^0$$

$$d[A] = -kdt$$

Integrating both the sides

$$[A] = -kt + C$$

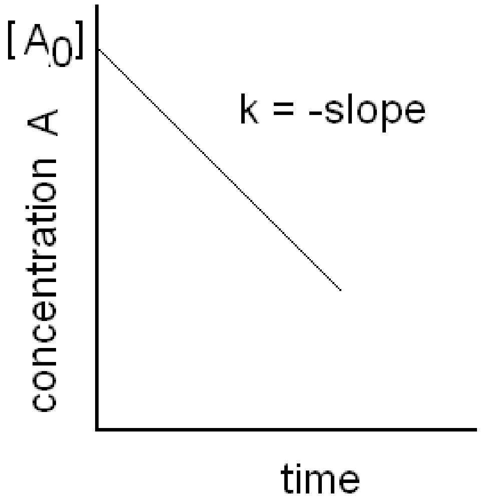
At t= 0 $[A] = [A_0]$ thus $C = [A_0]$

Where $[A_0]$ is initial concentration, on substituting value of C

$$[A] = -kt + [A_0]$$

$$k = \frac{1}{t}\{[A_0] - [A]\}$$

Where k is rate constant
t is reaction time
$[A_0]$ is initial reactant concentration
$[A]$ is final reactant concentration



Example of zero order reaction: The decomposition of gaseous ammonia on a hot platinum surface is a zero order reaction at high pressure

$$2NH_3(g) \xrightarrow[\text{pt catalyst}]{1130K} N_2(g) + 3H_2(g)$$

In this reaction, platinum metal acts as a catalyst. At high pressure the metal surface gets saturated with gas molecules. So, a further change in reaction conditions is unable to alter the amount of ammonia on the surface of the catalyst making rate of the reaction independent of its concentration. The thermal decomposition of HI on gold is another example of zero order reaction

Half-life period

Half –life period $t_{1/2}$ is the time in which half of the reaction has been completed i.e. half of the reactant concentration undergoes the reaction
It means final concentration of reactant $[A] = [A_0]/2$
And becomes $t_{1/2}$ then

$$k = \frac{1}{t_{1/2}}\left\{[A_0] - \frac{[A_0]}{2}\right\} = \frac{1}{t_{1/2}}\frac{[A_0]}{2}$$

$$t_{1/2} = \frac{1}{k}\frac{[A_0]}{2}$$

Thus half life period of zero order reaction is directly proportional to initial concentration of reactant $t_{1/2} \propto [A_0]$

First order reaction

In first order reaction the rate of reaction depends upon one concentration term only
For reaction A → product
Rate = k [A] or rate = k[B]
i.e only one concentration term affect the rate of reaction
Unit of rate constant = time^{-1}

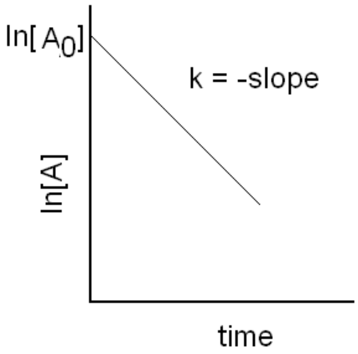
Integrated rate expression

For general reaction A → Product

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]^1$$

$$\frac{d[A]}{[A]} = -kdt$$

Integrating, we get
ln[A] = -kt +C
When t = 0 [A] = [A_0] , where [A_0] is initial concentration
ln[A_0] = C
Substituting value of C in equation
ln[A] = -kt + ln[A_0] ---------eq(1)
graph of equation (1) is straight line and negative of slope is rate constant k



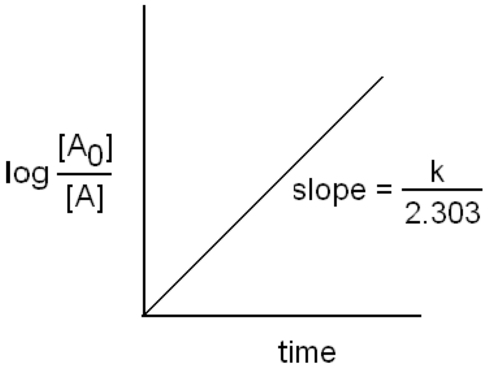
Rearranging equation (1)

$$ln\frac{[A]}{[A_0]} = -kt \quad or \quad [A] = [A_0]e^{-kt}$$

$$ln\frac{[A_0]}{[A]} = kt \quad -----eq(2)$$

$$log\frac{[A_0]}{[A]} = \frac{kt}{2.303}$$

Graph of the above equation is straight line passing through origin



$$k = \frac{2.303}{t} log\frac{[A_0]}{[A]} \quad ----eq(3)$$

At time t_1 Concentration be [A_1] from equation(1)
ln[A_1] = = - kt_1 + ln[A] -------eq(4)
At time t_2 concentration be [A_2] from equation(1)

$\ln[A_2] = = - kt_2 + \ln[A]$ -------eq(5)

Subtracting equation(5) from equation(4)

$\ln[A_1] - \ln[A_2] = k (t_2 - t_1)$

$$ln\frac{[A_1]}{[A_2]} = k(t_2 - t_1)$$

$$k = \frac{1}{(t_2 - t_1)} ln\frac{[A_1]}{[A_2]}$$

Here $t_2 - t_1 = t$ is time period

Half-life period

For half life period $t = t_{1/2}$ and $[A] = [A_0] /2$

$$k = \frac{2.303}{t_{1/2}} log\frac{[A_0]}{\left[\frac{A_0}{2}\right]}$$

$$t_{1/2} = \frac{2.303}{k} log2$$

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

Thus, half life period of the first order reaction is independent of any concentration

Amount of substance left after 'n' half life can be calculated as

$$amount\ left\ after'n'half\ life = \frac{[A_0]}{2^n}$$

Hydrogenation of ethane is an example of first order reaction

$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$

Rate = $k[C_2H_4]$

All natural and artificial radioactive decay of unstable nuclei take place by first order kinetics.

Decomposition of N_2O_5 and N_2O are some more examples of first order reactions

Note half life of nth order reaction $t_{1/2} \propto [A_0]^{1-n}$

$$t_{1/2} = \frac{(2^{n-1} - 1)}{(n-1)[A]_0^{n-1} k_n}$$

For reaction of type **n**A → Product

-Zero order

$$k = \frac{1}{\boldsymbol{n}t}\{[A_0] - [A]\} \ \ and\ t_{1/2} = \frac{1}{\boldsymbol{n}k}\frac{[A_0]}{2}$$

-First order reaction

$$k = \frac{2.303}{\boldsymbol{n}t} log\frac{[A_0]}{[A]} \ \ and\ \ t_{1/2} = \frac{0.693}{\boldsymbol{n}k}$$

Solved numerical

Q) A first order reaction takes 34.64 minutes for 50% completion. How much time will it take for 75% completion

Solution:

Half life = 34.64 minutes

Left over after first half life is 50% thus at the end of the second half life 50% of 50% = 25%is left over = 75% completion

Thus time for second half life = 34.64 minutes

Total time = 34.64 + 34.64 = 69.28 minutes

Q) 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 reaction in a closed vessel the total pressure developed is found to be 305.5 mm of Hg and on complete decomposition the total pressure is 587.5mm Hg. Calculate the rate constant of reaction

Solution

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

$$N_2O_5(g) \rightarrow 2NO_2(g) + (1/2)\ O_2(g)$$

	$N_2O_5(g)$	$2NO_2(g)$	$(1/2)\ O_2(g)$
Initial concentration	p_0	0	0
After 30 minutes	$p_0 - p$	2p	p/2
After complete Decomposition	0	$2p_0$	$p_0/2$

Total pressure after 30 minutes = $(p_0 - p) + 2p + (p/2) = 305.5$

$P_0 + (3p/2) = 305.5$ -------eq(1)

Total pressure after complete decomposition

$2p_0 + (p_0/2) = 587.5$

$(5p_0/2) = 587.5$ ------eq(2)

From equation (1) and (2) $p_0 = 235$ and $p = 47$

Given reaction is of first order thus and 2A → product thus

$$k = \frac{2.303}{nt}\log\frac{[A_0]}{[A]}$$

$$k = \frac{2.303}{2 \times 30}\log\frac{p_0}{p_0 - p} = \frac{2.303}{60} log 1.25$$

$$k = 3.72\times10^{-3}\ \text{min}^{-1}$$

Pseudo-Unimolecular reaction

The reactions which are not truly of the first order but become reactions of the first order under certain conditions are called pseudo-unimolecular or pseudo-first order reaction

For example, acidic hydrolysis of an ester

$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$

In this reactions concentration of water (one of the reactants) is in excess and its concentration remains constant throughout the reaction

Thus rate = k' $[CH_3COO\ C_2H_5]\ [H_2O]$

The term $[H_2O]$ can be taken as constant. The equation, thus, becomes

Rate = $k[CH_3COO\ C_2H_5]$

Where $k = k'[H_2O]$

Hydrolysis of cane sugar is another example

$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$

Molecularity of the reaction

Molecularity is defined as the number of atoms or molecules taking part in an elementary step leading to a chemical reaction. The overall chemical reaction may consist of many elementary steps. Each elementary reaction has its own molecularity which is equal to number of atoms or molecules participating in it. If the reaction takes place in more than one step there is no molecularity for the overall reaction. However molecularity and order are identical for elementary reaction (one step). There are many differences between the concepts of order and molecularity.

Sr.No	**Order of a reaction**	**Molecularity of a reaction**
1	It is the sum of powers raised on concentration terms in the rate expression	It is the number of molecules of reactants taking part in elementary step of a reaction
2	Order of a reaction is an experimental value, derived from rate expression	It is a theoretical concept.
3	Order of a reaction can be zero, fractional or integer.	Molecularity can neither be zero Nor be fractional.
4	Order of a reaction may have negative value.	Molecularity can never be negative
5	It is assigned for overall reaction	It is assigned for each elementary step of mechanism
6	It depends upon pressure, temperature and concentration (for pseudo order)	It is independent of pressure and temperature.

TEMPERATURE DEPENDANCE OF RATE CONSTANT

It is a common observation that rates of reactions increase with increase in temperature of the reaction mixture. Keeping the concentration of the reactants constant, the rate is found to be two times its initial value, when measured at a temperature 10 K greater than the initial temperature. However, the exact value of the rate constant determined at various temperature is predicted by using Arrhenius equation. This expression is obeyed by most of the reactions. Arrhenius equation is given as

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

taking log on both sides

$$lnk = lnA - \frac{E_a}{RT}$$

$$logk = logA - \frac{E_a}{2.303RT}$$

where k = rate constant, E_a = activation energy, A = frequency factor, or Arrhenius constant , R = gas constant, T = temperature in Kelvin.

If k_1 and k_2 are the rate constants measured at two different T_1 and T_2 temperatures respectively, then E_a can be determined as follows :
Arrhenius equation for two different temperatures T_1 and T_2 are :

$$logk_1 = logA - \frac{E_a}{2.303RT_1}$$

And

$$logk_2 = logA - \frac{E_a}{2.303RT_2}$$

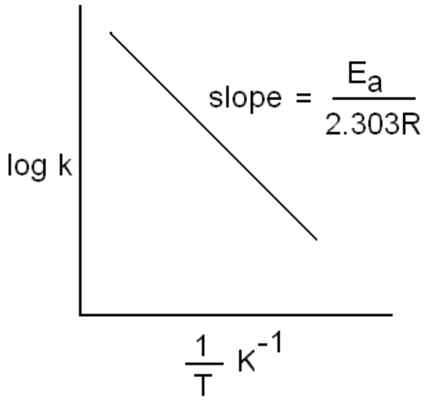
where k_1 and k_2 are the rate constants at temperature T_1 and T_2 respectively.

$$logk_2 - logk_1 = -\frac{E_a}{2.303RT_2} + \frac{E_a}{2.303RT_1}$$

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

If R = 1.987 cals.mol^{-1}, then unit of E_a is 10^{-3} k.cal.
Also, a plot of log k against 1/T values gives a straight line with slope value equals to $-Ea/2.303$ R and intercept value equals to log A. When E_a is a positive value, and if $T_2 > T_1$ then $k_2 > k_1$.
That is, rate constant value at higher temperature is greater than rate constant value at lower temperature.
Under such conditions, plot of log k against 1/T gives a negative slope straight line. From the slope of the straight line, E_a can be calculated.
Note

$\frac{k_2}{k_1}$ is known as temperature coefficient



Main characteristics of Arrhenius equation

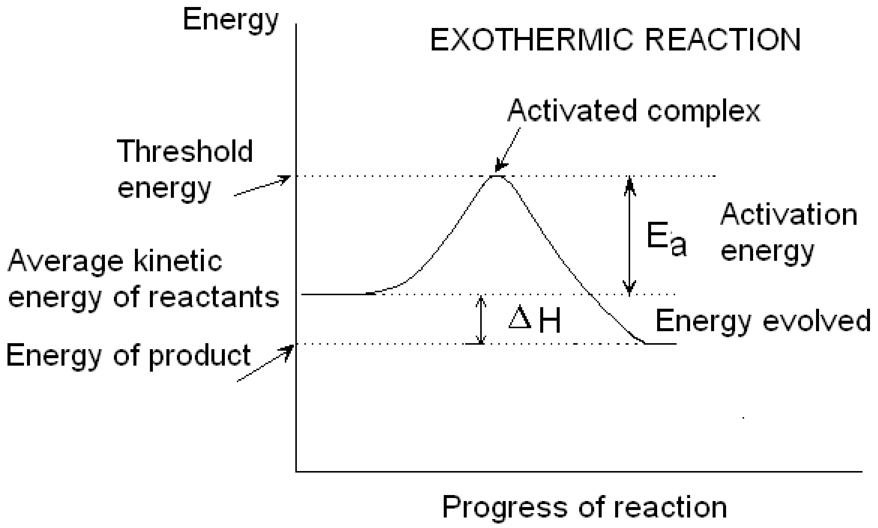
1) Larger the activation energy of reaction, smaller is the value of rate constant
2) Larger the activation of a reaction, greater is the influence of change in temperature
3) For lower temperature range, increase in temperature causes more change in the value of k than the same increase in temperature for high temperature range

Activation energy

The minimum amount of energy absorbed by the reactant molecules so that their energy becomes equal to the energy is called activation energy

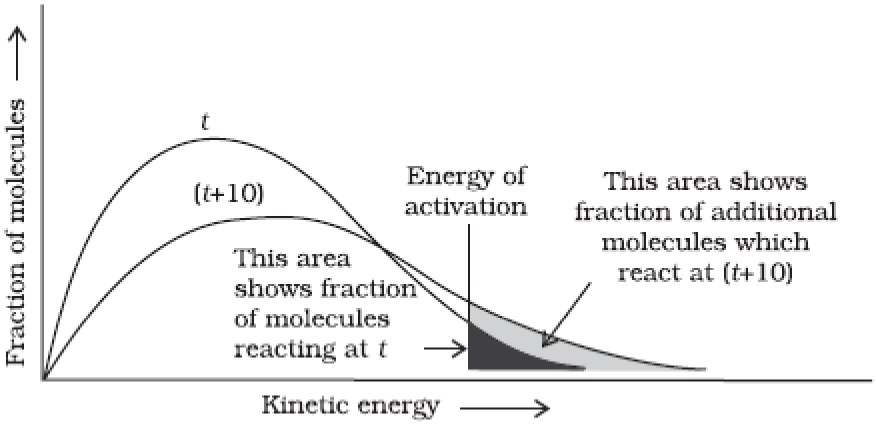
Or we can say that it is the difference between threshold energy and the average kinetic energy possessed by the reactant molecules

Activation energy = threshold energy – Average kinetic energy of reactant

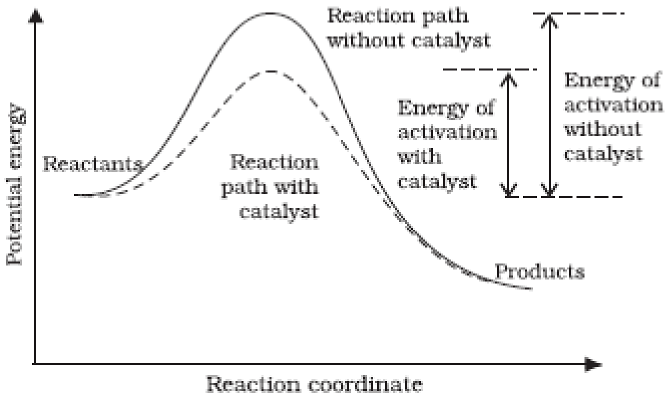


It has been found that for a chemical reaction with rise in temperature by 10^{O}, the rate constant is nearly doubled. It can be explained on the basis of activation energy

All the molecules in the reactant species do not have same kinetic energy. According to Boltzman and Maxwell , the distribution of kinetic energy may be described by plotting the reaction of molecules (N_E/N_T) with a given kinetic energy (E) Vs kinetic energy. Here N_E is the number of molecules with kinetic energy E and E_T is total number of molecules. The peak of the curve corresponds to the most probable kinetic energy. i.e kinetic energy of maximum fraction of molecules. There are decreasing number of molecules with energies higher than or lower than this value. Curve 1 represents the distribution at temperature t while curve 2 represent the distribution at temperature t+10. Clearly from the graph, for temperature t+10 curve broadens out. i.e spreads to the right side such that there is a greater proportional molecules with much higher energies capable to undergo reaction. The area under the curve must be constant since total probability must be one at all times It is clear from the graph at temperature (t+10) , the area showing fraction of molecules having energy equal to or greater than activation energy gets doubles leading to doubling the rate of reaction



Effect of catalyst



A catalyst is a substance which alters the rate of a reaction without itself undergoing any permanent chemical change.

For example, MnO_2 catalyses the following reaction so as to increase its rate considerably.

$$2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_2$$

The action of the catalyst can be explained by intermediate complex theory. According to this theory, a catalyst participates in a chemical reaction by forming temporary bonds with the reactants resulting in an intermediate complex.

This has a transitory existence and decomposes to yield products and the catalyst.

It is believed that the catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy between reactants and products and hence lowering the potential energy barrier

Characteristic of catalyst

1.A small amount of the catalyst can catalyse a large amount of reactants.

2. A catalyst does not alter Gibbs energy, ΔG of a reaction.

3. It catalyses the spontaneous reactions but does not catalyse non-spontaneous reactions.

4.It is also found that a catalyst does not change the equilibrium constant of a reaction rather, it helps in attaining the equilibrium faster.
5.it catalyses the forward as well as the backward reactions to the same extent so that the equilibrium state remains same but is reached earlier.

Solved numerical

Q) Temperature coefficient for the saponification of an ester by NaOH is 1.75 calculate the activation energy
Solution
Temperature coefficient i.e. $k_2/k_1 = 1.75$
In general practice T_1 = 25 ^{O}C i.e 298K and T_2 = 35^{O}C = 308K

$$log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

$$\log 1.75 = \frac{E_a}{2.303 \times 1987}\left[\frac{308 - 298}{298 \times 308}\right]$$

$E_a = 10.207$ kcal mol^{-1}

Q) For a first order reaction at 300^{O}C, activation energy is 35kcal mol^{-1} and the frequency constant 1.45×10^{11} sec^{-1}. Calculate the rate constant
Solution

$$logk = logA - \frac{E_a}{2.303RT}$$

R = 1.987 = 2 cal/K/mole, $E_a = 35\times10^3$cal, T = 573K

$$logk = log1.45 \times 10^{11} - \frac{35 \times 10^3}{2.303 \times 2 \times 573}$$

logk = 11.161 – 13.26 = -2.099
Taking antilog, k = 7.96×10^{-3} sec^{-1}

Q) From the following data for the reaction between A and B, calculate the order of the reaction with respect to A and with respect to B

[A]/moll^{-1}	[B]/mol L^{-1}	Initial rate/mol L^{-1}s^{-1}
2.5×10^{-4}	3.0×10^{-5}	5.0×10^{-4}
5.0×10^{-4}	6.0×10^{-5}	4.0×10^{-3}
1.0×10^{-3}	63.0×10^{-5}	1.6×10^{-2}

Solution
Let the order with respect to A be p and with respect to B be q. The rate law would be represented as
Rate = $k[A]^p [B]^q$
Therefore from first data of table $5.0\times10^{-4} = k [2.5\times10^{-4}]^p [3.0\times10^{-5}]^q$ ------eq(1)

Second date gives $4.0\times10^{-3} = k [5.0\times10^{-4}]^p [6.0\times10^{-5}]^q$ ---eq(2)

Third data for table $1.6\times10^{-2} = k\,[1.0\times10^{-3}]^p\,[6.0\times10^{-5}]^q$ ---eq(3)

Dividing equation (2) by (1)

$$\frac{4.0\times10^{-3}}{5.0\times10^{-4}}=\frac{k[5.0\times10^{-4}]^p[6.0\times10^{-5}]^q}{k[2.5\times10^{-4}]^p[3.0\times10^{-5}]^q}$$

$$8 = (2)^{p+q}$$

$$2^3 = (2)^{p+q}$$

$$\therefore p+q = 3$$

Similarly dividing equation(2) by (3)

$$\frac{4.0\times10^{-3}}{1.6\times10^{-2}}=\frac{k[5.0\times10^{-4}]^p[6.0\times10^{-5}]^q}{k[1.0\times10^{-3}]^p[6.0\times10^{-5}]^q}$$

$$\frac{1}{4}=\left(\frac{1}{2}\right)^p$$

Or $4 = 2^p$ Thus $p = 2$

So order with respect to A is two and with respect to B is one

Q) The time required for 10% completion of a first order reaction at 298K is equal to that required for its 25% completion at 308K. If the pre-exponential factor (A) for the reaction is 3.56×10^9 sec^{-1}, calculate its rate constant at 318K and also the energy of activation

Solution

For a first-order reaction, the rate constant expression is

$$k=\frac{2.303}{t}log\frac{[A_0]}{[A_t]}$$

At 298k

$$t_{298}=\frac{2.303}{k_{298}}log\frac{[A_0]}{0.9[A_0]}$$

At 308k

$$t_{308}=\frac{2.303}{k_{308}}log\frac{[A_0]}{0.75[A_0]}$$

Time taken at 298K (for completion of 10% of reaction) and at 308K(for completion of 25% of reaction) are same

$$\frac{2.303}{k_{298}}log\frac{[A_0]}{0.9[A_0]}=\frac{2.303}{k_{308}}log\frac{[A_0]}{0.75[A_0]}$$

$$\frac{k_{308}}{k_{298}}=\frac{0.1249}{0.0457}=2.73$$

Activation energy of the reaction can be calculated using

$$log\frac{k_{308}}{k_{298}}=\frac{E_a}{2.303R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$$

$$log2.73=\frac{E_a}{2.303\times8.314}\left[\frac{308-298}{298\times308}\right]$$

Ea = 76651 J mol^{-1} = 76.65 kJ mol^{-1}

Rate constant at 318K can be calculated using

$$logk = logA - \frac{E_a}{2.303RT}$$

$$logk_{318} = log3.56 \times 10^9 - \frac{76.65}{2.303 \times 8.314 \times 10^{-3} \times 318}$$

$K_{318} = 9.13 \times 10^{-4}\ _{s}^{-1}$

Q) A catalyst lowers the activation energy for a certain reaction from 75 to 20kJmol^{-1}. What will be the effect on the rate of the reaction at 20^{O}C, other things being equal?

Solution According to Arrhenius equation

$K = A\ e^{-Ea/Rt}$

In absence of catalyst $k_1 = Ae^{-75/RT}$ ---------eq(1)

In presence of catalyst, $k_2 = A\ e^{-20/RT}$ ---------eq(2)

Here we have assumed that the value of A is unchanged by the presence of catalyst

Dividing (2) by (1) we get

$$\frac{k_2}{k_1} = e^{\frac{55}{RT}}$$

$$ln\frac{k_2}{k_1} = \frac{55}{RT}$$

$$log\frac{k_2}{k_1} = \frac{55 \times 10^3}{2.303 \times 8.314 \times 293} = 9.8037$$

Taking antilog

$$\frac{k_2}{k_1} = 6.363 \times 10^9$$

Thus, in the presence of catalyst, rate of the reaction increases 6.39$\times 10^9$ times with respect to uncatalysed reaction

Collision theory of chemical reaction

According to this theory, the reactant molecules are assumed to be hard spheres and reaction is postulated to occur when molecules collide with each other.

The number of collisions per second per unit volume of the reaction mixture is known as collision frequency (Z).

Another factor which affects the rate of chemical reactions is activation energy For a bimolecular elementary reaction

A + B → Products

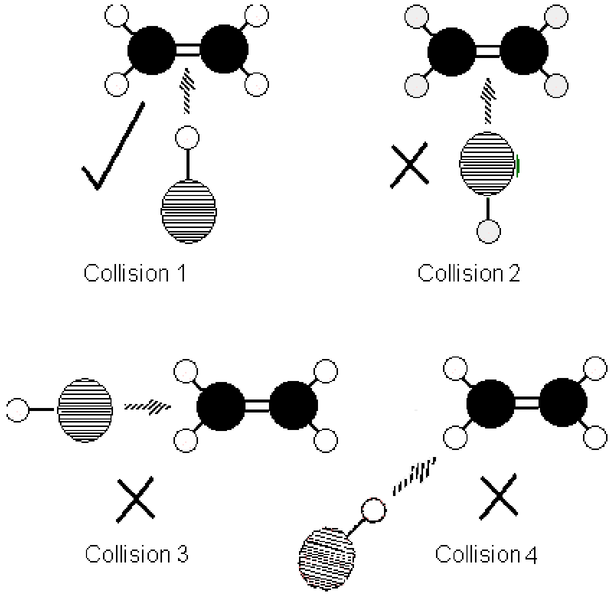
rate of reaction can be expressed as

Rate = $Z_{AB}\ e^{-Ea/\ RT}$ --------eq(1)

where Z_{AB} represents the collision frequency of reactants, A and B

and $e^{-Ea\ /RT}$ represents the fraction of molecules with energies equal to or greater than *E*a. Comparing this equation with Arrhenius equation, we can say that *A* is related to collision frequency. Equation (1) predicts the value of rate constants fairly accurately for the reactions that involve atomic species or simple molecules but for complex molecules significant deviations are observed. The reason could be that all collisions do not lead to the formation of products. The collisions in which molecules collide with sufficient kinetic energy (called threshold energy*) and proper orientation, so as to facilitate breaking of bonds between reacting species and formation of new bonds to form products are called as effective collisions.

Consider a simple reaction involving a collision between two molecules - ethene, $CH_2{=}CH_2$, and hydrogen chloride, HCl, for example. These react to give chloroethane.



$$CH_2{=}CH_2 + HCl \longrightarrow CH_3CH_2Cl$$

As a result of the collision between the two molecules, the double bond between the two carbons is converted into a single bond. A hydrogen atom gets attached to one of the carbons and a chlorine atom to the other. The reaction can only happen if the hydrogen end of the H-Cl bond approaches the carbon-carbon double bond. Any other collision between the two molecules doesn't work. The two simply bounce off each other. In any collision involving unsymmetrical species, you would expect that the way they hit each other will be important in deciding whether or not a reaction happens.

The proper orientation of reactant molecules lead to bond formation whereas improper orientation makes them simply bounce back and no products are formed.

To account for effective collisions, another factor *P*, called the probability or steric factor is introduced. It takes into account the fact that in a collision, molecules must be properly oriented i.e.

Rate = $PZ_{AB}\, e^{-Ea/RT}$

Thus, in collision theory activation energy and proper orientation of the molecules together determine the criteria for an effective collision and hence the rate of a chemical reaction. Collision theory also has certain drawbacks as it considers atoms/molecules to be hard spheres and ignores their structural aspect.

Rate of Reversible reaction

Most chemical reactions are not simple unimolecular or bimolecular reactions, but combination. The simplest of these is the reversible, or opposed, reaction. In reversible reactions, there is a pair of forward and reverse reactions.

For example,

$$aA + bB \leftrightarrow cC + dD$$

The rate equation for this reaction, assuming each step is elementary is

$$\text{Rate} = k_f\,[A]^a\,[B]^b - k_r\,[C]^c\,[D]^d$$

where k_f is the rate coefficient for the forward reaction that consumes A and B; k_r is the rate coefficient for the reverse reaction, which consumes X and Y and produces A and B. When the reaction is at equilibrium, the rate = 0. Therefore,

$$k_f\,[A]^a\,[B]^b = k_r\,[\,C]^c\,[D]^d$$

this equation can be used to give the equilibrium coefficient (K_{eq}) for the entire reaction:

$$k_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b} = \frac{k_f}{k_r}$$

Now it should make sense why increasing the reactant concentration will make more products. The forward rate increases, which uses up reactants and decreases the forward rate. At the same time, products are made, which increases the reverse reaction until both reaction rates are equal again.

Consecutive (Chain) Reactions

Another example of a complex reaction is one that occurs in several, consecutive steps. Take, for example, this reaction: $A \rightarrow B \rightarrow C$
where rate from A to B is k_1 and the rate from B to C is k_2. The rate laws for each of the steps is: Consumption of A

$$\frac{d[A]}{dt} = -k_1[A]$$

(production of B minus consumption of B)

$$\frac{d[B]}{dt} = k_1[A] - k_2[B]$$

(production of C)

$$\frac{d[C]}{dt} = -k_1[B]$$

The integrated rate law for A is:

$$[A_t] = [A_0]e^{-k_1 t}$$

Substituting this equation into the equation for rate B gives:

$$\frac{d[B]}{dt} = k_1[A_0]e^{-k_1 t} - k_2[B]$$

The concentration of B can be solved for using differential equations to give the equation:

$$[B_t] = [A_0]\left(\frac{k_1}{k_2} - k_2\right)e^{-k_1 t} - e^{-k_2 t}$$

Finally, since $[C] = [A]_0 - [B] - [A]$, we can substitute in and use differential equations to get the integrated rate law for C:

$$[C_t] = [A_0]\left\{1 + \left(\frac{k_1 e^{k_2 t} - k_2 e^{k_1 t}}{k_2 - k_1}\right)\right\}$$

Competing (Parallel) Reactions

Another common complex reaction is a competing, or parallel reaction. In a competing reaction, a substance reacts simultaneously to give two different products. For example,

A → B And A→ C
where k_1 is the rate constant for the formation of B and k_2 is the ate constant for formation of C.
The rate laws for this reaction are:
(rate of consumption of A by both reactions)

$$\frac{dA}{dt} = -(k_1 + k_2)[A]$$

(rate of production of B)

$$\frac{dB}{dt} = k_1[A]$$

(rate of production of C)

$$\frac{dC}{dt} = k_2[A]$$

Using substitution and differential equations as above, the integrated rate laws are:

$$[A_t] = [A_0]e^{-(k_1+k_2)}$$

$$[B_t] = \left(\frac{k_1}{k_1 + k_2}\right)[A_0]\left(1 - e^{-(k_1+k_2)}\right)$$

$$[C_t] = \left(\frac{k_2}{k_1 + k_2}\right)[A_0]\left(1 - e^{-(k_1+k_2)}\right)$$

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