B.sc II

Chemical Reaction Engineering

Paper - VII

Semester - III

36x

Kinetics of Homogeneous Reaction

Every Industrial chemical prozess is aimed at the production of a desired producat economically From a given raw material.

When a new molecules are fromed by the reamagement or redistribution of the constituent atoms, we say that a chemical Reaction is occured

In the Reaction process, the species losses its identity and assume a new froms may be decomposition, combination or by isomerisation.

Example. synthesis of methanol

$$\frac{1}{2} CO_2 + 2H_2 \rightarrow CH_3OH$$

Chemical Kineticas

The study of chemical Kineticas is the Rates at which chemical Reactions occur and the effecat of parameters, such as temperature, pressure and Reactant concentration or composition on the Reaction Rates.

it provides us information about the Reaction mechanisam, speed of chemical Reaction and type of the Rate equation.

Rate of Reaction →

The rate of Reaction is the rate of change of concentration of Reactant or producat per Unit time. since the rate of Reaction depend upon the concentration of Reactants it does not remain Unifrom during the course of Reaction because concentration of reactants gradually decrease with time

At beginin begining the rate of Reaction is rapid and gradually decreases with time as the Reactants are converted to producat.

the rate of of chemical Reaction is the rate at which the concentration of Reacting substances vary with a time and it is denoted by $\frac{dc}{dt}$

the rate of Reaction is proportional to concentration of Reactant. there fore

$$-\frac{dc}{dt} \propto c$$

$$-\frac{dc}{dt} = kc$$

K = Rate constant

the -ve Sign shows ~~that~~ the concentration of Reactant is decreases with time

The rate of Reaction can be defined in a number of ways, based on Unit volume of Reacting fluid in case of homogeneous System, based on Unit mass of solid in case of fluid-solid System and so on.

a) Based on Unit Volume of Reacting fluid

$$-r_A = -\frac{1}{V}\frac{dN_A}{dt} = \frac{\text{moles of A disappear}}{(\text{volume of fluid})(\text{Time})}$$

ⓑ Based on Unit mass of solid in fluid-solid system.

$$-r_A' = -\frac{1}{W}\frac{dN_A}{dt} = \frac{\text{moles of A disappeared}}{\text{mass of solid} \times \text{time}}$$

c) Based on Unit volume of solid in gas-solid system

$$-r_A'' = -\frac{1}{V_s}\frac{dN_A}{dt} = \frac{\text{moles A disapeared}}{(\text{volume of solid})(\text{time})}$$

d) Based on Unit Volume of Reactor

$$r_A = -\frac{1}{V_r}\frac{dN_A}{dt} = \frac{\text{moles of A disappeared}}{\text{volume of Reactor}}$$

The reaction rate is an intensive quantity and depends on concentration and temperature. the above rates are related by.

$$(-r_A)V = (-r_A')W = (-r_A)S = (-r_A'')V_s = (-r_A)V_r$$

Imp. Questions

1. Explain Elementary and Non elementary Reaction.
2. Differance betn elementary and non. elementary Reaction
3. molecularity of Reaction & order of Reaction.
4. Diff. moleculariity and order of Reaction
5. Kinetic models for nonelementary Reaction ✓
6. Temperature dependency from Arrhenius Law. ✓
7. Classification of chemical Reaction. ✓ CRE I By Ghiwani

P → 1) On doubling the concentration of Reactant The rate of Reaction is triples. find the Reaction order

Ans - $-r_A = KC_A^n$

At C_{A1} rate is, $-r_{A1} = KC_{A1}^n$

At C_{A2} rate is $-r_{A2} = KC_{A2}^n$

if. when $C_{A2} = 2C_{A1}$

then $-r_{A2} = 3(-r_{A1})$

$$\frac{-r_2}{-r_1} = \frac{KC_{A2}^n}{KC_{A1}^n}$$

Sustitute the value of $-r_{A_2} = 3(-r_A)$ in above eqn and also $C_{A_2} = 2C_{A_1}$

$$\frac{3(-r_{A_1})}{-r_{A_1}} = \frac{(2C_{A_1})^n}{(C_{A_1})^n}$$

$$3 = \frac{2^n \cdot C_{A_1}^n}{C_{A_1}^n}$$

$$3 = 2^n$$

$$\ln 3 = n \ln 2$$

$$1.0986 = n(0.693)$$

$$\frac{1.0986}{0.693} = n$$

$$\underline{\underline{n = 1.6}}$$

Q. Explain Representation of Elementary and non elementary Reaction

Q. Discuss the collision theory of bimolecular rea

P The pyrolysis of ethane proceeds with an activation energy of about 75000 How much faster is the decomposition at 650 °C than at 500 °C

Soln

we Know that

$$\ln\left[\frac{K_2}{K_1}\right] = \frac{E}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$T_1 = 500°C$, $T_2 = 650°C$

$T_1 = 500 + 273 = 773\ K$

$T_2 = 650 + 273 = 923\ K$

$R = 1.987\ cal/mol\ K$

$$\therefore \ln\left[\frac{K_2}{K_1}\right] = \frac{75000}{1.987}\left[\frac{1}{773} - \frac{1}{923}\right]$$

$$\ln\left(\frac{K_2}{K_1}\right) = 7.951$$

$$\therefore K_2/K_1 = \underline{2838} \quad \left[\therefore\ ~~7.951~~\ e^{7.951}\right]$$

$$K_2 = 2838\,K_1$$

At 650 °C the decomposition is faster by a factor 2838 than at 500 °C p The activation energy of a biomolecular reaⁿ is about 9150 cal/mol. How much faster is this Reaction takes place at 500K than at 400K

Ans $2A \longrightarrow$ product

$E = 9150$ cal/mole

$T_1 = 400K \quad T_2 = 500K$

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

$$= \frac{9150}{1.987}\left[\frac{1}{400} - \frac{1}{500}\right]$$

$= 2.303$

$k_2/k_1 = 10$

$\underline{k_2 = 10k_1}$

p. At 450 K the the rate of biomolecular reaction is ten times the rate at 400K. find the activation Energy for this reaction ⓐ From Arrhenius Law <b> From collision theory ⓒ what is the percentage differance in rate of reaction at 600K predicted by these two methods!

we know that
From Arhenium Law

$$\ln\left(\frac{r_2}{r_1}\right) = \frac{E}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$\because r_2 = 10 r_1$

$$\ln\left(\frac{10 r_1}{r_1}\right) = \frac{E}{1.987}\left[\frac{1}{400} - \frac{1}{450}\right]$$

$$\ln 10 = \frac{E}{1.987}\left[0.00027\right]$$

$$\frac{2.303 \times 1.987}{0.00027} = E$$

E = 16948 cal/mol.

E from collision Theory

$$\ln\left(\frac{r_2}{r_1}\right) = \frac{E}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] + \ln\left[\frac{(T_2)^{1/2}}{(T_1)^{1/2}}\right]$$

$$\ln\left(\frac{10 r_1}{r_1}\right) = \frac{E}{1.987}\left[\frac{1}{400} - \frac{1}{450}\right] + \ln\left[\frac{(450)^{1/2}}{(400)^{1/2}}\right]$$

$$2.303 = \frac{E}{1.987}\left[0.00027\right] + \ln\left[\frac{21.21}{20}\right]$$

$$2.303 = \frac{E}{1.987}\left[0.00027\right] + \ln 1.06$$

$[\ln 1.06 = 0.058]$

$$2.303 - 0.058 = \frac{E}{1.987}\left[0.00027\right]$$

$$\frac{2.24 \times 1.987}{0.00027} = E$$

$E = 16521$ Cal/mole.

ⓒ From Arrhenius Law: $\therefore T_3 = 600\,K$

$$\ln\left(\frac{r_3}{r_2}\right) = \frac{E}{R}\left[\frac{1}{T_2} - \frac{1}{T_3}\right] + \cancel{\ln\left[\right.}$$

$$\ln\left(\frac{r_3}{r_2}\right) = \frac{16948}{1.987}\left[\frac{1}{450} - \frac{1}{600}\right]$$

$$\ln\frac{r_3}{r_2} = 4.738$$

From collision theory

$$\ln\left(\frac{r_3}{r_2}\right) = \frac{E}{R}\left[\frac{1}{T_2} - \frac{1}{T_3}\right] + \ln\left[\frac{(T_3)^{\frac{1}{2}}}{(T_2)^{\frac{1}{2}}}\right]$$

$$\left(\ln\frac{r_3}{r_2}\right) = \frac{16521}{1.987}\left[\frac{1}{450} - \frac{1}{600}\right] + \ln\left[\frac{(600)^{1/2}}{(450)^{1/2}}\right]$$

$$= 4.15 + 0.139$$

$$= 4.289$$

% diff $\;\dfrac{4.738 - 4.289}{4.738} \times 100$

$= \underline{9.47\ \%}$

The rate of Reaction from collision theory is 9.4% more than its given by Arrhenius Law

P+ At 500 K the rate of bimolecular reaction is ten times the rate at 400K. Find the activation energy for this reaction ⓐ from arrhenius Law b) from collision theory ⓒ what is the % differance in rate of reaction at 600K predicted by these two methods.

a) we have

$$\ln\left[\frac{r_2}{r_1}\right] = \frac{E}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$r_2 = 10 r_1$

$T_1 = 400K$, $T_2 = 500K$

$R = 1.987$ cal/mol.K.

$$\ln\left(\frac{10 r_1}{r_1}\right) = \frac{E}{1.987}\left[\frac{1}{400} - \frac{1}{500}\right]$$

$E = 9150$ cal/mol

b) From collision theory

$$\ln\left(\frac{r_2}{r_1}\right) = \frac{E}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] + \ln\left(\frac{T_2^{1/2}}{(T_1)^{1/2}}\right)$$

$T_1 = 400K$, $T_2 = 500K$ $r_2 = 10 r_1$

$$\ln\left(\frac{100\,r_1}{r_1}\right) = \frac{E}{1.987}\left[\frac{1}{400} - \frac{1}{500}\right] + \ln\left[\frac{(500)^{1/2}}{[400]^{1/2}}\right]$$

$$E = 8707 \text{ cal/mole}$$

c> **From Arrhenius Law**

$$\ln\left(\frac{r_3}{r_2}\right) = \frac{E}{R}\left[\frac{1}{T_2} - \frac{1}{T_3}\right]$$

$$= \frac{9150}{1.987}\left[\frac{1}{500} - \frac{1}{600}\right]$$

$$\frac{r_3}{r_2} = 4.64$$

$$r_3 = 4.64\, r_2$$

From Collision theory

$$\ln\left(\frac{r_2}{r_3}\right) = \frac{E}{R}\left[\frac{1}{T_2} - \frac{1}{T_3}\right] + \ln\left(\frac{T_3^{1/2}}{T_2^{1/2}}\right)$$

$$\ln\left(\frac{r_3}{r_2}\right) = \frac{8707}{1.987}\left[\frac{1}{500} - \frac{1}{600}\right] + \ln\left[(600)^{1/2} / (500)^{1/2}\right]$$

$\frac{r_3}{r_2} = 4.72$

$r_3 = 4.64 r_2$

% differance in rates $= \frac{(4.72 - 4.64) r_2}{4.72 r_2} \times 100$

$= 1.7 \%$.

The rate of Reaction from collisin theory is 1.7 % more than it is given by Arrhenius Law.

Unit - 3

Interpretation of Batch Reactor Data

In order to obtain the size of a chemical reactor by making use of an appropriate design equation, one must know the rate equation for a specific reaction as the term - rate of reaction is involved in the design equation OR performance of a Reactor.

To determination of the complete rate equation involving two step

1) To find the order of Reaction
2) To find the temperature dependency of the rate constant (K and its variation with T):

Constant volume batch Reactor :-

The term constant volume batch Reactor means a constant-volume Reaction system, we really refer to volume of the Reaction mixture and volume of of reactor.

The reaction system that undergoes no change in the volume as the Reaction progress are called as co'stant-Volume system.

Example of constant-volume system :-

In case of gas phase Reaction with changing Number of moles carried out in a batch Reactor, the reactor is usually a sealed vessel, provided with proper instruments to measure pressure and temperature within the Reactor. the Volume of Reaction mixture within this Vessel is fixed and will not change and is therefore a constant volume system.

A gas phase Reaction process yielding Number of moles of product equal to the Number of moles of Reactants consumed

consider a Reaction.

$$CO + H_2O \rightarrow CO_2 + H_2$$

In this Reaction, two moles of producats are formed from two moles of Reactants.

The rate of reaction of any component, is given by

$$r_i = \frac{1}{V} \cdot \frac{dN_i}{dt}$$

for Constant-volume system as the volume of constant, we can take V inside the differential and the rate of reaction in terms of concentration is given by

$$r_i = \frac{1}{V} = \frac{d(N_i/V)}{dt} = \frac{dc_i}{dt}$$

as $c_i = N_i/V$.

If A is the reactant that is disapearing during course of reaction then the rate of disapearance of A i.e. $-r_A$ is given by

$$-r_A = -\frac{dC_A}{dt}$$

* Relation of concentration and conversion for Constant-Volume batch System.

The Concentration of A is the Number of moles of A per Unit Volume.

$$C_A = \frac{N_A}{V}$$

∴ C_A - is the Concentration

N_A → is the moles of A remained (unreacted at any time t during the course of Reaction.

N_{A0} → Initial moles of A

$$X_A \Rightarrow \frac{\text{moles of A reacted}}{\text{Initial moles of A}}$$

$$\therefore N_{A0} \cdot X_A = \frac{\text{moles of A reacted}}{\text{Initial moles of A}} \times \text{Initial moles of A}$$

$$\therefore N_{A0} \cdot X_A = \text{moles of A reacted.}$$

moles unreacted = Initial mol − Moles of A reacted

$$N_A = N_{A0} - N_{A0} X_A$$

$$= N_{A0}(1 - X_A)$$

But $\boxed{N_A = C_A \cdot V}$

$$C_A \cdot V = N_{A0} \cdot (1 - X_A)$$

$$C_A = \frac{N_{A0}(1 - X_A)}{V}$$

But $V = V_0$

$$C_A = \frac{N_{A0}}{V_0}(1 - X_A)$$

$$\therefore \frac{N_{A0}}{V_0} = C_{A0}$$

$$C_A = C_{A0} \cdot (1 - X_A)$$

the above equation relates the concentration of A at any time. t to the Initial concn. of A through the fractional conversion of A for any constant - volume system.

* Integrated rate equations for Different order Reaction..

* Irreversible Unimolecular - type first order Reaction.

when the rate of Reaction is direcately proportional to the concentration of only one Reactant the reaction is said to be first order.

Consider the Reaction

$$A \rightarrow \text{product}$$

the rate of disapearance of A is given by

$$-r_A = \frac{-dc_A}{dt} = Kc_A$$

rearranging we get

$$\frac{-dc_A}{c_A} = K \cdot dt.$$

Integrating the above equation within the limit,

reearang the above eqn and we get

$$-\frac{dC_A}{C_A} = k\,dt.$$

$C_A = C_{A0}$ at time 0

$C_A = C_A$ at time t

$$-\int_{C_{A0}}^{C_A}\frac{dC_A}{C_A} = k\int_0^t dt$$

$$-\left[\ln C_A\right]_{C_{A0}}^{C_A} = k(t)_0^t$$

$\ln C_A - \ln C_{A0}$

$-\left[\ln\frac{C_A}{C_{A0}}\right]$

$$-\ln\left[\frac{C_A}{C_{A0}}\right] = kt$$

$$k = \frac{1}{t}\ln\frac{C_{A0}}{C_A} \quad ①$$

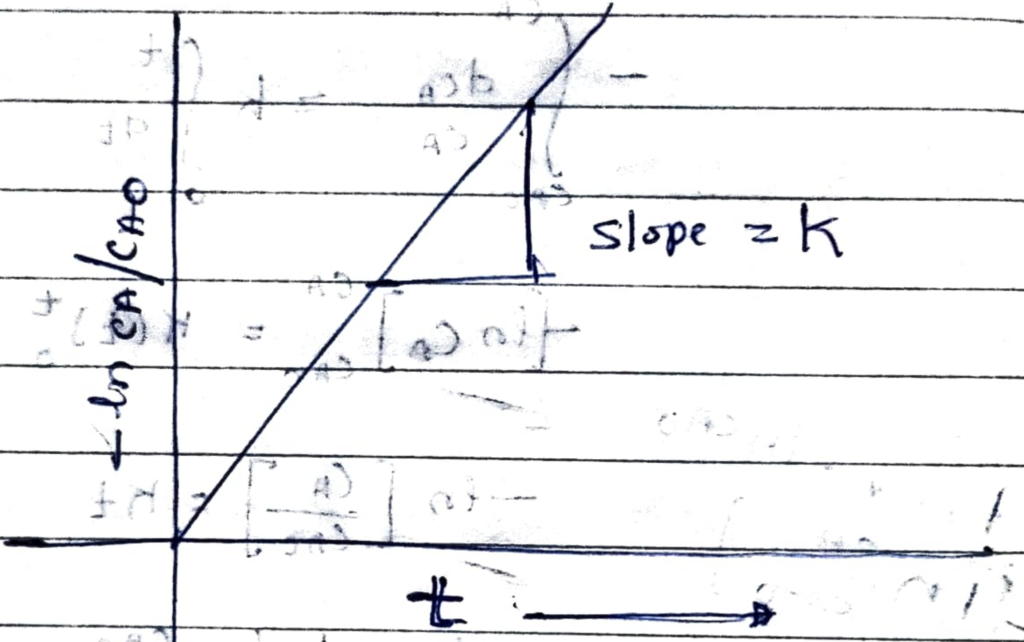
equation ① is the integrated rate equation for first order Reaction in terms of concentration. it is followed from the expression ① that k depends only the rate of concentration C_{A0}/C_A.

or

$$k = \frac{1}{t}\ln\frac{a}{a-x}$$

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

A plot of $-\ln C_A/C_{A0}$ versus t would give a straight line showing that the reaction is first order. the value of first order rate constant is equal to the slope of this line



* Irreversible Biomolecular/ Type second order reaction.

When the rate of Reaction is direcately proportional to the concentration raised to power Unity of two differant reactants or to the square of concentration of one Reactant, the reaction is said to be of second order.

~~for the~~ reaction 2A → producats.

OR

for the reaction A+B → producats,

with equal concentration of A and B, the rate expression can be given as

$$-r_A = -\frac{dC_A}{dt} = kC_A^2 \qquad ①$$

$$-\frac{dC_A}{C_A^2} = k \cdot dt$$

$$-\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A^2} = k\int_0^t dt$$

$$-\left[\frac{-1}{C_A}\right]_{C_{A0}}^{C_A} = kt$$

$$t = \frac{1}{K}\left[\frac{1}{C_A} - \frac{1}{C_{A0}}\right] \quad — ②$$

eqn ① is the integrated rate expression for second order Reaction in terms of Concentration.

Now we will develop the integrated rate expression in terms of conversion

$$2A \longrightarrow \text{product}$$

$$-r_A = -\frac{dC_A}{dt} = K C_A^2$$

But $C_A = C_{A0}(1 - X_A)$ — ~~②~~ ③

taking diff. of above eqn.

$$dC_A = C_{A0}(-dX_A)$$

$$dC_A = -C_{A0}\, dX_A$$

changing sign both side

$$\boxed{-dC_A = C_{A0} \cdot dX_A} \quad — ~~③~~ ④$$

the eqn ③ and ④ in eqn ①

$$-\frac{dc_A}{dt} = K c_A^2$$

$$\frac{C_{A0} \cdot dx_A}{dt} = K \cdot C_{A0}^2 (1-x_A)^2$$

rearrange the eqn

$$\frac{dx_A}{(1-x_A)^2} = \frac{K \cdot C_{A0}^2 \, dt}{C_{A0}}$$

$$\frac{dx_A}{(1-x_A)^2} = K \cdot C_{A0} \cdot dt$$

Integrating the above eqn by 0 To x_A and 0 To t

$$\int_0^{x_A} \frac{dx_A}{(1-x_A)2} = K \cdot C_{A0} \int_0^t dt$$

Substitute

For $y = 1 - x_A$

$dx_A = dy$

and Integrating by $y = 1$ and $y = 1 - x_A$

$\frac{1}{y^2}\int dy$

$\frac{1}{y^2} = y$

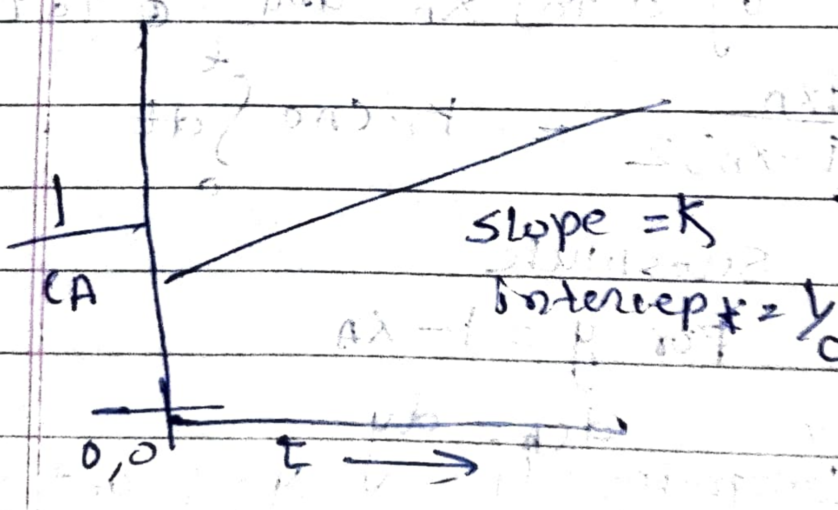
$= \frac{1}{y}$

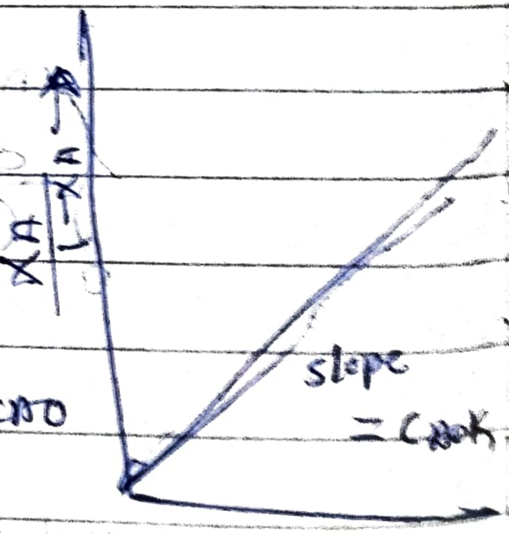
$$\int_{1}^{1-X_A} \frac{dy}{y^2} = K C_{A0}\int_0^t dt$$

$$\left[\frac{1}{y}\right]_1^{1-X_A} = K C_{A0} t$$

$$\left[\frac{1}{1-X_A}\right]^{1-X_A} = K C_{A0} t \qquad ④$$

The eqn ④ is the integrated rate eqn for second order reaction. in term of conversion.





Zero order Reaction

A reac^n is of zero order when the rate of reaction is independent of the concentration of the reactant.

A reaction of zero order is represented as

$$A \longrightarrow \text{product}$$

$$-r_A = -\frac{dC_A}{dt} = KC_A^0$$

$$-\frac{dC_A}{dt} = K$$

rearrage the eq^n

$$-dC_A = dt \cdot K$$

integrated the eq^n by CAo To CA.

$$-\int_{C_{A0}}^{C_A} dC_A = K\int_0^t dt$$

$$C_{A0} - C_A = Kt \quad \text{①}$$

eq^n ① is the integrated rate equation for zero order reaction in terms of conc^n

We know that

$$C_A = C_{A0}(1 - X_A)$$

Subtitute this value in eqn ①

$$C_{A0} - C_{A0}(1 - X_A) = Kt$$

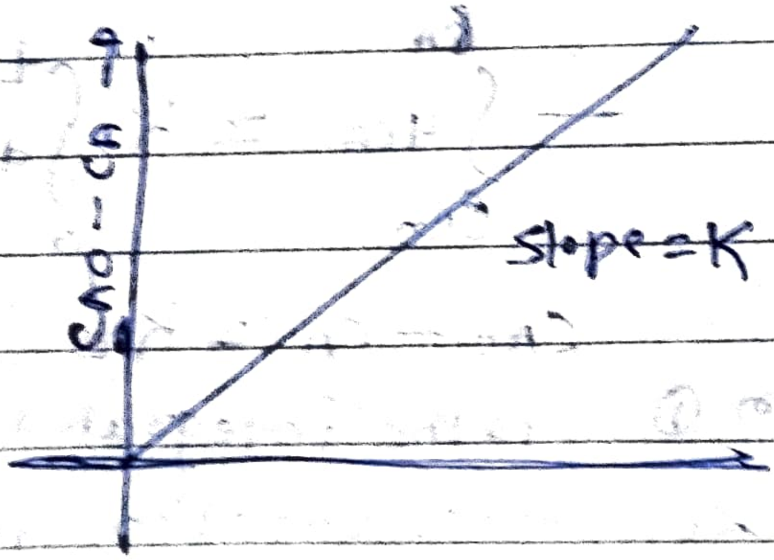
$$\cancel{C_{A0}} - \cancel{C_{A0}} + C_{A0} \cdot X_A = Kt$$

$$C_{A0} \cdot X_A = Kt \quad \text{—— ②}$$

The eqn two (2) is integrated rate eqn in terms of conversion

characteristics

plot a graph of $C_{A0} - C_A$ against t st. line passing through origin with slope equal to K.



Empirical rate equation of (nth) order

for the reac^n $A \longrightarrow$ products

$$-r_A = -\frac{dC_A}{dt} = K C_A^{n}.$$

rearrage the eq^n

$$-\frac{dC_A}{C_A^{n}} = K \cdot dt$$

Integrated by limit

$C_A = C_{A0}$ at $t = 0$

$C_A = C_A$ at $t = t$

$$-\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A^{n}} = K \int_0^t dt$$

$$-\left[\frac{C_A^{-n+1}}{-n+1}\right]_{C_{A0}}^{C_A} = Kt$$

$$\frac{1}{(n-1)}\left[\frac{1}{C_A^{n-1}} - \frac{1}{C_{A0}^{n-1}}\right] = Kt$$

$$\left[\frac{1}{C_A^{n-1}} - \frac{1}{C_{A0}^{n-1}}\right] = (n-1)kt, \quad n \neq 1$$

Half- life method

How, we will deal with the method of determinatio of overall order of irreversible reaction from the half-life.

The half life of a reaction, $t_{1/2}$ is defined as the time required for the concentration of the Reactant to fall to one-half of its Initial value.

∴ the reaction order and rate constant of a reaction can be determined from the data of half-life of a reaction as a function of the Initial Concentration obtained by performing experiments in Labratory.

For an irreversible Reaction

$$aA + bB + \cdots \longrightarrow \text{producat}$$

we write the rate of Expression are

$$-r_A = \frac{-dc_A}{dt} = k c_A^{\alpha} c_B^{\beta}$$

If the reactant are present in the Stoichiometric ratio Initially. they will remain at that ratio during the course of Reaction.

For the irreversible Reaction, Reactant A and B at any time:

$$\frac{C_B}{C_A} = \frac{b}{a} \qquad \boxed{C_B = \frac{b}{a} C_A}$$

$$-r_A = \frac{-dC_A}{dt} = k C_A^{\alpha} \left(\frac{b}{a} C_A\right)^{\beta} \quad \text{①}$$

$$= k C_A^{\alpha}\left[\left(\frac{b}{a}\right)^{\beta} \times (C_A)^{\beta}\right]$$

$$-r_A = k\left(\frac{b}{a}\right)^{\beta} \cdot C_A^{\alpha+\beta+\cdots n}$$

$$-r_A = k' C_A^{n}$$

Substitute this value in eqn ①

$$-\frac{dC_A}{dt} = k' C_A^{n}$$

$$\frac{-dC_A}{dt} = k' C_A^n$$

Rearrange the eqn and integrate with initial condition $C_A = C_{A0}$ at $t=0$

$$\int_{C_{A0}}^{C_A} \frac{-dC_A}{C_A^n} = k' \int_0^t dt$$

$$-\left[\frac{C_A^{-n+1}}{-n-1}\right]_{C_{A0}}^{C_A} = k't$$

$$\frac{1}{(n-1)}\left[\frac{1}{C_A^{n-1}} - \frac{1}{C_{A0}^{n-1}}\right] = k't$$

$$\frac{1}{C_A^{n-1}} - \frac{1}{C_{A0}^{n-1}} = k'(n-1)t$$

$$C_A^{-(n-1)} - C_{A0}^{-(n-1)} = k'(n-1)t$$

$$C_A^{1-n} - C_{A0}^{1-n} = k'(n-1)t \qquad \text{for } n \neq 1$$

the half life is the time required for the concentration of Reactant to fell to one half of its Initial value.

i.e. $t = t_{1/2}$ and $C_A = \frac{1}{2} C_{A0}$

$$\left(\frac{1}{2} C_{A0}\right)^{1-n} - C_{A0}^{1-n} = k'(n-1)\, t_{1/2}$$

$$\frac{C_{A0}^{1-n}}{2^{1-n}} - C_{A0}^{1-n} = k'(n-1)\, t_{1/2}$$

$$C_{A0}^{1-n}\left[2^{n-1} - 1\right] = k'(n-1)\, t_{1/2}$$

$$t_{1/2} = \frac{2^{n-1} - 1}{k'(n-1)}\, C_{A0}^{1-n} \quad \text{— ②}$$

Taking natural logrithms of both sides of equation ② we get

$$\ln(t_{1/2}) = \ln\left[\frac{2^{n-1} - 1}{k'(n-1)}\right] + (1-n)\ln C_{A0}$$

If

$$-\frac{dC_A}{dt} = K'' C_A^{\alpha}$$

rearrange and then integrated the eqn $C_B = C_{B0}$ at $t = 0$

then the eqn.

$$K'' = K (C_{B0}^{\beta})$$

$$\ln(t_{1/2}) = \ln\left[\frac{2^{n-1} - 1}{K'(n-1)}\right] + (1-n) \ln C_{B0}$$

• Calculation of Half-life of a first order reaction

We know that

$$K = \frac{2.303}{t} \log \frac{C_{A0}}{C_A} \quad -①$$

C_{A0} is a Initial concentration and C_A is the concentration of any time. i.e. Half life $t_{1/2}$ is time when Initial concentration reduce to ½ i.e.

$C_A = \frac{1}{2} C_{A0}$ substitute the eqn ①

$$K = \frac{2.303}{t_{1/2}} \log \frac{C_{A0}}{\frac{1}{2} C_{A0}}$$

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

$$K = \frac{2.303}{} \times 0.3010$$

~~$t_{1/2}$ =~~ $K = \frac{0.693}{t_{1/2}}$

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

Irreversible Reaction in parallel

In case of parallel reaction, the reactant is consumed by two different reactions to form different product. such reactions are also called as competing reactions.

Industrially important parallel reaction is the oxidation of ethylene to produce ethylene oxide along with formation of CO_2 and H_2O

$$CH_2=CH_2+\frac{1}{2}O_2 \longrightarrow C_2H_4O$$

$$CH_2=CH_2+3O_2 \rightarrow 2CO_2+2H_2O$$

consider that A is decomposing by two elementary Reaction in parallel

$$A \xrightarrow{k_1} R$$

$$A \xrightarrow{k_2} S$$

the rate of disapearance of A is given by

$$-r_A = \frac{dC_A}{dt} = K_1 C_A + K_2 C_A$$

$$-\frac{dC_A}{dt} = C_A (K_1 + K_2)$$

$$-\frac{dC_A}{C_A} = (K_1 + K_2) \cdot dt$$

Integrated the eqn by

CA = CAO and t = 0.

$$\int_{C_{A0}}^{C_A} -\frac{dC_A}{C_A} = K_1 + K_2 \int_0^t dt$$

and we get

$$-\ln\left(\frac{C_A}{C_{A0}}\right) = (K_1 + K_2)\, t \quad \text{—} ①$$

the rates of formation of R and S are given by

For R

$$r_R = \frac{dC_R}{dt} = K_1 C_A$$

and for S

$$R_S = \frac{dC_S}{dt} = K_2 C_A$$

$$\frac{r_R}{r_S} = \frac{dC_R/dt}{dC_S/dt} = \frac{K_1 C_A}{K_2 C_A}$$

$$= \frac{dC_R}{dC_S} = \frac{K_1}{K_2}$$

In which Integrating and we get

$$\frac{C_R - C_{R0}}{C_S - C_{S0}} = \frac{K_1}{K_2}$$

In this reaction system to know k_1 and k_2 we must fallow the concentration of atleast two components.

the concentration of third component is obtained by nothing that $C_A + C_R + C_S$ is constant.

A plot of $-\ln(C_A/C_{A0})$ v/s t yield a straight line with a slope equal to $K_1 + K_2$

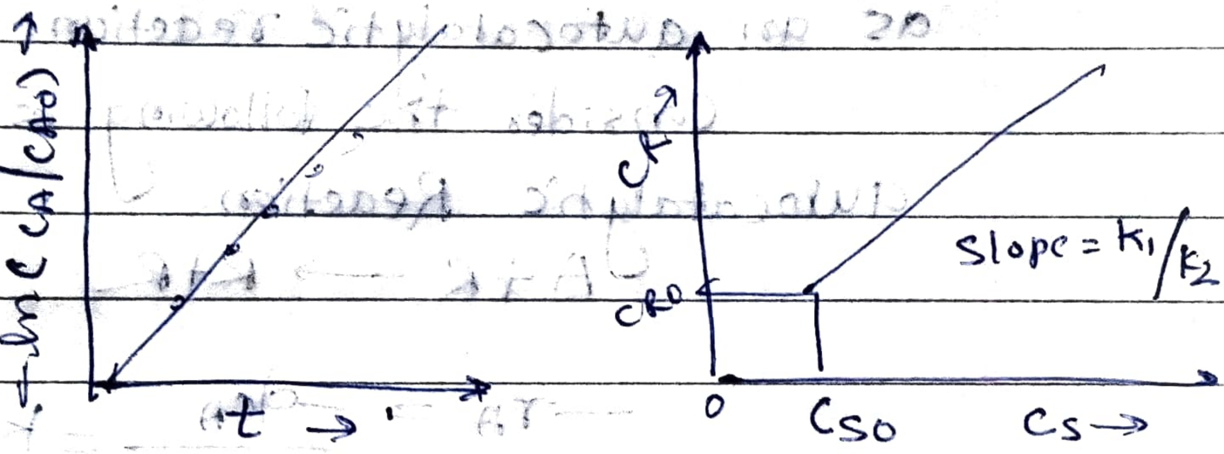


fig Evaluation of rate constant for first oder parallel Reaction.

Autocatalysic Reaction

A reaction in which one of the producat of the reaction acts as a catalyst is called as an autocatalytic reaction.

Consider the following simple autocatalytic Reaction.

$$A + R \rightarrow R + R$$

$$-r_A = \frac{-dC_A}{dt} = K C_A C_R$$

An a total Number of moles of A and R at any time t during the course of Reaction remain unchanged and stoichiometry of Reacting components and so we can write

$$C_0 = C_A + C_R = C_{A0} + C_{R0} = \text{constant}$$

at any time t

$$-r_A = \frac{-dC_A}{dt} = K C_A (C_0 - C_A)$$

| Because $C_R = C_0 - C_A$ |

Rearranging we get

$$\frac{-dC_A}{C_A(C_0 - C_A)} = k \cdot dt$$

Breaking into partial fraction, we get

$$-\frac{1}{C_0}\left[\frac{dC_A}{C_A} + \frac{dC_A}{C_0 - C_A}\right] = k\,dt$$

$$-\int_{C_{A0}}^{C_A} dC_A/C_A - \int_{C_{A0}}^{C_A} \frac{dC_A}{C_0 - C_A} = C_0 kt$$

$$\ln\left(\frac{C_{A0}}{C_A}\right) + \ln\left(\frac{C_0 - C_A}{C_0 - C_{A0}}\right) = C_0 kt$$

$$\ln \frac{C_{A0}(C_0 - C_A)}{C_A(C_0 - C_{A0})} = C_0 kt$$

Q. In haber process ammonia manufacturing $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ the rate of apearance of ~~NH_3~~ NH_3 is -

$$\frac{d[NH_3]}{dt} = 2\times10^{-4}\ mol\ L^{-1} s^{-1}$$ find

the rate of reaction of N_2, H_2.

Soln

$$\therefore \quad Rate = -\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$$

$$\frac{1}{2}\frac{d[NH_3]}{dt} = \frac{d[N_2]}{dt}$$

$$\frac{1}{2}\times2\times10^{-4} = \frac{d[N_2]}{dt}$$

$$1\times10^{-4} = \frac{d[N_2]}{dt}$$

similarly

$$\frac{1}{2}\frac{d[NH_3]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt}$$

$$\frac{1}{2}\times2\times10^{-4} = -\frac{1}{3}\frac{d[H_2]}{dt}$$

$$\frac{3}{2}\times2\times10^{-4} = -\frac{d[H_2]}{dt}$$

$$3\times10^{-4} = -\frac{d[H_2]}{dt}$$

3×10^{-4} lit^{-1} s^{-1}

p. the half-life period for a cetain First order reaction is 2.5×10^3 s. How long will it take for 1/4 of the receetant to be left behind

<u>Soln</u>

for the first order reaction

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

But $t_{1/2} = 2.5 \times 10^3$ s.

$\cancel{t_{1/2}} = 2.5 \times 10^3$ s

$$K = \frac{0.693}{2.5 \times 10^3}$$

$= 2.77 \times 10^{-4}$ s

let the time required to decrease the concentration of receetant of 1/4 th of its origrial concentration be t then

$C_{AO} = 1$ mol/lit, $C_A = \frac{1}{4}$ mol/lit

We know that eqn of concn of First order Reaction

$$K = \frac{1}{t} \ln \frac{C_{A0}}{C_A}$$

$$t = \frac{1}{K} \ln \frac{C_{A0}}{C_A}$$

$$t = \frac{1}{2.77 \times 10^{-4}} \ln \left[\frac{1}{1/4} \right]$$

= ~~5004.3~~

= 5000.5 Seconds.

② The half life period for a certain first order reaction is 3.6×10^{3} s. How long will it take for $\frac{1}{4}$ of reactant to be left behind.

For the first order reaction

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

$t_{1/2} = 3.6 \times 10^{3}$ s

$= 3.6 \times 10^{3}$ s

$$K = \frac{0.693}{3.6 \times 10^3}$$

$$K = 1.99 \times 10^{-4}\ s$$

But we know that

$$K = \frac{1}{t} \ln \frac{C_{A0}}{C_A}$$

~~K~~ $t = \frac{1}{K} \ln \frac{C_{A0}}{C_A}$

$C_{A0} = 1\ mol/16L$, $C_A = \frac{1}{4}\ mol/$

$$t = \frac{1}{1.99 \times 10^{-4}} \ln \left[\frac{1}{1/4}\right]$$

$$= 0.5025 \times 10^4 \times 1.38$$

$$= 6934.67 \text{ seconds}$$

3. Show that the decomposition of N_2O_5 at 68 °C is a first order reaction. Calculate the value of the rate constant.

Data

Time, min	0	1	2	3	4
$C_{N_2O_5}$ mol/lit	0.16	0.113	0.08	0.056	0.040

Soln :-

For the first order reaction, we have

$$K = \frac{1}{t} \ln \frac{C_{A0}}{C_A}$$

we write the eqn.

$$Kt = -\ln \frac{C_A}{C_{A0}}$$

① $C_A = 0.113$ mol/lit at $C_{A0} = 0.16$ $t=1$

$$K \times 1 = -\ln \frac{0.113}{0.16}$$

$$K = 0.3478\ \text{min}^{-1}$$

② $C_A = 0.08$ mol/lit, $C_{A0} = 0.16$, $t = 2$ min

$$K = \frac{-\ln(0.08/0.16)}{2} = 0.3466\ \text{min}^{-1}$$

③ $C_A = 0.056$, $C_{A0} = 0.16$, $t = 3$ min

$$K = \frac{-\ln(0.056/0.16)}{3} = 0.3499\ \text{min}^{-1}$$

④ $C_A = 0.040$, $C_{A0} = 0.016$, $t = 4$ min

$$K = \frac{-\ln \frac{0.040}{0.16}}{4}$$

$$K = 0.3466\ \text{min}^{-1}$$

the constant of Rate Constants K

indicates that the decomposition of N_2O_5 is First order reaction.

The average value of the rate constant (K) $= \frac{0.3478 + 0.3466 + 0.3499 + 0.3466}{4}$

$= 0.3477 \text{ min}^{-1}$ Ans

4) From the fallowing data show that decomposition of Hydrogen peroxide in aquenus solution is a First order Reaction What the Value of rate constant.

Time in min	0	10	20	30	40
N	25	20	15.7	12.5	9.6

where 'N' is the Number of ml of $KMnO_4$ required to decomposition at detonate volume H_2O_2.

solution :

As the decomposition is first order reaction

we know

$$K = \frac{1}{t} \ln\left(\frac{C_{A0}}{C_A}\right)$$

$C_{A'0} = 25$ ml

for $t = 10$ and $C_A = 20$

$$K = \frac{1}{10} \ln\left(\frac{25}{20}\right)$$

$= 0.0223 \text{ min}^{-1}$

for $t = 20$ min $C_A = 15.7$ ml

$$K = \frac{1}{20} \ln\left(\frac{25}{15.7}\right)$$

$= 0.02326 \text{ min}^{-1}$

for $t = 30$ min $C_A = 12.5$ ml

$$K = \frac{1}{30} \ln\left(\frac{25}{12.5}\right)$$

$= 0.0231 \text{ min}^{-1}$

for t = 40 min

$C_A = 9.8$ ml

$$K = \frac{1}{40} \ln \frac{25}{9.8}$$

$= 0.0239 \text{ min}^{-1}$

Average value of K
(Rate constant)

$$= \frac{0.0223 + 0.02326 + 0.0231 + 0.0239}{4}$$

$= 0.02314 \text{ min}^{-1}$

Since the value of K (Avg = 0.02314 min^{-1}) is almost constant the decomposition is first order.

5) Determine the order of Reaction from the following data

conc. of A mol/lit	1.0	1.0	0.02	0.04
conc. of B mol/l	0.02	0.04	1.0	1.0
Rate of Reaction mol/l. min	4.6×10^{-4}	9.2×10^{-4}	9.2×10^{-6}	3.68×10^{-5}

Determine the true rate constant also.

Solution. When the concentration of A is very large and constant, the rate depends upon the concentration of B only. therefore order of Reaction with respect to B is calculated as.

$$n_B = \frac{\ln r_1/r_2}{\ln C_{B_1}/C_{B_2}}$$

$r_1 = 4.6\times10^{-4}$ mol/l. min , $C_{B_1} = 0.02$ mol/l

$r_2 = 9.2\times10^{-4}$ mol/l. min. $C_{B_2} = 0.04$ mol

$$n_B = \frac{\ln(4.6\times10^{-4}/9.2\times10^{-4})}{\ln\left(\frac{0.02}{0.04}\right)}$$

$$= \frac{-0.301}{-0.301} = 1$$

When concentration of B is very large and constant the rate sl depends upon conc of A hence

$$n_A = \frac{\ln r_1' / r_2'}{\ln C_{A1} / C_{A2}}$$

$r_1' = 9.2 \times 10^{-6}$ $C_{A1} = 0.02$

$r_2' = 3.68 \times 10^{-5}$ $C_{A2} = 0.04$

$$n_A = \frac{\ln (9.2 \times 10^{-6} / 3.68 \times 10^{-5})}{\ln (0.02 / 0.04)}$$

$$= \frac{-0.602}{-0.301} = 2$$

There fore, the order of reaction

$$n = n_A + n_B$$

$$= 2 + 1 = 3$$

The rate equation may be given as.

$$\text{Rate} = k\, C_A^2 \cdot C_B$$

$$K = \frac{\text{Rate}}{C_A^2 \cdot C_B}$$

(i) $K = \frac{4.6 \times 10^{-4}}{(1)^2 \cdot (0.02)} = 2.3 \times 10^{-2}\ (\text{mol}/\text{lit})^{-2}\ \text{min}^{-}$

(ii) $K = \frac{9.2 \times 10^{-4}}{(1.0)^2\ (0.04)} = 2.3 \times 10^{-2}$ 〃

(iii) $K = \frac{9.2 \times 10^{-6}}{(0.02)^2\ (1.0)} = 2.3 \times 10^{-2}\ (\text{mol}/\text{lit})^{-2}\ (\text{min})^{-}$

(iv) $K = \frac{3.68 \times 10^{-5}}{(0.04)^2\ (1.0)} = 2.3 \times 10^{-2}$ 〃

Hence the true rate constat $= 2.3 \times 10^{-2}\ (\text{mol}/\text{lit})^{-2}\ \text{min}^{-}$

P·6 An aqueous solution of ethyl acetate is to sponified with sodium hydroxide the Initial concentration of ethyl acetate is 5 gm/lit and that of caustic is 0·10 Normal, the values of second order rate costant at 0°c and 20°c are $K = 0{\cdot}235$ and $0{\cdot}924$ $(l/mol)\ min^{-1}$ respectively. the reaction is irreversible. Calculate the time required to sponify 95% ~~Bs~~ of ester at 40°c

solution

$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa.$

$A + B \rightarrow R + S$

$C_{AO} = 5\ gm/lit = \dfrac{5}{\text{mol. wt of } CH_3COOC_2H_5} = \dfrac{5}{88}$

$= 0{\cdot}0568\ mol/lit$

$C_{BO} = 0{\cdot}10$ normal $= 0{\cdot}10$ molar (NaOH)

$= 0{\cdot}10\ mol/lit$

$e^{1.19}$ by cal = Alpha X ~~ln~~ power ^
Alpha x ln 1.19 = 3.2[illegible]

10/10

$k_1 = 0.235\ (l/mol)\ min^{-1}$ at $T_1 = 0°C = 273K$

$k_2 = 0.924\ (l/mol)\ min^{-1}$ at $t_2 = 20°C$
$= 20+273 = 293$

we have

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

$$\ln\left(\frac{0.924}{0.235}\right) = \frac{E}{1.987}\left[\frac{1}{273} - \frac{1}{293}\right]$$

$E = 10887$ Cal/mole

Calculate K at $40°C = 313K$

$$\ln\left(\frac{k_3}{k_2}\right) = \frac{10887}{1.987}\left[\frac{1}{293} - \frac{1}{313}\right]$$

$$\ln \frac{k_3}{k_2} = 5479.11\left[~~0.0034 - 0.0031~~\ 0.0002180\right]$$

$\ln \frac{k_3}{k_2} =$ ~~1.6443733~~ 1.194890

$\frac{k_3}{k_2} =$ ~~$e^{1.647732}$~~ $e^{1.194890}$

$k_3/k_2 = 3.30$ (by cal alpha x ln ^ 1.19

$K_3 = 3.30\, K_2$

$= 3.30 \times 0.924$

$= 305\, (l/mol)\ min^{-1}$

At 40°C $\underline{K = 3.05}$ lmol/min

For second order ~~reaction~~ irreverssible reaction the integrated rate expression is

$$\ln\left[\frac{m - X_A}{m(1-X_A)}\right] = C_{A0}(m-1)kt$$

$$M = \frac{C_{B0}}{C_{A0}} = \frac{0.10}{0.0568} = 1.76$$

$X_A = 0.95$ (95% sponification)
find t

$$\ln\left[\frac{1.76 - 0.95}{1.76(1-0.95)}\right] = 0.0568 \times (1.76-1) \times 3.05 \times t$$

$$t = 17 \text{ min}$$

time Required for sponify 95% ester = 17 min.

P- Following are results obtained for the decomposition of nitrous oxide in contalcat with gold surface at 900°C

Time (mine)	15	30	45	65	80
% N_2O decomposed	17	32	44.5	37	65

Show that Order of Reaction is Unity

solution :- For first order reaction We have

$$K = \frac{1}{t} \ln \left(\frac{C_{AO}}{C_A} \right).$$

$$\boxed{\frac{C_{AO}}{C_A} = \frac{1}{1-X_A}}$$

% decimposed = % converted = X_A%.

1) At t=15 min

$X_A = 17\% = 0.17$

$$K = \frac{1}{15} \ln \left[\frac{1}{1-X_A} \right]$$

$$= \frac{1}{15} \ln \left[\frac{1}{1-0.17} \right]$$

$$K = 0.01243 \ \text{min}^{-1}$$

ii) ~~At t 30 m~~ At $t = 30$ min

$X_A = 0.32$

Ans $\boxed{K = 0.01266 \text{ min}^{-1}}$

iii) At $t = 45$ min, $X_A = 0.445$

Ans $K = 0.01289$ min^{-1}

iv) $t = 65$ min $X_A = 0.57$

$K = 0.01289$ min^{-1}

v) $t = 80$ min. $X_A = 0.65$

$K = 0.01289$ min^{-1}

Since K fairly constant, ∴ reaction is First order.

---

p. Hydrolysis of ethyl acetate by NaOH using equal concentration of the reactants, was studied by titrating 25 ml of reaction mixture of a different time interval against standard acid from the data given below establish that this is a second order reaction

t in Min	0	5	15	25
ml acid used	16.00	10.24	6.13	4.32

soln :

We know that $K = \frac{1}{t}\left[\frac{1}{C_A} - \frac{1}{C_{A0}}\right]$

$\therefore C_{A0} = 16$

& $C_A = 10.24$ at 5 min, 6.13 at 15 min.

4.32 at 25 min

$\therefore K = \frac{1}{5}\left[\frac{1}{16} - \frac{1}{10.24}\right] = 0.0070$ L/mol/m

$K = \frac{1}{10}\left[\frac{1}{16} - \frac{1}{6.13}\right] = 0.0067$ L/mole/min

$K = \frac{1}{15}\left[\frac{1}{16} - \frac{1}{4.32}\right] = 0.00676$ L/mole/min.

The values of K being fairly constant. the reaction is the second order.

P A solution of H_2O_2 when titrated against $KMnO_4$ solution at different time intervals gave the following result.

t min	0	10	20
vol $KMnO_4$ for 10 ml H_2SO_4	23.8	14.7	9.1 ml

Show the decomposition of H_2O_2 is a first order reaction.

Soln We know that

$$K = \frac{1}{t} \ln \frac{C_{A0}}{C_A}$$

$$\therefore K = \frac{2.303}{t} \log \frac{C_{A0}}{C_A}$$

$C_{A0} = 23.8$

$C_A = 14.7$ at $t = 10$, 9.1 at $t = 20$

$$K = \frac{2.303}{10} \log \frac{23.8}{14.7} =$$

$$= \overset{0.2303}{\cancel{23.03}} \times \log 1.62 = 0.2303 \times 0.2095$$

$$= 0.04824$$

$$K = \frac{2.303}{20} \log \frac{23.8}{9.1} = 0.04240$$

The value k is almost constant. The decomposition of H_2O_2 is first order reaction.

Kinetic models for non-elementry Rean

To explain the kinetics of non-elementary rean, we assume that overall rean is the result of a series of elementaly rean that involves intermediate species. We can not measure and observe the intermediates formed as they are present in a very minwe quantities and left undected.

ther fore In testing of Kinetic model all that we have to do is

i> Assume the model

ii> obtain Kinetic expression

iii> see Whether the predicted rate expression is similar in from to the experimentaty found rate expression if not assume the new model.

Types of intermediate that can be formed

A> **Free radicals:** free atoms or larger Fragments of a stable molecules that contain one or more un paired eletron are called free radicals.

Examples

$H^\bullet$, $CH_3^\bullet$, $C_2H_5^\bullet$ etc.

ii> Ionic intermediates :

Electrically charged atom, molecule or fragment of molecule such as Na^+, OH^-, NH_4^+ are called ions.

example Na^+, OH^-, NH_4^+ are called ion

iii> molecule

molecule R in series reaction $A \rightarrow R \rightarrow S$.

In such reaction if the molecule R is highly reactive, it means life time is very small and its concentration in the reaction mixture is too small to measure. In such situation R may not be observed and thus can be considered as a reactive Intermediate.

iv> Transition Complexes.

The unstable forms of molecule, unstable association of molecule which decompose to give the product or by further collision return to the molecule in the normal state such unstable formed are called as transistion complexes.

The suggested schemes can be two types.

i) Non-chain Reaction
ii) chain Reaction.

Non-chain Reaction - In the non-chain Reaction, the intermediate is formed in the first Reaction which then disapears as its reacts further to yield the producat

Reactant → Intermediate
Intermediates* → producat

Chain Reaction

Reactant → (intermediate)* - Initiation
(Intermediate)* + (Reactant) → (Intermediate)** + producat -- propagation
(Intermediate)* → producat --- terminati

Q. For the Reaction $N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}(O_2)$
the value disapearance of N_2O_5 is given as 6.25×10^{-3} $mol\ L^{-1}\ s^{-1}$ what is the rate of formation of NO_2 & O_2

Sol/n

$$-\frac{d[N_2O_2]}{dt} = +\frac{1}{2}\frac{d[NO_2]}{dt} = +2\frac{d[O_2]}{dt}$$

$$\frac{1}{2}\frac{d[NO_2]}{dt} = -\frac{d[N_2O_2]}{dt}$$

$$\frac{d[NO_2]}{dt} = 2\times6.25\times10^{-3}$$

$$= 12.50\times10^{-3}\ mol\ L^{-1}\ s^{-1}$$

$$\frac{2d[O_2]}{2\,dt} = \frac{1}{2}\times6.25\times10^{-3}$$

$$= 3.125\times10^{-3}\ mol\ L^{-1}s^{-1}$$

Temperature - dependent term of rate eqn :-

For a reaction to occur, it is a first necessary to break or wealsen the bonds betn atom and molecule of the reactants which required a definate amount of energy. If the colliding molecule do not posses this energy, a collision between them does not result in the formation of new molecule.

the minimum amount of energy which the collinding molecules must have in order to bring about the reaction is known as activation energy.

Lower the value of of activation energy, higher will be the rate at which reaction will proceed and higher the value of activation energy, Lower will be the rate at which the Reaction proceeds.

for many reaction, the temperature dependence of the reaction rate constant K can be correlated by an equation of the type

$$K = K_0 e^{-E/RT} \quad -①$$

K_0 = pre exponential factor or frequency factor

E = Activation Energy J/mol or cal/mol

R = gas constant = 8.314 J/(mol.K)

= 1.987 cal/mol.K

T = absolute temperature K.

eqn ① is known as the arrhenius eqn or Law.

From the kinetic energy of gasses the factor $e^{-E/RT}$ gives the fraction betn the of the collision between molecules that together have this minimum energy that is bring about the chemical Reaction

The activation energy determining Experimentally by carrying out the reaction at th several different temperatures.

Taking the natural logrithm of eqn ① we get.

$$\ln K = \ln K_0 - \frac{E}{R}\left(\frac{1}{T}\right) \quad -②$$

Altrnatively.

The activation energy can also be obtained by measuring the rate constant. K_1 and K_2 at temp T_1 and T_2 respectively.

$$\ln k_1 = \ln k_0 - \frac{E}{RT_1} \quad ③$$

$$\ln k_2 = \ln k_0 - \frac{E}{RT_2} \quad ④$$

~~$\ln\left(\frac{K_2}{K_1}\right)$~~ Substract eqn ③ from eqn ④

$$\ln k_2 - \ln k_1 = \frac{-E}{RT_2} + \frac{E}{RT_1}$$

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{E}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$\ln\frac{K_2}{K_1} = \frac{E}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

If the concentration dependency of the rate of reaction is not known but rate of Reaction v/s. Temperature data available for diffreant concentrations E can be obtained from a plot of $\ln r$ v/s. $1/T$

If rate is known at two different temperature T_1 and T_2 then we can evaluate E with the help of equation

$$\ln\frac{r_2}{r_1} = -\frac{E}{R}\left[\frac{1}{T_2}-\frac{1}{T_1}\right]$$

Activation energy is usually reported in cal/mol or J/mol. In the above eqn we have to use T in K and R = 1.987 cal/mol or 8.314 J/mol.K

Temp. dependency from collision theory

$$\ln\frac{r_2}{r_1} = \frac{E}{R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]+\ln\left(\frac{T_2^{1/2}}{t_1^{1/2}}\right)$$

P. The gas phase Reaction beth methane (CH_4) and diatomic sulphur (S_2) is a given by equation

$CH_4(g) + 2S_2(g) \longrightarrow CS_2(g) + 2H_2S(g)$

At 550°C the rate constant fo this reaction is 1.1 litmol^{-1}sec and 625°C the rate constalt is 6.4 Lmol^{-1}sec. Calculate Ea fo this reaction

Sol^n

$K_1 = 1.1$ lit mol^{-1} sec

$K_2 = 6.4$ lit mol^{-1} sec

$T_1 = 550+273 = 823K$

$T_2 = 625+273 = 898K$

$R = 8.3145\ JK^{-1}mol^{-1}$

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{E}{R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$$

$$\ln\left(\frac{6.4}{1.1}\right) = \frac{E}{8.31}\left[\frac{1}{823}-\frac{1}{898}\right]$$

$E = 1.4\times10^5$ J/mol