ENGINEERS
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CHEMICAL ENGINEERING
REVISED AS PER GATE

CHEMICAL REACTION ENGINEERING

CHEMICAL ENGINEERING

Revised as Per New GATE Syllabus

STUDY MATERIAL

CHEMICAL REACTION ENGINEERING

Chemical Reaction Engineering: Theories of reaction rates; kinetics of homogeneous reactions, interpretation of kinetic data, single and multiple reactions in ideal reactors, non-ideal reactors; residence time distribution, single parameter model; non-isothermal reactors; kinetics of heterogeneous catalytic reactions; diffusion effects in catalysis.

C O N T E N T

CRE : Marking Analysis in GATE (2010 to 2024)			
Year	1 Mark	2 Marks	Total Marks
2024	1×4	2×4	12
2023	1×3	2×3	9
2022	1×4	2×3	10
2021	1×2	2×4	10
2020	1×2	2×6	14
2019	1×2	2×4	10
2018	1×2	2×5	12
2017	1×3	2×5	13
2016	1×3	2×4	11
2015	1×2	2×4	10
2014	1×2	2×3	8
2013	1×4	2×3	10
2012	1×3	2×3	9
2011	1×2	2×3	7
2010	1×1	2×4	9

List of Topics in GATE 2024 paper from CRE:

Collision theory, Reaction kinetics, Kinetics of parallel reaction), CSTR, Heterogeneous reaction, Homogenous reaction, Non-ideal reactor, Microbial fermentation.

CHAPTER-1

INTRODUCTION AND BASIC CONCEPT

Every industrial chemical process is designed to produce economically a desired product from a variety of starting material through a succession of treatment steps.
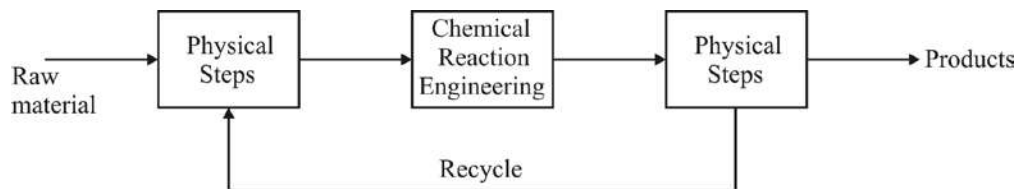
Figure: Typical chemical process.

Raw material undergoes a number of physical steps to put them in the form in which they can be reacted chemically. Then material passes through the reactor. The products of reaction must then undergo for further treatment. In chemical reaction engineering subject we are concerned with chemical treatment step of a process. CRE combines the study of chemical kinetics (reaction rates and reaction mechanisms) with the reactors in which the reaction occurs.

Chemical Reaction: When any chemical starts to losing their identity, then we can say it reacts. Chemical reaction takes place by decomposition, combination or change in configuration of molecules. Chemical reaction may be classified depending upon so many factors, given below:

* Based upon number of phase involved: Homogeneous and Heterogeneous reaction.
* Based upon catalyst used or not: Catalytic and non-catalytic reaction.
* Based upon the molecularity i.e. number of molecules that takes part in the reaction: Unimolecular, bimolecular and tri-molecular reaction.
* Based upon heat evolved or absorbed: Exothermic and endothermic reaction
* Based upon reaction takes place in one or both directions: Reversible or irreversible reaction.
* Based upon order of reaction: First order, second order and third order reaction.
* Based upon single or multiple reaction takes place: Single and multiple reaction.
* Based upon number of steps present in a reaction: Elementary and non-elementary reaction

Rate of Reaction: We define **rate of reaction** in terms of component. If the rate of change in number of moles of this component due to reaction is $\dfrac{dN_i}{dt}$ then,

$$\boxed{r_i = \frac{1}{V}\frac{dN_i}{dt} = \frac{\text{Moles of } i \text{ formed}}{(\text{Volume of fluid})\,(\text{Time})}}$$

i.e., the number of moles of component i formed per unit time per unit volume (mol/dm^{3}s). If species i is a reactant, the numerical value of r_i is a negative number (e.g. $r_i = -3\text{mol/dm}^3.\text{s}$ or $-r_i = 3\text{mol/dm}^3.\text{s}$)

If species i is a product, then $r_i =$ will be a positive number.
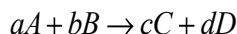
The rate of reaction can be a large value to essentially zero.

For constant volume system: $\quad r_i = \dfrac{d}{dt}\left(\dfrac{N_i}{V}\right) = \dfrac{d}{dt}(C_i) = \dfrac{dC_i}{dt}$

where, C_i is the concentration of species i in reaction mixture.

Relative rates of reaction:

For the reaction:

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

The relation between the rate of participants A, B, C, D in chemical reaction with their stoichiometric coefficient

is:
$$\frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_C}{c} = \frac{r_D}{d}$$

Also, if we compare $\dfrac{-r_A}{a} = \dfrac{r_C}{c}$

$$-r_A = \frac{a}{c} r_c$$

Rate of disappearance of A = $\dfrac{a}{c}$ (Rate of formation of C)

Factors affecting rate of reaction:
Many variable may affect the rate of a chemical reaction. In homogeneous system the temperature, pressure and composition affect the rate of reaction.

In heterogeneous system factors that affect the rate of reaction are rate of mass transfer *i.e.,* heat transfer nature of catalyst if present.

Note (1) Rate of reaction can also be given as:

i) Based on unit mass of solid in fluid-solid system,
$$r_i' = \frac{1}{W}\frac{dN_i}{dt} = \frac{\text{moles of i formed}}{(\text{mass of solid})(\text{time})}$$

ii) Based on unit interfacial surface in two-fold systems or based on unit surface of solid in gas-solid system,
$$r_i'' = \frac{1}{S}\frac{dN_i}{dt} = \frac{\text{moles of } i \text{ formed}}{(\text{surface}) (\text{time})}$$

iii) Based on unit volume of solid in gas-solid systems,
$$r_i''' = \frac{1}{V_s}\frac{dN_i}{dt} = \frac{\text{moles of } i \text{ formed}}{(\text{volume of solid}) (\text{time})}$$

iv) Based on unit volume of reactor, if different from the rate based on unit volume of fluid,
$$r_i'''' = \frac{1}{V_r}\frac{dN_i}{dt} = \frac{\text{moles of i formed}}{(\text{volume of reactor})(\text{time})}$$

(2) Relation between different rate of reactions:
$$(r_i)V = (r_i')W = (r_i'')S = (r_i''')V_s = (r_i'''')V_r$$

Rate law:

An algebraic equation that relates the reaction rate and concentration is known as rate law.

$$A + B \rightarrow \text{PRODUCTS}$$

$$-r_A = k_A(T)\left[f_n(C_A, C_B)\right] \qquad or \qquad -r_A = k_A C_A^{\alpha} C_B^{\beta}$$

$k_A \rightarrow$ Rate constant/ specific reaction rate
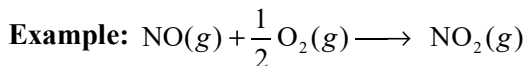
Order of reaction (n) = $\alpha + \beta$

For the reaction where all the stoichiometric coefficients are 1, e.g.

A + B $\rightarrow$ C + D
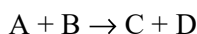
$$k_A = k_B = k_C = k_D = k$$

Important. Rate Laws Are determined by experimental observation.

1. A homogeneous reaction is one which takes place in only one phase; *i.e.,* all the reacting material and products and catalyst (if any) will be present in a similar phases.
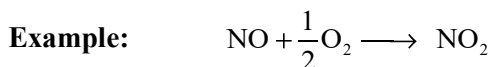
Example: $NO(g) + \dfrac{1}{2}O_2(g) \longrightarrow NO_2(g)$

A hetrogeneous reaction is one which involves the presence of more than one phase.

Example: $SO_2(g) + \dfrac{1}{2}O_2(g) \xrightarrow{V_2O_5(s)} SO_3(g)$
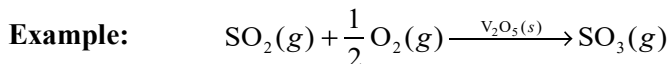
2. Catalytic reaction are those reaction which involves use of catalyst to enhance the rate of reaction.

Example: $\underset{\text{Ethylene}}{C_2H_4} + H_2 \xrightarrow[\text{Heat}]{Ni} \underset{\text{Ethane}}{C_2H_6}$

Non catalytic reactions are those reaction which does not involve use of catalyst.

Example: $NO + \dfrac{1}{2}O_2 \longrightarrow NO_2$

3. (*a*) **Unimolecular Reaction:** Reaction of single molecule.

Example: $\begin{matrix} H_2C — CH_2 \\ | \quad\quad | \\ H_2C — CH_2 \end{matrix} \xrightarrow{\text{Decomposition}} 2C_2H_4$
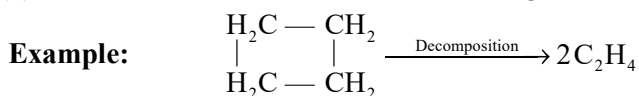
(*b*) **Bimolecular Reaction:** Reaction between two molecules.

$2HI(g) \xrightarrow{\text{Decomposition}} I_2(g) + H_2(g)$
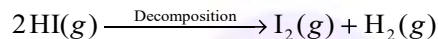
(*c*) **Trimolecular Reaction:**

$2NO + O_2 \xrightarrow{\text{Oxidation}} 2NO_2$
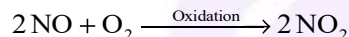
4. The reaction may be classified as exothermic and endothermic reaction.
Exothermic reaction is one in which heat is evolved.

Example: $CO + 2H_2 \xrightarrow{Cu} CH_3OH + Heat$
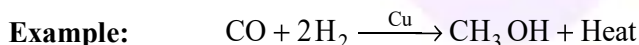
Endothermic reaction is one in which heat is absorbed

$\underset{\text{ethyl alcohol}}{C_2H_5OH} \xrightarrow[\text{Dehydration}]{Al_2O_3} C_2H_4 + H_2O - Heat$
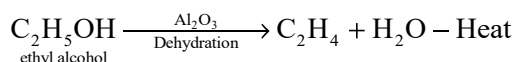
5. The reaction may be classified as reversible and irreversible reaction. Reversible reaction are those in which forward and reverse reaction takes place simultaneously.

$C_2H_5OH + CH_3COOH \underset{}{\overset{H^+}{\rightleftharpoons}} CH_3COOC_2H_5 + H_2O$
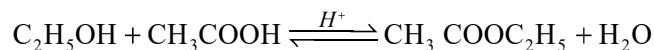
Irreversible reaction are those which can proceed only in one direction.

$C_6H_6 + HNO_3 \longrightarrow C_6H_5NO_2 + H_2O$
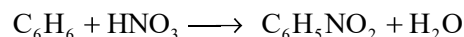
6. The reaction may be classified as first order, second order and third order reaction.
First order reaction:

Example: $N_2O_5 \xrightarrow{\text{Decomposition}} NO_2 + \dfrac{1}{2}O_2$
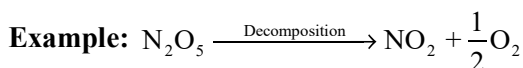
Second order reaction: (Saponification of ester)
Example: $CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$

Third order reaction:
Example: $2NO + H_2 \longrightarrow N_2O + H_2O$
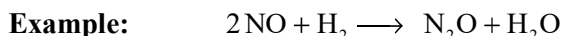
Solved Example

Q.1. For a homogeneous reaction system, where C_i is the concentration of i at time t, N_i is the no. of moles of i at time t, V is the reaction volume at time t and t is the reaction time. The rate of reaction for species i is defined as

(a.) $\dfrac{dC_i}{dt}$ (b.) $-\left(\dfrac{dC_i}{dt}\right)$ (c.) $\dfrac{1}{V}\dfrac{dN_i}{dt}$ (d.) $-\left(\dfrac{1}{V}\dfrac{dN_i}{dt}\right)$

Ans. c

Q.2. For an elementary reaction $A + 2B \xrightarrow{\ k\ } 3C$

(a.) Rate of appearance of C is equal to rate of disappearance of A

(b.) Rate of disappearance of A is equal to rate of disappearance of B.

(c.) Rate of appearance of C is equal to rate of disappearance of B.

(d.) Rate of appearance of C is 3 times rate of disappearance of A.

ANS: d

$$\dfrac{-r_A}{1} = \dfrac{-r_B}{2} = \dfrac{r_C}{3}\begin{bmatrix}\text{Relative Rates}\\ \text{of reaction}\end{bmatrix}$$

$-r_A$ = rate of disappearance of A

$-r_B$ = rate of disappearance of B

r_C = rate of appearance of C

$\therefore \boxed{r_C = 3(-r_A)}$

Q.3. Rate expression of reaction

$-r_A = 0.02 C_A^2 \ \text{mol/cm}^3\text{min}$

If concentration is to be expressed in mol/l and time in hours, the value of rate constant would be

(a.) $0.12\,\text{hr}^{-1}(\text{mol}/l)^{-1}$ (b.) $0.012\,\text{hr}^{-1}(\text{mol}/l)^{-1}$

(c.) $12\,\text{hr}^{-1}(\text{mol}/l)^{-1}$ (d.) $1.2\,\text{hr}^{-1}(\text{mol}/l)^{-1}$
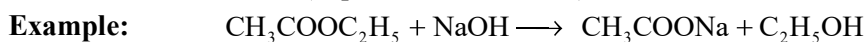
ANS: (c)

$1L = 10\text{cm}^3$

$1\text{hr} = 60\text{min}$

$$-r_A = 0.02 C_A^2 \dfrac{mol}{\left(\dfrac{1}{10}\right)^2 \left(\dfrac{1}{60}\right)hr}$$

$$-r_A = 0.02 C_A^2 \times 600 \dfrac{mol}{l\ hr}$$

$-r_A = 12 C_A^2 mol\ l^{-1} hr^{-1}$

Clearly $k = 12$

unit of $k = \dfrac{r_A}{C_A^2} = \dfrac{molL^{-1}hr^{-1}}{mol^2 l^{-2}}$ $\Rightarrow$ *unit of* $k = mol^{-1}l\ hr^{-1}$

$\boxed{k = 12 hr^{-1}(mol/l)^{-1}}$

Q.4. The rate of reaction for a gas phase reaction is expressed as

$$\frac{-dp_A}{dt} = 2.56 P_A^2 \, atm/hr$$

The Units of rate constant are

(a.) $hr^{-1}(atm)^{-1}$ (b.) $hr^{-1}(atm)^3$ (c.) $hr^{-1}atm$ (d.) $hr^{-1}(mol/L)^{-1}$

ANS: (a) $k = \dfrac{-dp_A/dt}{p_A^2} = \dfrac{atm/hr}{atm^2} = atm^{-1}hr^{-1}$

Q.5. For a gas reaction at T(K), the rate is given by:

$$\frac{-dp_A}{dt} = k' p_A^2 \, atm/hr$$

If the rate equation is expressed as:

$$-r_A = \frac{-1}{V}\frac{dN_A}{dt} = kC_A^2 (mol/L - hr)$$

The rate constant k is given by

(a.) k = k'rT   (b.) k = k'   (c.) k = k' $(RT)^2$ (d.) k = k'/RT

ANS: (a)

$$\frac{-dp_A}{dt} = k' p_A^2 \qquad\qquad \boxed{C_A = \frac{p_A}{RT}}$$

$$\frac{-d}{dt}(C_A RT) = k' C_A^2 (RT)^2$$

$$-RT\frac{dc_A}{dt} = k' C_A^2 (RT)^2$$

$$-\frac{dc_A}{dt} = k' C_A^2 (RT)$$

$$-r_A = k' C_A^2 (RT)$$

$$kc_A^2 = k' C_A^2 (RT)$$

$$k = k'(RT)$$

Q.6. The irreversible reaction is the special case of reversible reaction if concentration of reactant at equilibrium condition is _____

(a) 6   (b) 4   (c) 2   (d) 0

ANS: (d)

Summery

1. When solid catalyst present in liquid or gas phase condition, it is also considered as heterogeneous reaction.
2. For nth order reaction unit of rate constant K is given by (concentration)$^{1-n}$ time^{-1}.
3. Variable affecting rate of reaction are T, P, concentration heat transfer, mass transfer in heterogeneous system.

CHAPTER-2

KINETICS OF REACTION

In homogeneous system, the possible factors that affect the rate of reaction are temperature, composition and pressure.

Hence for homogeneous system we can write rate of reaction as a function of concentration and temperature.

$$-r_A = f[\text{Temperature dependent term, Concentration dependent term}]\frac{\text{mol}}{l.s}$$

According to rate law rate of reaction is directly proportional to the reactant concentration. Rate law is also called rate equation, kinetic expression.

Consider a irreversible reaction

$$a\,A + b\,B .... \longrightarrow r\,R + s\,S ....$$
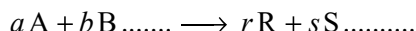
According to rate law we can write

$$-r_A = kf(C_A, C_B) = k\,C_A^a\,C_B^b ....$$

Where K is rate constant *a* and *b* are the power of concentration of reactant A, B ….. on which rate of reaction depends.

Kinetics Model for Non-Elementary Reactions:

To explain the kinetics of non elementary reaction we assume that a sequence of elementary reaction is actually occurring but we can not observe the intermediate formed because they are only present in very minute quantity. Hence we observe only initial reactant and final products that appears to be a single reaction.

For example: $A_2 + D_2 \longrightarrow 2\,AD$

If the kinetic of reaction shows that reaction is non-elementary then we can postulate a series of elementary steps.

$$A_2 \rightleftharpoons 2\,A^*$$

$$A^* + D_2 \rightleftharpoons AD + D^*$$

$$A^* + D^* \rightleftharpoons AD$$
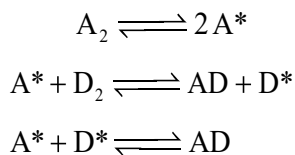
where * sign shows unobserved intermediate.

Types of Intermediate:

(*i*) Free radicals:

Free atoms that contain one or more unpaired electrons are called free radicals.

Example: $CH_3^{\bullet}, C_2H_5^{\bullet}, I^{\bullet}, H^{\bullet}, CCl_3^{\bullet}$

They are highly reactive and unstable.

(*ii*) Ions and Polar Substance: Electrically charged atoms, molecules or fragments of molecules are called ions.

Example: N_3^-, N_a^+, OH^-, I^-

(*iii*) Molecules: Consider a consecutive reaction,

$$A \longrightarrow B \longrightarrow C$$
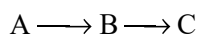
If the intermediate B is highly reactive its mean life time will be very small and its concentration in the reacting mixture can become too small to measure.

In this condition B may not be observed and can be considered to be a reactive intermediate.

(iv) Transition Complex: Unstable forms of molecule or unstable association of molecules which can either decompose to give product or by further collision return to molecules in the normal state. Such unstable forms are called transition complex.

Reaction scheme involving these four kinds of intermediate can be of two types:

(*a*) Non chain reaction:

      Reactants $\longrightarrow$ (Intermediates) $*$

      (intermediates) $*$ $\longrightarrow$ Products

(*b*) Chain Reaction:

      Reactant $\longrightarrow$ (Intermediate) $*$ [Initiation]

      (Intermediate) $*$ + Reactant $\longrightarrow$ (Intermediate) $*$ + Product   [Propagation]

      (Intermediate) $*$ $\longrightarrow$ Product   [Termination]

Testing Kinetics Models:

Now we will see that how to test correspondence between experiment and a proposed mechanism.
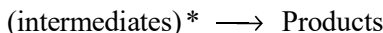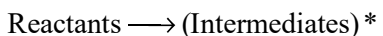
In matching the predicted rate expression with the experimentally found, we rely on the following rule:

(*i*) If any component takes part in more than one reaction then its net rate of change is equal to sum of the rates of change of components *i* in each of the elementary reaction in which it is participated.

      $r_{i,\,net} = \Sigma r_i$

(*ii*) As the intermediates are highly reactive they have very short life time and they are present in very small quantities, hence their net rate of formation is taken as zero.

      $\therefore$ $r_A^* = 0$

This is called Pseudo Steady State Approximation (PSSA).

TEMPERATURE DEPENDENT TERM OF A RATE EQUATION:

For many reactions and particularly elementary reactions, the rate expression can be written as a product of a temperature dependent term and a concentration dependent term.

      $r_i = f_1(\text{temperature}) \, f_2(\text{concentration})$

      $r_i = K \, f_2(\text{concentration})$

For such reactions the temperature dependent term, the reaction rate constant has been found in practically all cases.

(a) Temperature dependency from Arrhenius law:

From Arrhenius law rate constant K is given by: $\boxed{k = k_o e^{-\frac{E}{RT}}}$

where, K_o = the frequency or pre-exponential factor.

        E = is called activation energy of the reaction.

        R = gas constant

        T = absolute temperature, K

At the same concentration, but at two different temperature, Arrhenius law indicate that

$$\boxed{\ln\frac{r_2}{r_1} = \ln\frac{k_2}{k_1} = \frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

$$\ln\left(\frac{t_1}{t_2}\right) = \frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Unit of k_o = unit of k

k_o is not a function of temperature. k_o (also known as frequency factor) does not affect the temperature sensitivity of reaction

Also $$\boxed{\ln\left(\frac{k(T_2)}{k(T_1)}\right) = \frac{\Delta H_{R_x}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

Here $K(T_2)$ and $K(T_1)$ are equilibrium constant at T_1 & T_2 respectively & ΔH_{RX} is the heat of reaction

Also $$\boxed{\frac{d}{dT}(\ln k) = \frac{E}{RT^2}}$$

If temperature is low change in k w.r.t T is high and vice versa.

Q.1. From Arrhenius law, a plot of ln k versus 1/T gives a straight line with a slope of (-E/R). The units of E/R are

(a.) K/cal   (b.) cal/K   (c.) cal   (d.) K

Solution:(d) $\dfrac{E}{R} = \dfrac{cal\ mol^{-1}}{cal\ mol^{-1}\ K^{-1}} = K$

Q.2. From the chemical reaction $A \xrightarrow{k} B$ an increase in temperature from 295K to 305K causes the rate of reaction to double. The energy of activation for this reaction must be

(c.) 12389Kcal/mol   (b.) 12.38Kcal/mol   (c.) 1.2Kcal/mol   (d.) 1238Kcal/mol

Solution: (b)

$$\ln\frac{r_2}{r_1} = \frac{E}{R}\left(\frac{1}{T} - \frac{-1}{T_2}\right) \qquad \boxed{\begin{array}{l} R = 1.987 cal\ mol^{-1}\ K^{-1} \\ r_2 = 2r_1 \end{array}}$$

$$\ln\left(\frac{2r_1}{r_1}\right) = \frac{E}{1.987}\left(\frac{1}{295} - \frac{1}{305}\right)$$

On solving E = 12389.47 cal/mol

Or E = 12.38Kcal/mol
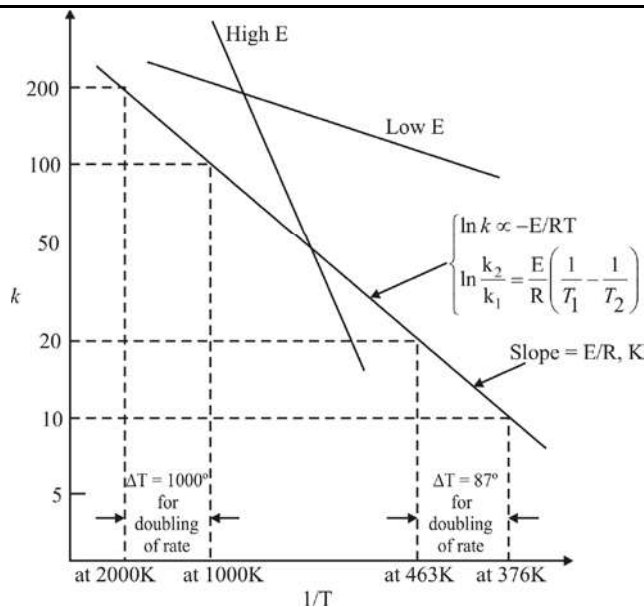
Figure: Sketch showing temperature dependency of the reaction rate.

Activation Energy and Temperature Dependency:

The temperature dependency of reaction is determined by the activation energy and temperature level of the reaction as shown in figure. Conclusion from figure are as follows:

(*i*) From the Arrhenius law, the value of the frequency factor k_o does not affect the temperature sensitivity.

(*ii*) Any given reaction is much more temperature sensitive at a low temperature than at a high temperature.

(*iii*) Reactions with high activation energy are very temperature sensitive, reaction with low activation energy are relatively temperature insensitive.

(*iv*) From Arrhenius law a plot of ln k vs $\dfrac{1}{T}$ given a straight line with large slope for large E and small slope for small E.
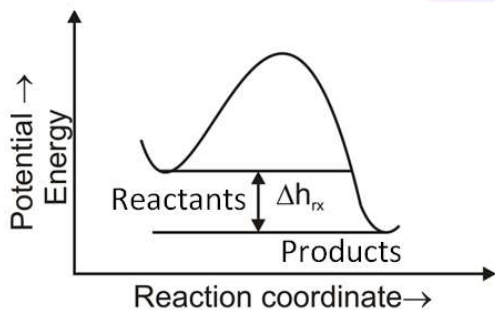
Activation Energy:

The excess energy of the reactants required to dissociate into products.
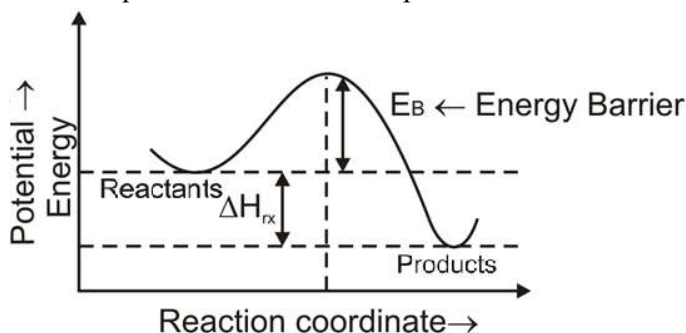
$\Rightarrow$ In Exothermic reaction, reactants have more energy than products

$\Delta H_{\text{Reaction}} =$ Energy of product - Energy of Reactant

$\Delta H_{\text{Reaction}} = -$ve (for exothermic reactions)
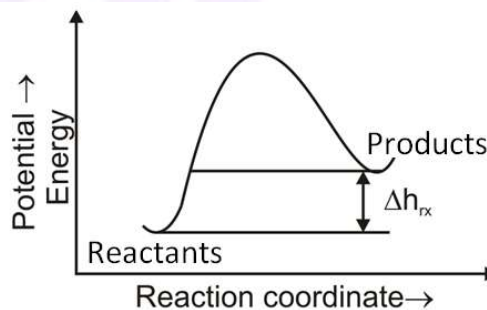
Exothermic reaction   Endothermic reaction

(b) Temperature Dependency from the Collision Theory:

Collision theory is based upon the concept that before molecule react, there must be collision between the reactant molecules and only those collision in which the colliding molecules have a certain minimum amount of energy are effective. Further this concept leads to the rate expression based upon the frequency of molecular collisions and the fraction collisions that are effective.

From collision theory rate constant K is given by:

$$\boxed{K \propto T^{\frac{1}{2}} e^{-\frac{E}{RT}}} \qquad \ln\left(\frac{k_2}{k_1}\right) = \frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + \frac{1}{2}\ln\left(\frac{T_2}{T_1}\right)$$

(c) Temperature Dependency from Transition State Theory:

The fundamental postulate of the theory is that (*i*) The reacting molecules must form unstable intermediate called activated complex before being converted (*i.e.*, there is formation of activated complex) to product. (*ii*) There exists an equilibrium between the activated complex and reactants at all the time.

According to transition state theory rate constant is given by:

$$\boxed{k \propto T\, e^{-\frac{E}{RT}}} \qquad \textbf{or} \quad \ln\left(\frac{k_2}{k_1}\right) = \frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + \ln\left(\frac{T_2}{T_1}\right)$$

This equation describe the temperature dependency from Transition State Theory.

**Difference between Collision Theory and Transition State Theory:**

Collision Theory	Transition State Theory
1. Collision theory does not agree more closely with experiments.	1. Transition state theory agrees more closely with experiments.
2. Collision theory is based on **Kinetic theory** of gases.	2. Transition state theory is based on statistical mechanics.
3. Collision theory view that decomposition of activated complex is very rapid.	3. Transition state theory view that formation of activated complex is very rapid.
4. Collision theory view that formation of **activated complex is slow and rate controlling.**	4. Transition state theory view that **decomposition of activated** complex is slow and rate controlling.
5. $k \propto T^{\frac{1}{2}}\, e^{-\frac{E}{RT}}$	5. $k \propto T\, e^{-\frac{E}{RT}}$

Summary:

1. In General the rate constant is expressed as $K = K_0 T^m e^{-E/RT}$, $m = 0$ for Arrhenius law $M = \dfrac{1}{2}$ collision theory, m = 1 transition state theory.

2. In differential form, Arrhenius law is given by $\dfrac{d(\ln k)}{dT} = \dfrac{E}{RT^2}$

3. $\ln \dfrac{r_2}{r_1} = \ln \dfrac{K_2}{K_1} = \ln \dfrac{t_1}{t_2} = \dfrac{E}{R}\left[\dfrac{1}{T_1} - \dfrac{1}{T_2}\right]$ for Arrhenius law.

SOLVED EXAMPLE

1. The decomposition of N_2O_5 is postulated to occur by the following mechanism.

$$N_2O_5 \underset{K_2}{\overset{K_1}{\rightleftharpoons}} NO_2 + NO_3^*$$

$$NO_3^* \xrightarrow{K_3} NO^* + O_2$$
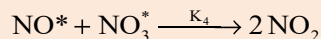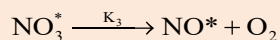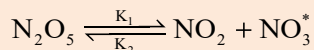
$$NO^* + NO_3^* \xrightarrow{K_4} 2NO_2$$

using steady state approximation derive an expression for rate of decomposition of N_2O_5.

Solution: We know that

Rate of decomposition is given by

$$\frac{-d[N_2O_5]}{dt} = K_1[N_2O_5] - K_2[NO_2][NO_3^*] \qquad \ldots(a)$$

By steady state hypothesis.

$$\frac{d[NO^*]}{dt} = K_3[NO_3^*] - K_4[NO^*][NO_3^*] = 0 \qquad \ldots(i)$$

$$\frac{d[NO_3^*]}{dt} = K_1[N_2O_5] - K_2[NO_2][NO_3^*] - K_3[NO_3^*] - K_4[NO^*][NO_3^*] \qquad \ldots(ii)$$

From equation (i)

$$[NO^*] = \frac{K_3[NO_3^*]}{K_4[NO_3^*]} = \frac{K_3}{K_4} \qquad \ldots(iii)$$

Put equation (iii) in equation (ii)

$$K_1[N_2O_5] = K_2[NO_2][NO_3^*] + K_3[NO_3^*] + K_3[NO_3^*]$$

$$\Rightarrow \quad [NO_3^*] = \frac{K_1[N_2O_5]}{K_2[NO_2] + 2K_3} \qquad \ldots(iv)$$

Put equation (iv) in equation (a)

We get,

$$\frac{-d[N_2O_5]}{dt} = K_1[N_2O_5] - K_2[NO_2]\left(\frac{K_1[N_2O_5]}{K_2[NO_2] + 2K_3}\right)$$

$$= K_1[N_2O_5]\left(1 - \frac{K_2[NO_2]}{K_2[NO_2] + 2K_3}\right)$$

---

2. At 500 K the rate of a bimolecular reaction is ten times the rate at 400 K. Find the activation energy for this reaction.

(a) From Arrhenius law (b) From Collision theory

Solution: (a) We have from Arrhenius law

$$\ln(r) = -\frac{E}{RT} + \ln K_o$$

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

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

We have, $r_2 = 10\,r_1$

$T_1 = 400$ K

$T_2 = 500$ K

$R = 1.987$ cal/mol K

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

$$E = 9150 \text{ cal/mol K}$$

(b) From Collision theory we know that

$$K \propto T^{\frac{1}{2}}\,e^{-\frac{E}{RT}}$$

$$r = K'_o\,T^{\frac{1}{2}}\,e^{-\frac{E}{RT}}$$

$$\ln r = -\frac{E}{R}\left(\frac{1}{T}\right) + \ln T^{\frac{1}{2}} + \ln K'_o$$

$$\ln r_1 = -\frac{E}{R}\left(\frac{1}{T_1}\right) + \ln T_1^{\frac{1}{2}} + \ln K'_o$$

$$\ln r_2 = -\frac{E}{R}\left(\frac{1}{T_2}\right) + \ln T_2^{\frac{1}{2}} + \ln K'_o$$

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

$$T_1 = 400 \text{ K}, \qquad\qquad T_2 = 500 \text{ K}$$

$$r_2 = 10\,r_1$$

$$\ln\left(\frac{10\,r_1}{r_1}\right) = \frac{E}{1.987}\left[\frac{1}{400} - \frac{1}{500}\right] + \ln\left[\frac{(500)^{\frac{1}{2}}}{(400)^{\frac{1}{2}}}\right]$$

$$E = 8707 \text{ cal/mol} \qquad \textbf{Ans.}$$

3. On doubling the concentration reactant rate of reaction triples. Find the reaction order.

Solution: Let $-r_A = K\,C_A^n$

Suppose at concentration C_{A_1} rate of reaction is $-r_{A_1} = K\,C_{A_1}^n$

At concentration C_{A_2} rate of reaction is $-r_{A_2} = K\,C_{A_2}^n$

If $C_{A_2} = 2\,C_{A_1}$ we have $-r_{A_2} = 3\,(-r_{A_1})$

$$\frac{-r_{A_2}}{-r_{A_1}} = \frac{C_{A_2}^n}{C_{A_1}^n}$$

$$\frac{3(-r_{A1})}{-r_{A_1}} = \frac{(2\,C_{A_1})^n}{(C_{A_1})^n} \quad\Rightarrow\quad 3 = 2^n$$

$\Rightarrow$ $\ln 3 = n \ln 2$ $\Rightarrow$ $\boxed{n = 1.58 \approx 1.6}$

4. A certain reaction has a rate given by $-r_A = 0.005\,C_A^2$ mol/cm^3 min

If the concentration is expressed in mole/lit and time in hours. What would be the value and units of rate constants.

Solution: $-r_A = 0.005\,C_A^2$, mol/cm^3 min

$$-r_A = 0.005\left(\frac{cm^3}{mol\,.\,min}\right)C_A^2\left(\frac{mol}{cm^3}\right)^2,\ \frac{mol}{cm^3\,min}$$

CHAPTER-3

INTERPRETATION OF BATCH REACTOR DATA

- The determination of rate equation is usually two step procedure, first the concentration dependency is found at fixed temperature and then the temperature dependence of the rate constant is found, yielding the complete rate equation.
- Value of the constants of the equation can only be found by experiments.
- Equipment by which experimental information is obtained can be divide into two types of reactors $\longrightarrow$ batch and flow.
- By performing the experiment to determine extent of reaction at various times and this can be done by carrying out a chemical reaction in experimental batch reactor and then by calculating:
  (*i*) Total pressure of reaction system at different time during reaction.
  (*ii*) Concentration of a given component at different times during the course of reaction.
  (*iii*) Volume of a reacting system at different times during the course of reaction.
  (*iv*) Physical property of a fluid such as the electrical conductivity or refractive index at different time during the course of reaction.
- Experimental batch reactor is usually operated isothermally and at constant volume.
- Batch reactor is simple device adaptable to small scale laboratory setups and it needs little auxiliary equipments.
- There are two method for analyzing kinetic data:
  Integral method and differential methods.

In Integral method:

(a) Guess the reaction order & integrate the given reaction

e.g. $A \rightarrow B$

if $n = 1$

$$(-r_A) = kC_A^1$$

For constant volume reaction system

$$(-r_A) = -\frac{1}{V}\frac{dN_A}{dt} = -\frac{dC_A}{dt} = kC_A$$

(b) Integrate the above kinetic in such a way that left hand side becomes of function of time as below.

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

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

(c) From time versus concentration data plot the curve, if it follow a straight line passing through origin then assumed order is correct.

(d) If it is not then go through step (a) and again repeat it.

Plot of Concentration as a function of time for different order reactions

zero order reaction   second order reaction   First order Reaction
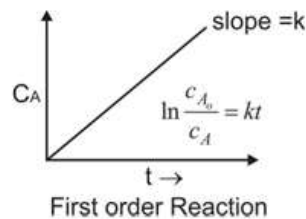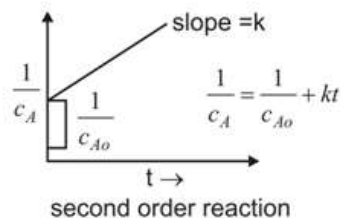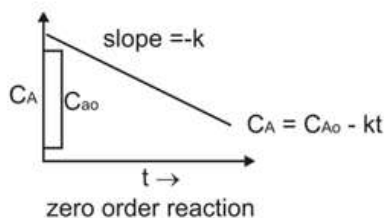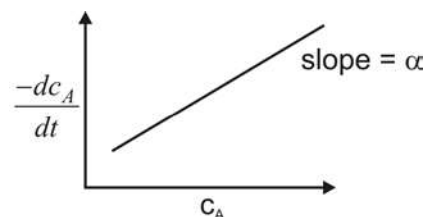
In differential method:

$$\frac{-dc_A}{dt} = kc_A^\alpha$$

Take ln on both sides

$$\ln\left(\frac{-dC_A}{dt}\right) = \ln k + \alpha \ln C_A$$

Plot $\frac{-dC_A}{dt}$ versus ln C_A on a Log – Log graph. The slope will be reaction

order α

Q.1. The differential method of analyzing kinetic data

(a.) Requires more accurate or larger amounts of data

(b.) Can be used only after finding $\frac{1}{V}\frac{dN}{dt}$ from the data

(c.) Is used in more complicated situations

(d.) All of these

Solution: Since (a), (b) and (c) are correct regarding differential method of analyzing data $\therefore$ (d) is the correct option.

- Difference between integral method and differential method of analysis:

Integral Methods	Differential Methods
1. Integral method is easy to use and is recommended when testing specific mechanism or simple rate expression.	1. Differential method is useful in more complicated situation but require more accurate or larger amount of data.
2. Integral method can only test rate form.	2. The differential method can be used to develop a rate equation to fit the data.

Constant Volume Batch Reactor:

Constant volume batch reactor means volume of reaction mixture, and not the volume of reactor. This term actually means a constant density reaction system.

In a constant volume system the measure of reaction rate of component *i* becomes.

$$r_i = \frac{1}{V}\frac{d\,N_i}{dt} = \frac{d\left(\dfrac{N_i}{V}\right)}{dt} = \frac{d\,C_i}{dt}$$

For ideal gases, where,

$$C_i = \frac{p_i}{RT}$$

Summary:

1. When data of N vs t is scattered we should use integral method.

2. $X_A = 1 - \dfrac{C_A}{C_{A0}}$ and $d_{XA} = -\dfrac{dC_A}{C_{A0}}$.

3. In integral method use plot $\dfrac{1}{C_A}$ vs t graph to find order of the reaction.

4. For zero order reaction $C_{A0} - C_A = Kt$ (C_A vs t gives straight line) for $t < \dfrac{C_{A0}}{K}$

   $C_{A0} = 0$ for $t \geq \dfrac{C_{A0}}{K}$

5. For nth order reaction $t_{1/2} = \dfrac{(0.5)^{1-n} - 1}{K(n-1)} C_{A0}^{1-n}$.

6. For irreversible parallel reaction

   $A \xrightarrow{\;K_1\;} R$

   $A \xrightarrow{\;K_2\;} S$

   $\ln \dfrac{C_{A0}}{C_A} = (K_1 + K_2)t$

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

7. For series ration $A \xrightarrow{\;K_1\;} R \xrightarrow{\;K_2\;} S$

   $C_{B,\,maximum} = C_{A0} \left(\dfrac{K_1}{K_2} \right)^{\frac{K_2}{K_2 - K_1}}$, $t_{max} = \dfrac{\ln(K_2 / K_1)}{K_2 - K_1}$

8. Auto catalytic Reaction:
   Maximum rate of reaction obtain when $C_A = C_R$

9. For gas phase reaction, $\dfrac{dC_A}{dt} = \dfrac{C_{A0}}{\varepsilon_A} \dfrac{d(\ln v)}{dt}$

CHAPTER-4

DESIGN EQUATION FOR IDEAL REACTORS

General mole balance Equation

$$\begin{bmatrix} \text{Rate of flow} \\ \text{of species i} \\ \text{into the system} \end{bmatrix} - \begin{bmatrix} \text{Rate of flow} \\ \text{of i out of} \\ \text{the system} \end{bmatrix} + \begin{bmatrix} \text{Rate of Generation} \\ \text{of i by chemical} \\ \text{reaction within} \\ \text{system} \end{bmatrix} = \begin{bmatrix} \text{Rate of accumulation} \\ \text{of i within the system} \end{bmatrix}$$

In – out + Generation = Accumulation

$$F_{io} - F_i + G_i = \frac{dN_i}{dt}$$

$$G_i = r_i V$$

$$\frac{moles}{time} = \frac{moles}{time \times Volume} \times Volume$$

r_i is the rate of formation of species i.

If r_i varies with the position in system volume,

$$G_i = \int^v r_i dV$$

∴ Mole balance equation becomes

$$F_{io} - F_i + \int^v r_i dV = \frac{dN_i}{dt}$$

Note: This general mole balance equation is used to develop the design equation for various types of industrial reactors.

Types of Industrial Reactors:

1. **Batch Reactor:** Reactants are initially charged into the reactor and left to react for certain period

   Uses:
   - For small scale operation
   - For testing new processes
   - For processes that are difficult to convert into continuous operations.

   Advantages:
   - High conversion are obtained when reactants are left for long time

   Disadvantages:
   - Difficult for large scale production
   - High labour cost involved.

   This is an unsteady state operation where composition changes with time. However, at any instant, composition is uniform throughout the reactor.