

Reaction Engineering (Ch34009) Part-1(JKB)

Chapter-1 Introduction

Introduction

- The reaction engineering is one of the major subjects in chemical engineering and it is part of basic science.
- The technology or know-how of the manufacturing processes are first obtained from the laboratory and pilot plant studies.
- The knowledge of reaction engineering is essential in every step of starting from laboratory to pilot plant studies as well as designing of a reactor.

Course Content:

- Basic concepts of chemical kinetics.
- Reaction mechanism and derivation of rate equation.
- Concepts of ideal reactors (a) Batch reactor. (b) Continuous stirred tank reactor (CSTR) and (c) Plug flow reactor.
- Search for rate model :Analysis of reactor data i)Differential reactor
ii) Integral reactor
- Isothermal Reactor design for single reaction. Mass balances for homogeneous and heterogeneous reactions.

- Multiple reactors : Parallel and Series connection.
- Multiple reaction systems: Parallel and Series reactions.
- Non ideal reactors: Residence time distribution(RTD)

Book Recommended:

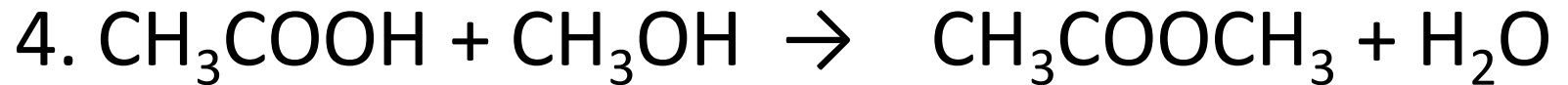
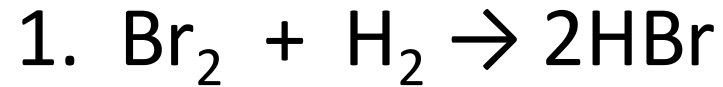
1. Chemical Reaction Engineering, - O. Levenspiel
2. Elements of Chemical Reaction Engineering- H.S. Fogler
3. Chemical Engineering Kinetics- J. M. Smith

Type of Reactions: Homogeneous and Heterogeneous

- Single-phase reaction is called homogeneous and multiphase-reaction is called heterogeneous reaction.
- Heterogeneous reaction are Gas-solid catalytic reactions, Gas - liquid, organic – aqueous phase reactions.
- The non-catalytic types.

Examples of homogeneous reactions

Some common examples of homogeneous reactions are hydrogen-bromine reaction, decomposition of nitrous oxide, decomposition of hydrogen iodide, esterification of acetic acid and methanol.



Examples of heterogeneous reactions

Rate of reaction

The rate of reaction in various forms are expressed as

$$\begin{aligned} -r'_A &= \frac{1}{W} \frac{dN_A}{dt} = k' C_A \\ r''_A &= \frac{1}{S_i} \frac{dN_A}{dt} = k'' C_A \end{aligned} \quad (1.1)$$

C_A is the concentration of A at any instant of time t in kmol/m^3 . Where, $-r_A$ is for homogeneous reaction in $\text{kmol/m}^3.\text{s}$ and The rates, $-r'_A$ and $-r''_A$ are expressed in $\text{kmol/kg-catalyst.s}$ and $\text{kmol/surface area.s}$ for the case of heterogeneous reactions. k, k'' and k''' are the corresponding rate constant based on the reactor volume, weight of the catalyst and interfacial area respectively.

If we consider the reaction as



- then the relation between various rates in terms of various species are

$$-r_A = -\frac{a}{b}r_B = \frac{a}{c}r_C$$

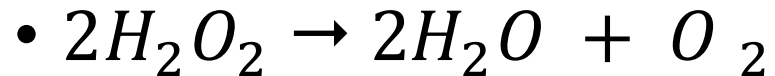
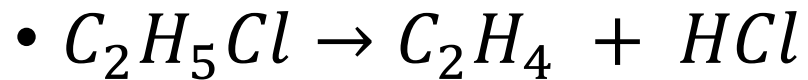
- The negative sign in $-r_A$ represents the disappearance of the reactant A and for the rate of formation it should be represented as $+r_C$.
- An elementary reaction represents the reaction in molecular level or with their ions in a single step. The reactions are called unimolecular, bimolecular and trimolecular types with their corresponding order of reaction as first, second and third order respectively.

Elementary Reactions

If the reaction is the decomposition of one molecule of species A as by the reaction stoichiometry, $A \rightarrow B$, it is called unimolecular reaction.

If the reaction stoichiometry is $2A \rightarrow B$, it is second order and bimolecular.

For example, the decomposition of ethyl chloride or hydrogen peroxide



These are mono molecular reactions and the rate of these monomolecular reactions are described by first-order kinetics.

These are elementary types.

Non-elementary Reactions

The non-elementary reactions take place in multiple steps and all individual reaction steps may be of elementary. These reactions follow the complex mechanism and may be observed in both homogeneous and heterogeneous reactions.

Example : The manufacture of nitric acid by oxidation of ammonia in presence of Pt-metal oxide catalyst

Catalytic oxidation of ammonia

The overall reaction: $4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O}$

1. Oxidation of nitric oxide: $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$

2. Formation nitric acid: $4\text{NO}_2 + 2\text{H}_2\text{O} + \text{O}_2 \rightarrow 4\text{HNO}_3$

One rate equation was proposed for the formation of HNO_3 as

$$r = k[\text{NH}_3]^{0.36}[\text{O}_2]^{0.14}$$

Examples of non-elementary reactions

- In the decomposition of acetaldehyde, $CH_3CHO \rightarrow CH_4 + CO$ The reaction rate is given by

$$-r_{CH_3CHO} = k[CH_3CHO]^{3/2}$$

- In hydrogen-bromine reaction $H_2 + Br_2 \rightarrow 2HBr$, the reaction rate is given as a complex form

$$-r_{HBr} = \frac{k_1[H_2][Br_2]^{3/2}}{[HBr] + k_2[Br_2]}$$

The individual elementary steps of the reaction are used to postulate the mechanism of the overall reaction of non elementary processes.

Kinetic Rate Models: Non Elementary Reactions

- In order to explain the non-elementary reaction we consider the following reaction and the rate equation for the above reaction is given by
- $A \rightarrow B + \frac{1}{2}C$
- $-r_A = \frac{kC_A^2}{1+k'C_A}$
- The reaction is a non-elementary type as there is no direct relation between rate equation and its stoichiometry.

Derivation of Rate Models

- The rate equation can be derived from the proposed mechanism considering all the steps. The above reaction may also be written as
- $2A \rightarrow 2B + C$
- A several consecutive steps may be considered in the overall reaction of the above reaction.
- we can assume a mechanism
- Step 1 : $A \rightleftharpoons A^*$
-
- Step 2 : $A^* + A \rightleftharpoons 2B + C$

Derivation of Rate Models

From steps (1) and (2),

- $-r_A = k_1 C_A - k_2 C_A^* + k_3 C_A C_A^* - k_4 C_B^2 C_C \quad (1)$

- $-r_A^* = k_1 C_A - k_2 C_A^* - k_3 C_A C_A^* + k_4 C_B^2 C_C \quad (2)$

- The rate of formation of the intermediate A^* is assumed to be negligible.

- So that, $-r_A^* = 0$ and $C_A^* = \frac{k_1 C_A + k_4 C_B^2 C_C}{k_2 + k_3 C_A}$

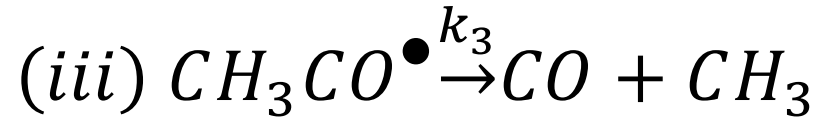
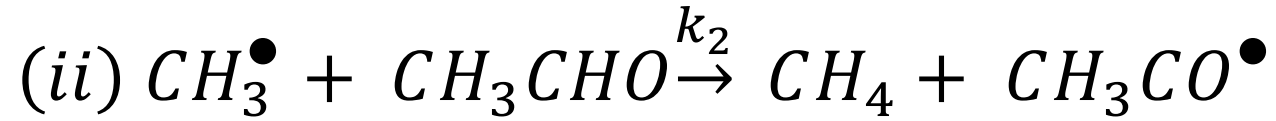
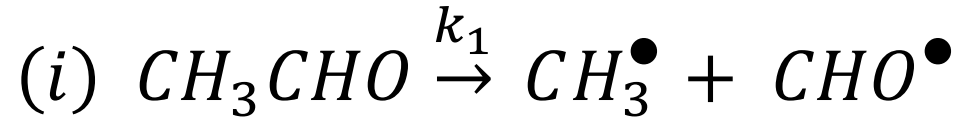
Substituting C_A^* in Equation (1), we have

$$-r_A = \frac{k C_A^2}{1 + k' C_A}$$

Derivation of Rate Models

- Where, k_4 is assumed to be zero, $k = \frac{2k_1k_3}{k_2}$ and $k' = \frac{k_3}{k_2}$.
- If the second term of the denominator of Equation(2.9) is neglected for $k_2 \gg k_3$ and k' is neglected, the rate of the reaction may be approximated by a second-order rate kinetics.

The mechanism of the decomposition of acetaldehyde is given by the methyl radical formation



The rate of decomposition of acetaldehyde is

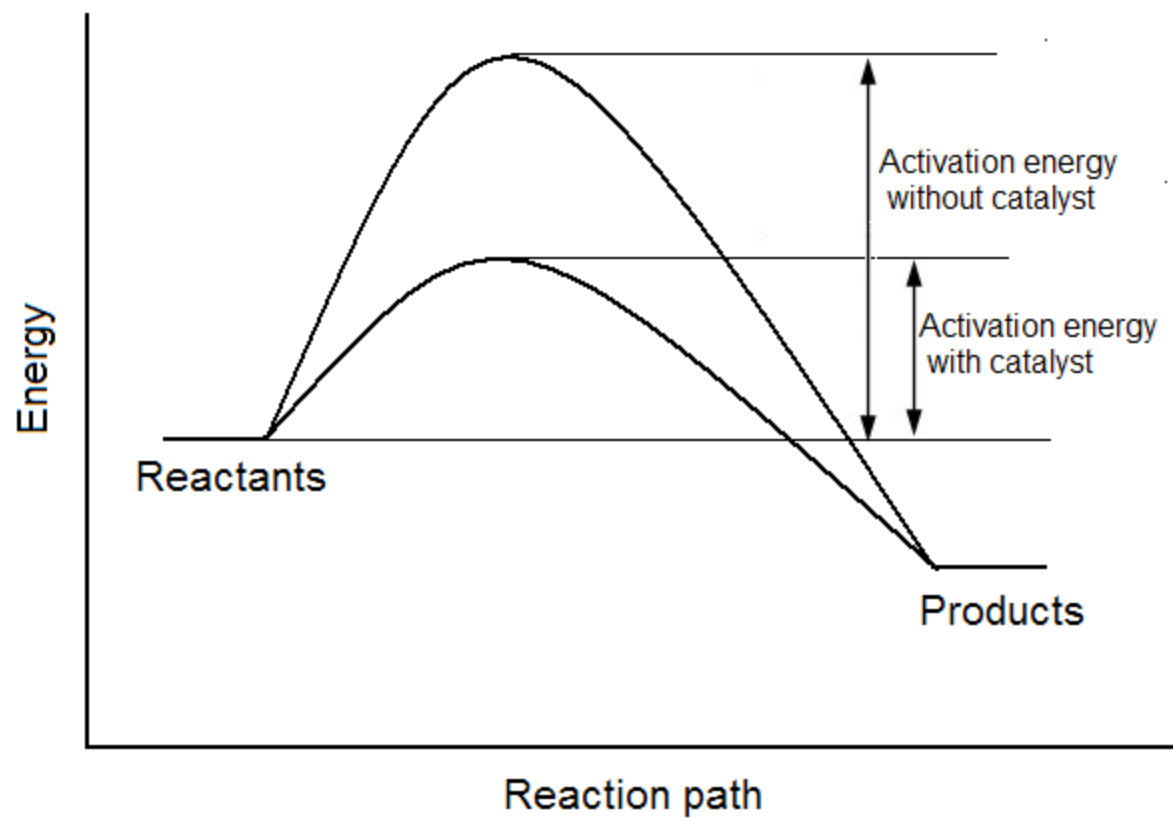
$$-\frac{dC_{\text{CH}_3\text{CHO}}}{dt} = k_2 \left(\frac{k_1}{k_4} \right)^{1/2} C_{\text{CH}_3\text{CHO}}^{3/2} = k' C_{\text{CH}_3\text{CHO}}^{3/2}$$

where the order of the reaction is 3/2.

Catalytic reactions

- The rate of a chemical reactions may be enhanced by a very large factor by employing a substance which accelerates the speed of reaction by introducing a low energy path from reactants to products. The substance is called catalyst and it remains unchanged by the reaction.
- In some cases, in absence of a catalyst the reactions occur so slowly than that of presence catalyst.
- The Energy requirements for the reactant to attain the activation stage in presence of catalyst is less than the energy requirement without catalyst.

The plot of energy variation during the progress of a reaction



Rate constant and Specific reaction rate

In these cases, the rate of reaction can be expressed as

$$-r_A = k C_A^n$$

The proportionality constant, k is called the rate constant or the specific reaction rate.

which is an empirical rate equation, 'n' is the order of the reaction which may have any fractional or integer value. The unit of k for n^{th} order reaction would be given by

$$\frac{\text{kmol per m}^3 \text{ per sec}}{(\text{kmol per m}^3)^n} = (\text{m}^3)^{n-1} (\text{kmol})^{1-n} \text{s}^{-1}$$

The unit of rate constant for a first order reaction is time^{-1} or in S.I unit s^{-1} and for second order reaction $\text{m}^3 \text{kmol}^{-1} \text{s}^{-1}$

Temperature dependency of rate constant

- The participating molecules are to be brought together and collide each other with an extra energy, that will cause the formation of chemical bond between them before commencing the reaction.
- The reacting molecules should gather an excess of a minimum energy E or to reach at a higher energy state, then they possess collision. The minimum energy E is known as Activation energy.
- Collision Theory, Transition State Theory and Arrhenius Theory may be used to see the temperature dependency of rate constant.

Collision Theory

- According to this theory, the rate is proportional to the number of the effective collisions per unit volume per unit time.
- For gas-phase bimolecular elementary reaction between A and B, The number collision suffers A with B per unit time is the frequency of collision, which is proportional to the mean velocity determined from kinetic theory of gases
- We now assume that the molecule A is stationary and B is moving with a mean velocity of \bar{u} . The average velocity of a molecule is obtained from the kinetic theory of gases as

$$\bar{u} = \left(\frac{8RT}{\pi M} \right)^{1/2}$$

- The region for collision between A and B may be assumed as a cylinder of radius d_{AB} .
- The collision between A and B occurs when the center of A is at a distance of collision diameter, d_{AB} from the center of B.

$$\text{where } d_{AB} = \frac{d_A + d_B}{2}$$

The molecules of A and B are assumed spherical of diameters d_A and d_B

So, The area of cross-section for collision between two molecules = the area of the circle of radius, $\frac{d_{AB}}{2} = a_{AB} = \frac{\pi}{4} d_{AB}^2$

Collision Theory

- $\bar{u} = \left(\frac{8RT}{\pi M}\right)^{1/2} = \left(\frac{8k_B T}{\pi m_{AB}}\right)^{\frac{1}{2}}$
- where, k_B is the Boltzmann constant and M is obtained , $\frac{1}{m_{AB}} = \frac{1}{M_A} + \frac{1}{M_B}$
- The swept volume for a moving molecule of B for experiencing collision with A will be $a_{AB}\bar{u}$ is the volume of the cylinder
- $a_{AB}\bar{u} = \frac{\pi}{4} d_{AB}^2 \left(\frac{8k_B T}{\pi m_{AB}}\right)^{\frac{1}{2}}$

Collision Theory

- The frequency of collision between molecules A and B
- $f = N_A N_B \frac{\pi}{4} d_{AB}^2 \left(\frac{8k_B T}{\pi m_{AB}} \right)^{\frac{1}{2}}$
- where, N_A and N_B are the number of molecules of A and B are proportional to C_A and C_B
-
- Rate of collision $\propto C_A C_B T^{1/2}$
- So, the frequency of collision
- Rate of collision $\propto C_A C_B T^{1/2}$
- The rate is proportional to the number of these effective collisions per unit volume per unit time.

Collision Theory

The fraction having excess of the minimum energy E will $e^{-\frac{E}{RT}}$.

Rate of reaction = [rate of collisions between A and B] \times
[successful collisions for reaction]

$$= \left[10^6 N_{AV}^2 C_A C_B \left(\frac{\pi}{4} d_{AB}^2 \right) \left(\frac{8k_B T}{\pi m_{AB}} \right)^{\frac{1}{2}} \right] \times \left[e^{-\frac{E}{RT}} \right]$$
$$= \left[10^6 N_{AV}^2 \left(\frac{\pi}{4} d_{AB}^2 \right) \left(\frac{8k_B T}{\pi m_{AB}} \right)^{\frac{1}{2}} \right] \times \left[e^{-\frac{E}{RT}} \right] C_A C_B = k C_A C_B$$

the reaction rate, $-r_A \propto C_A C_B T^{1/2} e^{-\frac{E}{RT}}$

Where the term $e^{-E/RT}$ is the Boltzmann expression for evaluating the fraction having energy excess over E .

Transition State Theory

- The transition state theory is also known as activated-state theory.
- As per this theory, the reacting molecules will reach the maximum energy level to form an activated complex.
- The activated molecules then undergo the chemical change to form the product.

This mechanism can be explained as



- $K = \frac{[A^*]}{[A]}$

- $\ln K = \frac{-\Delta G}{RT} = \frac{-\Delta H + T\Delta S}{RT}$

Transition State Theory

- The second step is a first-order irreversible reaction whose rate is expressed as

$$\frac{dP}{dt} = k'[A] = k_1[A^*]$$

Where, k' = first-order rate constant in s^{-1} . k_1 = the rate constant in the formation of P from the activated complex

The rate may be written as $-r_A = k_1[A^*] = k_1K[A]$

As per the transition state theory, applying statistical and quantum mechanics, Where, $K = e^{\frac{\Delta S}{R}} e^{-\frac{\Delta H}{RT}}$

Transition State Theory

The rate constant , $k_1 = \frac{kRT}{Nh}$

- where R = gas constant, T = absolute temperature, N = Avogadro's number , h = Planck's constant and k = transmission coefficient.
- If the reaction rate evaluated in terms of second, the value of k_1 is approximately equals to $2 \times 10^{10} \text{ T s}^{-1}$.
- $k' = 2 \times 10^{10} \text{ T } e^{\Delta S/T} e^{-\Delta H/RT} \text{ s}^{-1}$
- The above equation is called Eyring equation.
- $-r_A \propto C_A C_B T e^{-\frac{\Delta H - \Delta S}{RT}}$ or, $-r_A \propto C_A C_B T e^{\frac{-\Delta E}{RT}}$

Arrhenius Law

- According to this law, the rate of reaction between A and B = $kC_A C_B$.
- The rate constant, k is given by
- $k = k_0 e^{-\frac{E}{RT}}$
- $-r_A = kC_A C_B = k_0 e^{-\frac{E}{RT}} C_A C_B$
- where k_0 is the pre-exponential constant and E is the activation energy