

# CHEMICAL ENGINEERING

## Chemical Reaction Engineering



Comprehensive Theory  
*with Solved Examples and Practice Questions*





### **MADE EASY Publications Pvt. Ltd.**

**Corporate Office:** 44-A/4, Kalu Sarai (Near Hauz Khas Metro Station), New Delhi-110016 | **Ph. :** 9021300500

**Email :** infomep@madeeasy.in | **Web :** www.madeeasypublications.org

## **Chemical Reaction Engineering**

© Copyright by MADE EASY Publications Pvt. Ltd.  
All rights are reserved. No part of this publication may be reproduced, stored in or introduced into a retrieval system, or transmitted in any form or by any means (electronic, mechanical, photo-copying, recording or otherwise), without the prior written permission of the above mentioned publisher of this book.



**MADE EASY Publications Pvt. Ltd.** has taken due care in collecting the data and providing the solutions, before publishing this book. In spite of this, if any inaccuracy or printing error occurs then **MADE EASY Publications Pvt. Ltd.** owes no responsibility. We will be grateful if you could point out any such error. Your suggestions will be appreciated.

EDITIONS

First Edition : 2021

Second Edition : 2022

Third Edition : 2023

**Fourth Edition : 2024**

# CONTENTS

## Chemical Reaction Engineering

### CHAPTER 1

#### Overview of Chemical Reaction Engg. .... 1-7

1.1	Introduction .....	1
1.2	Classification of Reactions.....	2
1.3	Definition of Reaction Rate.....	3
	<i>Student Assignments</i> .....	6

### CHAPTER 2

#### Kinetics of Homogeneous Reactions ..... 8-20

2.1	Introduction .....	8
2.2	Classification of Chemical Reactions.....	9
2.3	Temperature Dependent Term of a Rate Equation.....	13
	<i>Student Assignments</i> .....	18

### CHAPTER 3

#### Interpretation of Batch Reactor Data ..... 21-49

3.1	Introduction .....	21
3.2	Kinetics of Homogeneous Elementary Reaction .....	21
3.3	Constant Volume Batch Reactor .....	22
3.4	The Conversion (Fractional Conversion).....	23
3.5	Flow Reactors with Variable Volumetric Flow Rate .....	26
3.6	Integral Method of Analysis of Data .....	27
3.7	Empirical Rate Equations of nth Order .....	33
3.8	Multiple Reactions .....	37
	<i>Student Assignments</i> .....	47

### CHAPTER 4

#### Design of Isothermal Ideal Reactors ..... 50-106

4.1	Batch Reactor.....	50
4.2	Flow/Continuous Reactors.....	50
4.3	Semi-Batch Reactor.....	53
4.4	Space-Time and Space Velocity.....	56
4.5	Ideal CSTR.....	57
4.6	Steady State Plug Flow Reactor.....	61
4.7	Design for Single Reactions .....	65
4.8	Reactors in Series.....	68
4.9	Recycle Reactor .....	83
4.10	Design of Ideal Reactors for Multiple Reactions.....	87
4.11	Qualitative Analysis of Multiple Reaction .....	94
4.12	First Order Followed by Zero-Order Reaction .....	98
4.13	Zero-Order Followed by First-Order Reaction.....	98
	<i>Student Assignments</i> .....	102

### CHAPTER 5

#### Design of Non-Isothermal Ideal Reactors..... 107-122

5.1	Standard Heat of Formation.....	107
5.2	Heat of Reaction and Temperature.....	107
5.3	Energy Balance in Ideal CSTR.....	109
5.4	Energy Balance over PFR.....	110
	<i>Student Assignments</i> .....	121

**CHAPTER 6****Design of Non-Ideal Reactors ..... 123-148**

6.1	Introduction .....	123
6.2	Tracer Experiment .....	124
6.3	Pulse Tracer Experiment on Ideal Reactors .....	126
6.4	Step Tracer Experiment with Ideal Reactors .....	131
6.5	Zero Parameter Model.....	143
	<i>Student Assignments</i> .....	146

**CHAPTER 7****Heterogeneous Reactions, Rate and Performance Equation for Catalyst Deactivation Boiling ..... 149-173**

7.1	Single Cylindrical Pore, First-Order Reaction.....	149
7.2	Performance Equations for Reactors containing Porous Catalyst Particles.....	157

7.3	Kinetics of Heterogeneous Reaction.....	158
7.4	Deactivating Catalysts .....	165
7.5	Batch-Solids : Determining the Rate for Independent Deactivation.....	167
	<i>Student Assignments</i> .....	171

**CHAPTER 8****Kinetics of Enzyme Reactions ..... 174-182**

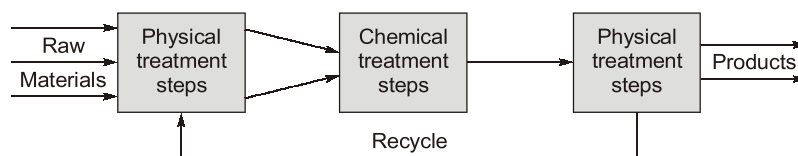
8.1	Introduction .....	174
8.2	Michaelis-Menten Kinetics (M-M Kinetics) .....	175
	<i>Student Assignments</i> .....	182

# Overview of Chemical Reaction Engineering

## 1.1 INTRODUCTION

Chemical Reaction Engineering is the study of knowledge of Chemical Kinetics along with Chemical reactors in which reaction or chemical process takes places.

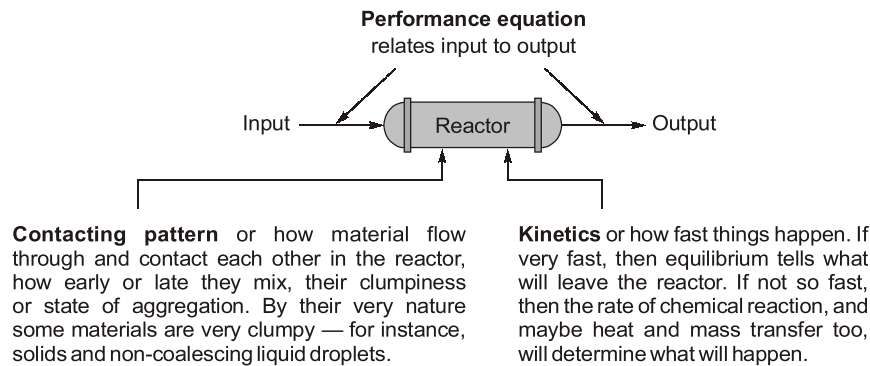
Every industrial chemical process is designed to produce economically a desired product from a variety of starting materials through a succession of treatment steps. The raw materials undergo a number of physical treatment steps to put them in the form in which they can be reacted chemically. Then they pass through the reactor. The products of the reaction must then undergo further physical treatment-separations, purifications, etc. for the final desired product to be obtained.



**Figure:** Typical Chemical Process

Design of equipment for the physical treatment steps is studied in the unit operations. Reactor design uses information, knowledge, and experience from a variety of areas-thermodynamics, chemical kinetics, fluid mechanics, heat transfer, mass transfer, and economics. Chemical reaction engineering is the synthesis of all these factors with the aim of properly designing a chemical reactor.

To find what a reactor is able to do we need to know the kinetics, the contacting pattern and the performance equation. We show this schematically in figure.



**Figure:** Information needed to predict what a reactor can do

- Chemical kinetics and reactor design are heart of Chemical process industries. Hence selection of reactor system that operates in safest mode and most efficient can be the key of economic success and failure of process industries.

In this subject we will study the expression to relate input to output for various kinetics and various contacting patterns, or

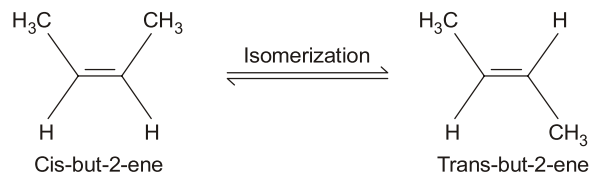
$$\text{Output} = f[\text{input, kinetics, contacting}] \quad \dots(1.1)$$

This is called the **performance equation**.

- Chemical kinetics involves only rate of reaction while the physical kinetics involves rate of mass and transfer of heat. Physical kinetics play an important role in heterogenous reaction.
- Chemical Reaction is said to have taken place when any particular chemical species loses its identity during the course of reaction.

There are three basic ways through which species may lose identity:

- 1. Decomposition Reaction:** A decomposition reaction is a reaction in which a compound breaks down into two or more simpler substances. The general form of a decomposition reaction is:  $AB \rightarrow A + B$ .
- 2. Combination Reaction:** A combination reaction (also known as a synthesis reaction) is a reaction where two or more elements or compounds (reactants) combine to form a single compound (product). Such reactions are represented by equations of the following form:  $X + Y \rightarrow XY$ .
- 3. Isomerization Reaction:** The chemical process by which a compound is transformed into any of its isomeric forms, i.e., forms with the same chemical composition but with different structure or configuration and, hence, generally with different physical and chemical properties.



**Figure:** Number of carbon atoms and hydrogen are same but configuration is different.

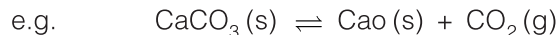
## 1.2 CLASSIFICATION OF REACTIONS

- 1. Homogeneous Reaction:** A reaction is homogeneous if it takes place in one phase alone. In homogeneous reactions all reacting materials are found within a single phase, be it gas, liquid, or solid.

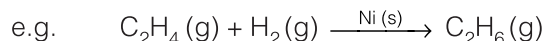


- If the reaction is catalytic, the catalyst must also be present within the same phase.
- All non-catalytic gas phase reactions are homogeneous.

**2. Heterogeneous Reaction:** A reaction is heterogenous if it requires the presence of atleast two phases to proceed.



- Heterogenous systems are frequently catalytic, but not necessarily so.



- Reaction in which the reactants and products are gases and the catalyst is a solid, are heterogeneous.

Table shows the classification of chemical reactions according to our scheme with a few examples of typical reactions for each type.

	Non-catalytic	Catalytic
Homogeneous	Most gas-phase reactions	Most liquid-phase reactions
	Fast reactions such as burning of a flame	Reactions in colloidal systems Enzyme and microbial reactions
Heterogeneous	Burning of coal Roasting of ores Attack of solids by acids Gas-liquid absorption with reaction Reduction of iron ore to iron and steel	Ammonia synthesis Oxidation of ammonia to produce nitric acid Cracking of crude oil Oxidation of $\text{SO}_2$ to $\text{SO}_3$

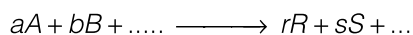
**Table:** Classification of Chemical Reactions Useful in Reactor Design

### Variables Affecting the Rate of Reaction

- In homogeneous systems the temperature, pressure, and composition are obvious variables.
- In heterogeneous systems more than one phase is involved. So, material may have to move from phase to phase during reaction; hence, the rate of mass transfer can become important.
- An exothermic reaction taking place at the interior surfaces of a porous catalyst pellet. Heat released by reaction is not removed fast enough, a severe nonuniform temperature distribution can occur within the pellet. So, heat transfer may play important roles in determining the rates of heterogeneous reactions.

## 1.3 DEFINITION OF REACTION RATE

The rate of chemical reaction



defined as the number of molecules of a given species (say, A) formed or transformed per unit time  $t$  per unit volume  $V$  of the system. Thus, the rate of disappearance of component A is,

$$\text{Rate of disappearance of A, } (-r_A) = -\frac{1}{V} \times \frac{dNA}{dt} = \frac{(\text{Moles of A disappearance})}{(\text{Volume of fluid})(\text{Time})}$$

- If we define rate as  $\left(-\frac{dN_i}{dt}\right)$ , then this definition depends upon the mass and volume of reaction mixture which is extensive property.
- If we define rate as  $\left(-\frac{1}{V} \times \frac{dN_i}{dt}\right)$  then this does not depend upon quantity. Thus, this is intensive property.

### 1.3.1 For Homogeneous Reaction System

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

### 1.3.2 For Heterogeneous Reaction System Rate of Reaction defines in Various Forms

1. Based on unit mass of solid in fluid-solid systems,

$$r'_i = \frac{1}{W} \frac{dN_i}{dt} = \frac{\text{Moles } i \text{ formed}}{(\text{Mass of solid})(\text{Time})}$$

2. Based on unit interfacial surface in two-fluid systems or based on unit surface of solid in gas-solid systems,

$$r''_i = \frac{1}{S} \frac{dN_i}{dt} = \frac{\text{Moles } i \text{ formed}}{(\text{Surface})(\text{Time})}$$

3. Based on unit volume of solid in gas-solid systems,

$$r'''_i = \frac{1}{V_s} \frac{dN_i}{dt} = \frac{\text{Moles } i \text{ formed}}{(\text{Volume of solid})(\text{Time})}$$

4. Based on unit volume of reactor, if different from the rate based on unit volume of fluid,

$$r''''_i = \frac{1}{V_r} \frac{dN_i}{dt} = \frac{\text{Moles } i \text{ formed}}{(\text{Volume of reactor})(\text{Time})}$$

- In homogeneous systems, the volume of fluid in the reactor is often identical to the volume of reactor. In such a case  $V$  and  $V_r$  are identical.
- In heterogeneous systems all the above intensive definitions of reaction rate are related by

$$\begin{aligned} (\text{Volume of fluid})r_i &= (\text{Mass of solid})r'_i = (\text{Surface of solid})r''_i = (\text{Volume of solid})r'''_i \\ &= (\text{Volume of reactor})r''''_i \end{aligned}$$

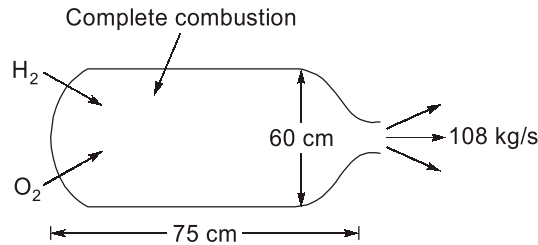
or,

$$Vr_i = Wr'_i = Sr''_i = V_s r'''_i = V_r r''''_i$$

#### Example 1.1

A rocket engine burns a stoichiometric mixture of fuel (liquid hydrogen) in oxidant (liquid oxygen). The combustion chamber is cylindrical, 75 cm long and 60 cm in diameter, and the combustion process produce 108 kg/s of exhaust gases. If combustion is complete, find the rate of reaction of hydrogen and of oxygen.





**Solution:**

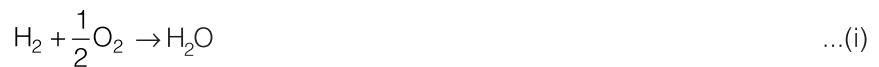
We want to evaluate

$$-r_{H_2} = \frac{1}{V} \frac{dN_{H_2}}{dt} \text{ and } -r_{O_2} = \frac{1}{V} \frac{dN_{O_2}}{dt}$$

Let us evaluate terms. The reactor volume and the volume in which reaction takes place are identical. Thus,

$$V = \frac{\pi}{2} (0.6)^2 (0.75) = 0.2121 \text{ m}^3$$

Next, let us look at the reaction occurring.



Molecular weight :            2 gm   16 gm   18 gm

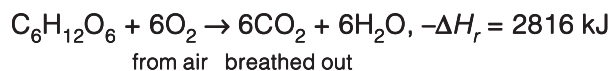
Therefore,                      H<sub>2</sub>O produced/s =  $108 \text{ kg/s} \left( \frac{1 \text{ kmol}}{18 \text{ kg}} \right) = 6 \text{ kmol/s}$

So, from Eq. (i),                      H<sub>2</sub> used = 6 kmol/s  
O<sub>2</sub> used = 3 kmol/s

$$\begin{aligned} -r_{H_2} &= \frac{1}{0.2121 \text{ m}^3} \times 6 \text{ kmol/s} \\ &= 2.829 \times 10^4 \text{ mol used}/(\text{m}^3 \text{ of rocket})/\text{s} \\ -r_{O_2} &= -\frac{1}{0.2121 \text{ m}^3} \times 3 \text{ kmol/s} = 1.415 \times 10^4 \text{ mol}/\text{m}^3\text{s} \end{aligned}$$

**Example 1.2**

A human being (75 kg) consumes about 6000 kJ of food per day. Assume that the food is all glucose and that the overall reaction is



Find man's metabolic rate (the rate of living, loving and laughing) in terms of moles of oxygen used per m<sup>3</sup> of person per second.

**Solution:**

We want to find

$$-r'''_{O_2} = -\frac{1}{V_{\text{person}}} \frac{dN_{O_2}}{dt} = \frac{\text{mol } O_2 \text{ used}}{(\text{m}^3 \text{ of person})\text{s}} \quad \dots(i)$$

Let us evaluate the two terms in this equation. First of all, from our life experience we estimate the density of man to be

$$\rho = 1000 \text{ kg/m}^3$$

Therefore, for the person in question

$$V_{\text{person}} = \frac{75 \text{ kg}}{1000 \text{ kg/m}^3} = 0.075 \text{ m}^3$$

Next, noting that each mole of glucose consumed uses 6 moles of oxygen and releases 2816 kJ of energy, we see that we need

$$\frac{dN_{\text{O}_2}}{dt} = \left( \frac{6000 \text{ kJ/day}}{2816 \text{ kJ/mol glucose}} \right) \left( \frac{6 \text{ mol O}_2}{1 \text{ mol glucose}} \right) = 12.8 \text{ mol O}_2/\text{day}$$

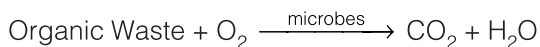
Inserting into eq. (i)

$$\begin{aligned} -r''_{\text{O}_2} &= \frac{1}{0.075 \text{ m}^3} \times \frac{12.8 \text{ mol O}_2 \text{ used}}{\text{day}} \times \frac{1 \text{ day}}{24 \times 3600 \text{ s}} \\ &= 0.002 \text{ mol O}_2 \text{ used/m}^3 \cdot \text{s} \end{aligned}$$

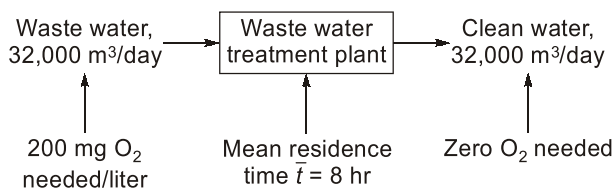


### Student's Assignments

- Q1** Consider a municipal water treatment plant for a small community (see fig.). Waste water, 32,000 m<sup>3</sup>/day, flows through the treatment plant with a mean residence time of 8 hour, air is bubbled through the tanks, and microbes in the tank attack and break down the organic material.

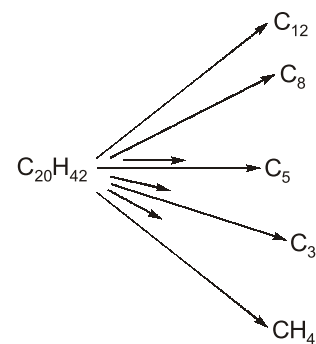


A typical entering feed has a BOD (biological oxygen demand) of 200 mg O<sub>2</sub>/litre, while the effluent has a negligible BOD. Find the rate of reaction or decrease in BOD in the treatment tanks.

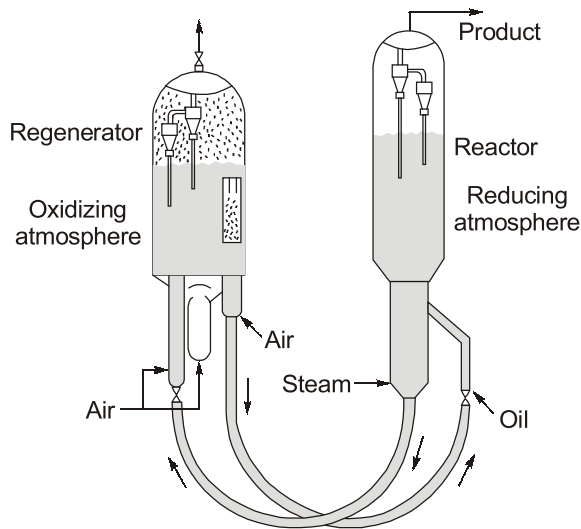


- Q2** FCC reactors are among the largest processing units used in the petroleum industry. Figure shows an example of such units. A typical unit is 4-10 m ID and 10-20 m high and contains about 50 tons of  $\rho = 800 \text{ kg/m}^3$  porous catalyst. It is fed about 38,000 barrels of crude oil per day (6000 m<sup>3</sup>/day at a density  $\rho \approx 900 \text{ kg/m}^3$ ), and it cracks these long chain hydrocarbons into shorter molecules.

To get an idea of the rate of reaction in these giant units, let us simplify and suppose that the feed consists of just C<sub>20</sub> hydrocarbon, or



If 60% of the vaporized feed is cracked in the unit, what is the rate of reaction, expressed as  $-r'$  (mols reacted/kg catalyst) and as  $r'''$  (mols reacted/m<sup>3</sup> catalyst)?



■ **Explanation**

**1. (Sol.)**

Find the rate of reaction defined as

$$r_{O_2} = \frac{\text{mol } O_2 \text{ used}}{s \text{ (m}^3 \text{ of tank)}}$$

Evaluate terms

$$\bar{t} = \frac{V}{v} \text{ or } V = \bar{t}v$$

or Volume of treatment tanks

$$= \left(\frac{1}{3} \text{ day}\right)(32000 \text{ m}^3/\text{day}) = 10667 \text{ m}^3$$

O<sub>2</sub> used:

$$(200 \text{ mg/lit}) (1 \text{ gm}/1000 \text{ mg}) (\text{mol}/32 \text{ gm})$$

$$(1000 \text{ lit}/\text{m}^3) (32000 \text{ m}^3)(\text{day}) = 2 \times 10^5 \text{ mol } O_2/\text{day}$$

Thus, the rate of reaction

$$\frac{2.0 \times 10^5 \text{ mol } O_2/\text{day}}{10667 \text{ m}^3} = 18.75 \text{ mol}/\text{m}^3 \cdot \text{day}$$

$$= 2.17 \times 10^{-4} \text{ mol}/\text{m}^3 \cdot \text{s}$$

**2. (Sol.)**

Find  $-r'_{C_{20}H_{42}}$  and  $-r'''_{C_{20}H_{42}}$  (evaluate terms)

$$V_{\text{cat}} = \frac{50000 \text{ kg}}{800 \text{ kg}/\text{m}^3} = 62.5 \text{ m}^3 \text{ of catalyst}$$

$$W_{\text{cat}} = 50000 \text{ kg}$$

$$mW_{C_{20}H_{42}} = [20(12) + 42(1)] \frac{1}{1000}$$

$$= 0.282 \text{ kg/mol}$$

$$F_{\text{feed}} = (6000 \text{ m}^3/\text{day})(900 \text{ kg}/\text{m}^3)$$

$$= 5400000 \text{ kg/day}$$

So,  $-\frac{dN_{C_{20}H_{42}}}{dt}$

$$= \left(\frac{5400000 \text{ kg/day}}{0.282 \text{ kg/day}}\right) \left(\frac{\text{day}}{24(3600)\text{s}}\right)(0.6)$$

$$= 133 \text{ mol reacted/s}$$

Thus, the rate of disappearance of C<sub>20</sub>H<sub>42</sub>

$$-r' = \frac{1}{W_{\text{cat}}} \frac{dN}{dt} = \frac{1}{50000}(133)$$

$$= 0.0027 \text{ mol/kg cat.s}$$

$$-r''' = \frac{1}{V_{\text{cat}}} \frac{dN}{dt} = \frac{1}{625}(133)$$

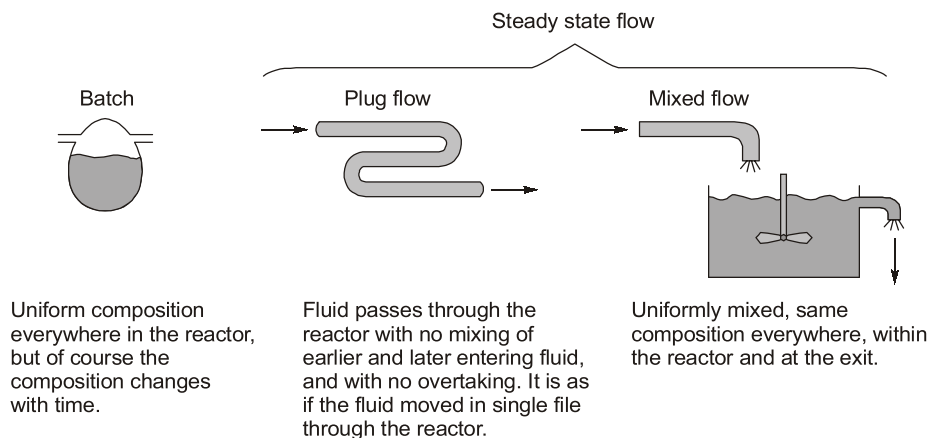
$$= 2.13 \text{ mol}/\text{m}^3 \text{ cat.s}$$



# Kinetics of Homogeneous Reactions

## 2.1 INTRODUCTION

Ideal reactors have three ideal flow or contacting patterns. We show these in figure, and we very often try to make real reactors approach these ideals as closely as possible.



**Figure:** Ideal reactor types

We particularly like these three flows or reacting patterns because they are easy to treat (it is simple to find their performance equations) and because one of them often is the best pattern possible (it will give the most of whatever it is we want). Later we will consider recycle reactors, staged reactors, and other flow pattern combinations, as well as deviations of real reactors from these ideals.

### The Rate Equation

Suppose a single-phase reaction  $aA + bB \longrightarrow rR + sS$ . The most useful measure of reaction rate for reactant A is

$$r_A = -\frac{1}{V} \frac{dN_A}{dt} = \frac{\text{(Amount of A disappearing)}}{\text{(Volume) (Time)}} \left[ \frac{\text{mol}}{\text{m}^3 \cdot \text{s}} \right] \quad \dots(2.1)$$

Rate of disappearance of A

Note that this is an intensive measure

The minus sign means disappearance

In addition, the rates of reaction of all materials are related by

$$\frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_R}{r} = \frac{r_S}{s} \quad \dots(2.2)$$

or,

$$-\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{r} \frac{d[R]}{dt} = \frac{1}{s} \frac{d[S]}{dt} \quad \dots(2.3)$$

- Rate of reaction is independent of type of reactor.
- Rate of reaction depend upon properties of reaction mixture and reaction condition at any given point. (i.e., Concentration, Temperature, Pressure). Thus, we can write

$$-r_A = f \left[ \begin{array}{l} \text{Temperature} \\ \text{dependent} \\ \text{terms} \end{array} , \begin{array}{l} \text{Concentration} \\ \text{dependent} \\ \text{terms} \end{array} \right] \quad \text{as an example} \quad k C_A^a = k_0 e^{-E/RT} C_A^a \quad \dots(2.4)$$

$\left(\frac{\text{mol}}{\text{m}^3}\right)^{1-a} \text{s}^{-1}$ 
Activation energy

Reaction order
Temperature dependent term

## 2.2 CLASSIFICATION OF CHEMICAL REACTIONS

### 2.2.1 Elementary and Non-elementary Reactions

Consider a single reaction with stoichiometric equation



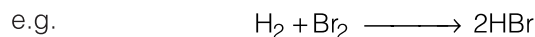
If we postulate that the rate-controlling mechanism involves the collision or interaction of a single molecule of  $A$  with a single molecule of  $B$ , then the number of collisions of molecules  $A$  with  $B$  is proportional to the rate of reaction. But at a given temperature the number of collisions is proportional to the concentration of reactants in the mixture.

Hence, the rate of disappearance of  $A$  is given by

$$-r_A = k C_A C_B \quad \dots(2.5)$$

Such reactions in which the rate equation corresponds to a stoichiometric equation are called **Elementary Reactions**.

- Elementary Kinetics are that kinetics in which exponents of concentration matches exactly with reaction stoichiometric coefficients irrespective of reaction is elementary or non-elementary. When there is no direct correspondence between stoichiometry and rate, then we have **non-elementary reactions**. It has multi-step reaction, involves number of elementary steps and takes place through particular sequence and path-ways.



$$r_{HBr} = \frac{k_1 [H_2] [Br_2]^{1/2}}{k_2 + [Br_2]}$$

### 2.2.2 Molecularity and Order of Reaction

**Order of reaction** can only be defined for kinetics which follow power law model. In general, term, suppose rate of reaction



May be written,

$$-r_A = -\frac{1}{a} \frac{d[A]}{dt} = k[A]^\alpha [B]^\beta \quad \dots(2.6)$$

- Order with respect to  $A = \alpha$
- Order with respect to  $B = \beta$
- Overall Order,  $n = \alpha + \beta$
- For non-elementary kinetics, the order can be determined within some limits.
- Order is experimentally determined quantity, it can be any real numbers, fractions.
- It can be noted that when the order of reaction is a fraction, the reaction is generally a chain reaction or follows some other complex mechanism. An example of a chemical reaction with a fractional reaction order is the pyrolysis of acetaldehyde. This reaction has an order of 2.5.

**Molecularity** of an elementary reaction refers to the number of atoms, molecules, or ions which must undergo a collision with each other in a short time interval for the chemical reaction to proceed.

- Molecularity of a reaction can never be zero.
- Molecularity of a reaction can never be fraction, but only positive integer.
- Molecularity has been found to have the values of one, two or occasionally three.

#### NOTE



1. The molecularity refers only to an elementary reaction.
2. No reaction can have molecularity more than three. If molecularity is greater than three then reaction is non-elementary.
3. Since kinetics is experimentally determined quantity thus multiplying with any constant in reaction does not change its kinetics.

### Rate Constant, $k$

Suppose a homogeneous chemical reaction,  $A \rightarrow B$

Having order =  $n$

$$\text{Rate of reaction, } -r_A = k[A]^n$$

$$\text{Unit of rate of reaction} = \frac{\text{Moles}}{(\text{Volume})(\text{Time})}$$

$$\text{Unit of concentration} = \frac{(\text{Moles})}{(\text{Volume})}$$

So, 
$$\text{Unit of rate constant} = (\text{Time})^{-1} \left( \frac{\text{Moles}}{\text{Volume}} \right)^{(1-n)}$$

Order of reaction, $n$	Unit of rate constant
$n = 0$	$\frac{(\text{moles})}{(m^3)(\text{sec})}$
$n = 1$	$(\text{time})^{-1}$
$n = 1.5$	$\frac{(m^3)^{0.5}}{(\text{moles})^{0.5}(\text{time})}$
$n = 2$	$\frac{(m^3)}{(\text{moles})(\text{time})}$

**Example 2.1**

The experimental determined overall order of the reaction  $A + B \rightarrow C + D$  is two. Which one of the following is correct?

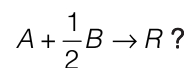
- (a) Reaction is elementary with molecularity of 2.
- (b) The molecularity of reaction is 2 but reaction may not be elementary.
- (c) The reaction is elementary but molecularity may not be 2.
- (d) The reaction may be elementary with molecularity 2.

**Solution: (d)**

The order of a reaction is determined by experiment. It can not be predicted without experiment data. The order need not correspond to the stoichiometry unless the reaction is elementary.

**Example 2.2**

A chemical reaction  $2A + B \rightarrow 2R$  has the rate expression  $-r_A = 2[A][B]^{0.5}$ . What is the rate equation for the following reaction if stoichiometric equation is written as



**Solution :**

The rate equation remains unaffected as it does not depend in any way on the stoichiometric equation. For an elementary reaction, rate constant necessary need to specify the component of the reaction e.g.,



If the rate is measured in terms of  $B$ , the rate equation is

$$-r_B = k_B[B][D]^2$$

If it refers to  $D$ , the rate equation is  $-r_D = k_D[B][D]^2$

Or if it refers to the product  $T$ , then  $r_T = k_T[B][D]^2$

But from the stoichiometry  $-r_B = -\frac{1}{2}r_D = \frac{1}{3}r_T$

Hence,  $k_B = -\frac{1}{2}k_D = \frac{1}{3}k_T$

**Representation of a Non-elementary Reaction**

A non-elementary reaction is one whose stoichiometry does not match its kinetics. For example,



Rate: 
$$r_{NH_3} = k_1 \frac{[N_2][H_2]^{3/2}}{[NH_3]^2} - k_2 \frac{[NH_3]}{[H_2]^{3/2}}$$

**Example 2.3**

The irreversible reaction  $A + B \rightleftharpoons AB$  has been studied kinetically, and the rate of formation of product has been found to be well correlated by the following rate equation:

$$r_{AB} = k[B]^2 \dots \text{Independent of concentration of } A \dots (2.7)$$

What reaction mechanism is suggested by this rate expression if the chemistry of the reaction suggests that the intermediate consists of an association of reactant molecules and that a chain reaction does not occur?

**Solution:**

If this were an elementary reaction, the rate would be given by

$$r_{AB} = k[A][B] \quad \dots(2.8)$$

Since equation (1) and (2) are not of the same type, the reaction evidently is non-elementary. Consequently, let us try various mechanisms and see which gives a rate expression similar in form to the experimentally found expression.

Hypothesize a two-step reversible scheme involving the formation of an intermediate substance  $A_2^*$ ; not actually seen and hence thought to be present only in small amounts. Thus,



which really involves four elementary reactions



Let the  $k$  values refer to the components disappearing; thus  $k_1$ , refers to  $A$ ,  $k_2$ , refers to  $A_2^*$ , etc.

Now write the expression for the rate of formation of  $AB$ . Since this component is involved in equation 7 and 8, its overall rate of change is the sum of the individual rates. Thus

$$r_{AB} = k_3[A_2^*][B] - k_4[A][AB] \quad \dots(2.15)$$

Because the concentration of intermediate  $[A_2^*]$  is so small and not measurable, the above rate expression cannot be tested in its present form. So, replace  $[A_2^*]$  by concentrations that can be measured, such as  $[A]$ ,  $[B]$  or  $[AB]$ . This is done in the following manner. From the four elementary reactions that all involve  $A$ : We find

$$r_{A_2^*} = \frac{1}{2} k_1[A]^2 - k_2[A_2^*] - k_3[A_2^*][B] + k_4[A][AB] \quad \dots(2.16)$$

Because the concentration of  $A_2^*$  is always extremely small we may assume that its rate of change is zero.

$$r_{A_2^*} = 0 \quad \dots(2.17)$$

or,

This is the steady-state approximation.

$$[A_2^*] = \frac{\frac{1}{2} k_1[A]^2 + k_4[A][AB]}{k_2 + k_3[B]} \quad \dots(2.18)$$



**Transition complexes  $[A_2^*]$ :** The numerous collisions between reactant molecules result in a wide distribution of energies among the individual molecules. This can result in strained bonds, unstable forms of molecules, or unstable association of molecules which can then decompose to give products, or by further collisions return to molecules in the normal state.

Such unstable forms are called transition complexes. Here  $[A_2^*]$  is transition complex intermediate.

Combining eqns. 2.16 and 2.17 we then find which, replaced in eqn. 2.15, simplifying and cancelling two terms (two terms will always cancel if you are doing it right), gives the rate of formation of  $AB$  in terms of measurable quantities. Thus,

$$r_{AB} = \frac{\frac{1}{2}k_1k_3[A]^2[B] - k_2k_4[A][AB]}{k_2 + k_3[B]} \quad \dots(2.19)$$

If  $k_4$  is very small, this expression reduces to

$$r_{AB} = \frac{1}{2}k_1[A]^2 \quad \dots(2.20)$$

If  $k_4$  is very small,  $r_{AB}$ , reduces to

$$r_{AB} = \frac{\left(\frac{k_1k_3}{2k_2}\right)[A]^2[B]}{1 + \left(\frac{k_3}{k_2}\right)[B]} \quad \dots(2.21)$$

## 2.3 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 composition dependent term,

$$\begin{aligned} r_i &= f_1(\text{temperature}) \cdot f_2(\text{composition}) \\ &= k \cdot f_2(\text{composition}) \end{aligned} \quad \dots(2.22)$$

### 2.3.1 Arrhenius Theory

In ideal conditions every molecules are easily converted to product but in real condition only few molecules have enough energy to be converted into product. In order to converted reactant species or molecule in product though energy is required to break the bond energy them. That minimum amount of energy to break the bond in order to convert the reactant into product possessed by few molecules among all. This minimum amount of energy is called activation energy.

Hence **activation energy is defined as minimum amount of energy that must be possessed by reactant species to convert into product.**

- Lower the value of activation energy faster the reaction rate.
- Addition of catalyst speeds up the rate of reaction actually not by lowering the activation energy but it speeds up rate of reaction by following an alternate path which have lower activation energy i.e. catalyst doesn't affect the previous activation energy but it follows an alternate path which has lower activation energy.
- Catalyst does not participate in the reaction i.e. mass of catalyst before and after the reaction is same.
- Catalyst does not effect the equilibrium.