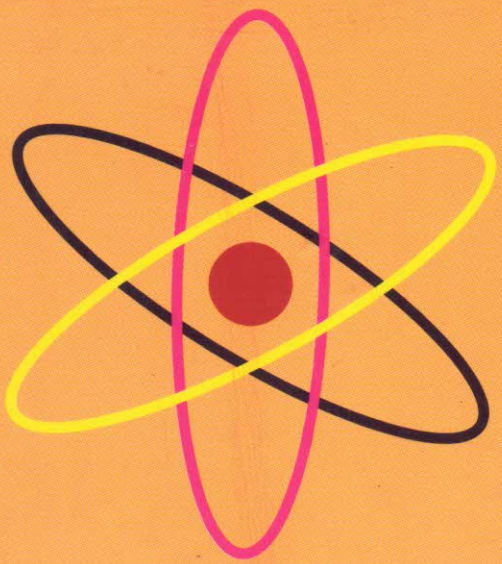
Elements of Reaction Engineering

Srivastav R.P.S.



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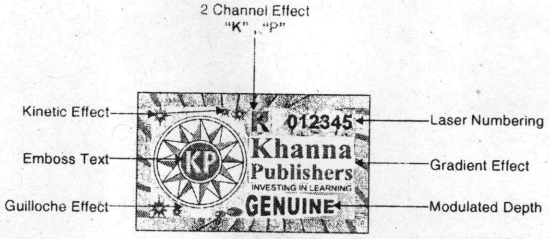

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PREFACE

Chemical reaction engineering (C.R.E.) deals with that activities of engineering where something new is produced from old materials. Designing of a reactor and understanding fully in depth of reactions need more emphasis in reaction engineering.

Generally those working in industries have number of questions such as how to attack a particular problem dealing with chemical reactions, how best to get optimum products and how to optimize the variables for best required design. The book aims at giving them some clue to find out the solutions of the above problems in fastest and easiest way. The above questions can be answered if qualitative analysis, simplest design techniques, comparison between reactors on quantitative and qualitative basis are taken up. Readers must develop a feel for the subject as well as intuitive sense to understand inside the problem.

Although number of books in the subjects are available but non deals with the basic need of budding engineers. All these books talk high with quality and standard and deal with complicated problems to tackle. Attempts have been made to describe the theory in simple mathematical manner with the help of explanations wherever required. Most of the equations have been derived from the first principle and complicated part have been simplified.

It is author's feeling that the book should serve as introductory book for students, guidelines for teacher and a help for designer and/or practicing engineers.

Many solved problems from industrial environment have been added. Few challenging problems will serve as brain-storming sessions for students.

CRE can easily be divided in two sections. First section can take care of fundamental approach to homogeneous reactions while other to hetrogeneous reactions. It is necessary to cover first part in one semester (pre final year) and remaining part in another semester (final year). Maturity of the students and basic knowledge of other subjects may help students to understand the second part better.

Chapter 2 deals with initial understanding and basic concept of homogeneous reactions and its application in industrial sector. Chapter 3 emphasis on batch reactors. Chapter 4 and 5 deal with design concepts and reactor design respectively. Chapter 6 takes care of energy and pressure effects on chemical reactions. Chapter 7 behaviour of non-ideal reactor and chapter-8 fluid mixing.

Part II, Hetrogeneous Reactions begins with the basics of the subject. Chapter 2 covers catalysis and its rate in a reactor. Chapters 3 to 5 covers multiphase reactions dealing fluid-solid, fluid-fluid and solid-solid reactions. Catalysts and Transport processes are covered in Chapter 6 and 7 respectively. Chapter 8 deals with reactor design for hetrogeneous reactions.

The above pattern was followed by the author while offering a course in C.R.E. at University level. However, it will be prevelge of teachers to follow the way it suits them most.

The author will be highly obliged if some omission or errors are pqinted out. It will be his endower to acknowledge them in proceeding editions.

With pleasure the author would like to acknowledge help, inspiration, encourgement and healthy critisims received from the well wishers. friends, students and the family members. The special thanks are due to Mrs. Madauri Lata, Dr. E.B.P. Pillai, Autogizachew adugna, Dean Polytechnic Institute, Bahirdar, Ato Almayedo Kerlo Shibeshi for their inspiration, correcting the manuscripts and their valuable suggestions from time to time.

The author is indebted to Prof. Birjesh Chandra, Ato Solomen, Ato Julfikar and Ato Mohammad for their healthy suggestion and help rendered by them.

The author thinks readers will not be disappointed by adopting this book as their text book for the course "Chemical Reaction Engineering" I & II. The author is sure that they will always find something new to scratch their head.

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CONTENTS

PART I : HOMOGENEOUS REACTIONS

1

Introduction

INTRODUCTION

Due to enhancement in world population, need for more industrialization have become must. In this context chemicals play vital role. As the day starts with chemicals and ends with chemicals.

Morning—Tooth Paste, Bread, Butter, Oil, Cloths, etc.

Afternoon—Lunch, Drinks, etc.

Evening—Tea, Biscuits, etc.

Night—Insecticides, Blanket, etc.

To keep healthy—Fruits, Medicines, etc.

To look beautiful—Powder, Cream, Oil, Vasline, etc.

These are the basic requirement of a human being in day to day life. All these chemicals are manufactured in industries. An industries operates as shown in Fig. 1.1.

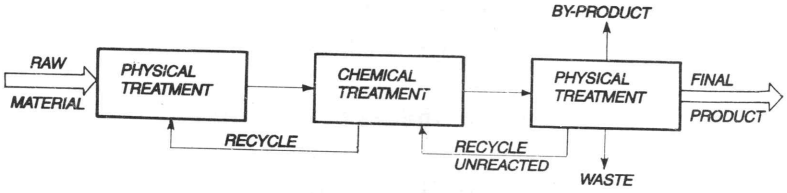


Fig. 1.1. Typical Chemical Process.

First physical treatment deals with beneficiation of raw material/enrichment of raw matent and last physical treatment takes care of separation of final product, by product, waste and/or unreacted.

First physical treatment—Crushing/grinding, filteration, size separation, sieving etc. are encountered.

Second physical treatment—Distillation, extraction, leaching, ion exchange, dialysis, reverse osmosis etc. are involved.

Chemical treatment deals with chlorination, nitration, sulfonation, bleaching, hydrogenation etc.

It is obvious from Fig. 1.1 that the chemical treatment is heart of the chemical industries. The role played by reaction engineering is to keep heart alive all the times. By simulating, updating, maintaining on most economical manner.

Design of a reactor is no more routine matter. It involves many alteration, optimization with over all cost of reactor in mind. Reactor design requires depth knowledge of many subjects of chemical engineering, *viz.* thermodynamics, fluid mechanics, heat transfer, separation process, economics, optimal process modelling and simulation etc. The reaction engineering uses all these informations for a better design. A designer has to satisfy his customer by suitably answering the following two questions which is generally asked.

(*a*) What changes to occur ?

(*b*) How fast these change will occur ?

To answer the first question one has to take the help of thermodynamics whereas second requires the depth knowledge of chemical kinetics, physical chemistry, heat transfer etc. If some one wish to ponder on both the question together. It will amount to landing in hot water. Hence let us start with the simplest situations and build up the analysis with the help of previous knowledge to solve the difficult problems. Let us make beginning with classification of reactions.

1.1. CLASSIFICATION OF REACTIONS

There are various ways to classify a reactions, however, the simplest will be taken up.

(*a*) **On the basis of phases present in reactant/product**

(*i*) Homogeneous (*ii*) Heterogeneous

It is homogeneous if all the reactants products are present in one phase whereas if more than one phase is present it is known as heterogeneous reaction.

(*b*) **Based on Catalyst**

(*i*) Catalytic reactions (*ii*) Non-catalytic reactions

A catalytic reaction is one where a catalyst is must to proceed the reaction whereas non catalytic reaction does not require any catalyst to proceed with. A catalyst does not take part in reaction however it either promote or retard the rate of reaction. A simple distinction with these classifications are depicted in Table 1.1.

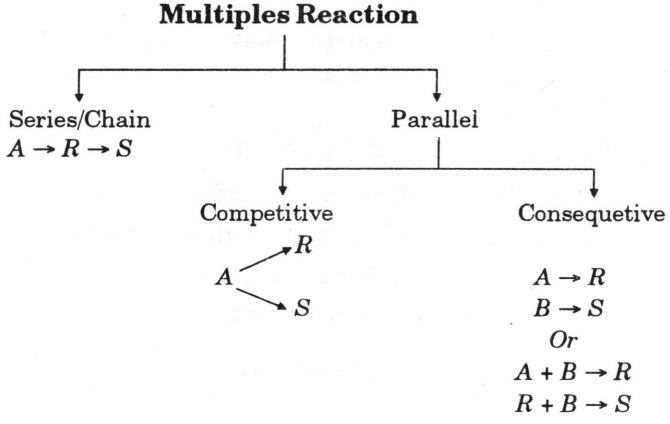
Table 1.1. Classification of Chemical Reactions

	Non-Catalytic	*Catalytic*
Homogeneous	*Most Gas Phase Reactions*	*Most Liquid Phase Reactions*
	Fast Reactions i.e. Burning of Flames	*Reaction in Colloidal System*
Heterogeneous	Burning of coal, roasting of ores, gas-liquid absorption with reaction, mass transfer with chemical reaction, production of iron and steel from iron ores.	Ammonia synthesis, cracking of naphtha oxidation of SO_2 to H_2SO_4, nitric acid production from ammonia.

(*c*) **Based upon concentration**

(*i*) Single (*ii*) Multiples.

If a single stoichiometric equation is applicable it is known as single while in the case of more than one stoichiometric equations they are termed as multiple. Multiples reaction can be further subdivided as



(*d*) **Viewed on the basis of equilibrium**

(*i*) Reversible (*ii*) Irreversible

(*iii*) Elementary (*iv*) Non-elementary reactions.

In a situation when products formed again decomposes to give reactants the reaction is known as reversible and in a case no decomposition of products take place it is irreversible reactions.

Where rate equation corresponds to stoichiometric equation it is termed as elementary reaction. If it does not correspond to stoichiometric equation it is non-elementary reaction. However, it is not always must that an equilibrium for reversible reaction. should exist in elementary reactions. Elementary reactions may also be unidirectional.

1.2. CHEMICAL KINETICS

It search for the factors which influence the rate. It quantify and justify the values of rate. Its study plays important role as :

(*a*) It is a tool to know the nature of reacting system. It also takes care of the chemical bonds involved, their structure and energy evolved/released if bonds are broken.

(*b*) Organic chemist views it as a tool to understand chemical bonding and molecular structure. Their compounding is of more interest for them.

(*c*) It provides a method to study heat and mass transfer and suggests methods to understand rate phenomena in other fields.

(*d*) For chemical engineer it gives information about design of equipments.

Any way chemical kinetics may be expressed the way one wish to use. Some more lights may be thrown if the thermodynamic approach is discussed.

1.3. THERMODYNAMICS APPROACH

It generally provides two vital informations :

(*a*) Amount of heat liberated or absorbed during reaction.

(*b*) Maximum possible extent of reaction.

A chemical reaction may be expressed as ;

$$bB + aA \rightleftharpoons rR + sS,\ \Delta H_r \begin{cases} + \text{ve, endothermic} \\ - \text{ve, exothermic} \end{cases}$$

The heat of reaction, ΔH_r, is the heat transferred either from or to surroundings when reactants give products. The thermodynamics allows to calculate the equilibrium constants, K, from the standard Gibbs free energies, G° ;

$$\Delta G^\circ = r\Delta G^\circ_R + s\Delta G^\circ_S - b\Delta G^\circ_B - a\Delta G^\circ_A = -RT \ln K \quad ...(1.1)$$

If the value of equilibrium constant, K, is known, the expected maximum yield can be estimated.

1.4. VARIABLES TO AFFECT

There may be n numbers of variables which will affect the chemical reaction. It depends on type of reactions also. Table 1.2 depicts the parameter affecting a chemical reaction.

Table 1.2. Variables affecting a reaction

Types of Reaction	*Variables Affecting*
Homogeneous	Temperature, pressure and composition.
Heterogeneous	Rate of mass transfer between layers and rate of heat transfer.
Series	Slowest step of the series.

1.5. ROLE OF REACTION RATE

Rate can be defined on number of ways. Before jumping into rate let us select one component, i, if the rate of change in number of moles in this component is $\frac{dN_i}{dt}$, then, rate can be defined on various basis.

(a) Based on unit volume of fluid :

$$r_i = \frac{1}{V} \cdot \frac{dN_i}{dt} = \frac{\text{moles of } i \text{ formed}}{(\text{Volume of fluid})(\text{Time})} \quad ...(1.2)$$

$$= \frac{dN_i}{dt} \quad ...(1.3)$$

(b) Based on unit mass of solid ;

$$r_i' = \frac{1}{W} \cdot \frac{dN_i}{dt} = \frac{\text{moles of } i \text{ formed}}{(\text{Mass of solid})(\text{Time})} \quad ...(1.4)$$

$$= \frac{dN_i}{dt} \quad ...(1.5)$$

(c) Based on unit surface area of solids ;

$$r_i'' = \frac{1}{S} \cdot \frac{dN_i}{dt} = \frac{\text{moles of } i \text{ formed}}{(\text{Surface area of solids})(\text{Time})} \quad ...(1.6)$$

$$= \frac{dN_i}{dt} \quad ...(1.7)$$

(d) Based on unit volume of solids ;

$$r_i''' = \frac{1}{V_s} \cdot \frac{dN_i}{dt} = \frac{\text{moles of } i \text{ formed}}{(\text{Volume of solid})(\text{Time})} \quad ...(1.8)$$

$$= \frac{dN_i}{dt} \quad ...(1.9)$$

(*e*) Based on unit volume of the reactor ;

$$r_i^{iv} = \frac{1}{V_r} \cdot \frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{Volume of reactor})(\text{Time})} \quad ...(1.10)$$

$$= \frac{dN_i}{dt} \quad ...(1.11)$$

Generally in the homogeneous reactions volume of the fluid and volume of the reactor is same. As fluid should fill up the complete reactor. Hence equations (1.3) and (1.10) can be exchanged wherever required.

For heterogeneous system all situations are existing, hence equations from (1.3) to (1.10) are all used as per need.

If one examine equation (1.3) to (1.10) he may relate reaction rate as ;

$$\left\{\begin{matrix}\text{Volume}\\ \text{of fluid}\end{matrix}\right\} r_i = \left\{\begin{matrix}\text{Mass of}\\ \text{solid}\end{matrix}\right\} r_i' = \left\{\begin{matrix}\text{Surface area}\\ \text{of solids}\end{matrix}\right\} r_i''$$

$$= \left\{\begin{matrix}\text{Volume of}\\ \text{solid}\end{matrix}\right\} r_i''' = \left\{\begin{matrix}\text{Volume of}\\ \text{reactor}\end{matrix}\right\} r_i^{iv} \quad ...(1.12)$$

or $$Vr_i = Wr_i' = Sr_i'' = V_s r_i''' = V_r r_i^{iv} \quad ...(1.13)$$

The equation (1.13) gives a clue to define a rate.

Rate is nothing but the way a component disappearance or formed per unit time.

The rate depends on the conditions of the systems.

$$r_i = f(\text{Conditions of system}) \quad ...(1.14)$$

These conditions are temperature, pressure and composition.

So,

$$r_i = f(\text{Temperature, Pressure, Composition}) \quad ...(1.15)$$

From the knowledge of general science the temperature and pressure are interrelated. Thus equation (1.15) reduces to

$$r_i = f(\text{Temperature, Composition}) \quad ...(1.16)$$

Effect of these will be discussed in detail in chapter 2.

SOLVED PROBLEMS

Problem 1.1. *A first order reaction A → B is carried out in a tubular reactor with constant volumetric flow rate. Derive an equation relating the reactor volume to the entering and exit concentration of reactant, the rate constant and volumetric flow rates. Determine the reactor volume to reduce the exiting concentration to 10% of entering. Assume volumetric flow rate as 10 litres / min and specific reaction rate constant as 0.23 / min.*

Solution. The mole balance for tubular reactor,

$$\frac{dF_A}{dV} = r_A \qquad ...(1.1.1)$$

For the first order reaction, $-r_A = kC_A$.

As the volumetric flow rate is constant

$$\frac{dF_A}{dV} = \frac{d(C_A v_0)}{dV} = v_0 \frac{dC_A}{dV} = r_A \qquad ...(1.1.2)$$

Substituting for r_A

$$-r_A = -v_0 \frac{dC_A}{dV} = kC_A$$

or $$-\frac{v_0}{k}\left(\frac{dC_A}{dV}\right) = d_V$$

or on integration, $$V = \frac{v_0}{k} \ln \frac{C_{A0}}{C_A}$$

$$= \frac{10}{0.23} \ln \frac{C_{A0}}{0.1\, C_{A0}}$$

$$= 100 \text{ litres.} \quad \textbf{Ans.}$$

Problem 1.2. *Write the mole balance for dimethyl ether in terms of reactor volume, concentration and rate of disappearance of dimethyl ether for both a constant volume and constant pressure batch reactor.*

Solution. Let reaction be $A \longrightarrow M + H + C$ ...(1.1.3)

where, A = Dimethyl ether, M = Methane,

H = Hydrogen and C = Carbon.

For both types of reactors, $\frac{1}{V} \cdot \frac{dN_A}{dt} = r_A$ ...(1.1.4)

Assume. No patial variations in r_A for both reactors.

(a) Constant volume batch reactor ;

Assume. Reactor being perfectly mixed.

$$\frac{1}{V} \cdot \frac{dN_A}{dt} = \frac{d(NA/V)}{dt} = \frac{dC_A}{dt} = r_A \qquad ...(1.1.5)$$

(b) Constant pressure batch reactor ;

$$N_A = C_A V$$

$$\frac{1}{V} \cdot \frac{dN_A}{dt} = \frac{1}{V} \frac{d(C_A \,.\, V)}{dt} = \frac{dC_A}{dt} + \frac{C_A}{V} \cdot \frac{dV}{dt} = r_A \qquad ...(1.1.6)$$

or $$r_A = \frac{dC_A}{dt} + C_A \frac{d \ln V}{dt} \,. \quad \textbf{Ans.}$$

UNSOLVED PROBLEMS

1.1. Find the variation of the rate of the reaction $2NO + O_2 \longrightarrow 2NO_2$ with the two-fold increase in the initial oxygen concentration. Repeat the problem with the two-fold increase of the initial concentration of NO. Compare the results obtained in two cases.

1.2. Find the $H_2 : CO$ ratio need for the highest rate of methane synthesis if the reaction rate is given by the following equation :

$$(-r_A) = k_1 pH_2 \left\{ \frac{pC_0}{pCH_{3OH}} \right\}^{0.25} - k_2 \frac{pCH_{3OH}^{0.5}}{pC_0^{0.25}} .$$

1.3. The rate of the reaction $2A + B \longrightarrow D$ is given by the first order equation for each component. After 20 minutes 20% of A has reacted. Calculate the concentration of component A after 40 minutes.

1.4. A polymerization reaction takes place at a constant temperature in homogeneous phase. For the initial monomer concentration of 0.3, 0.5 and 0.9 $\frac{\text{mole}}{\text{liter}}$, 30% of the monomer reacts in 40 minutes. Find out the reaction rate.

1.5. A gas mixture contains NO and air. Find the oxygen concentration to provide the maximum rate of oxidation of NO. The temperature is below 150°C, A clue (an irreversible reaction). The rate of reaction is $(-r_A) = kC_{NO}^2 C_{O_2}$.

1.6. Water vapour is 1.85 mole % dissociated at 2000°C and one atmosphere pressure at equilibrium. Calculate the equilibrium dissociation at 25°C and 1 atm.

1.7. Write the mole balance for dimethyl ether in terms of the reactor volume, concentration and rate of formation of dimethyl ether for both a constant pressure and a constant volume batch reactor.

1.8. Differentiate between rate of reaction for homogeneous and heterogeneous reactions. State the properties on which each of them depend.

1.9. A reaction has the stoichiometric equation $A + B \longrightarrow 2R$, state the order of reaction.

1.10. A certain reaction has a rate, $(-r_A) = 5 \times 10^{-3} C_A^2 . \frac{\text{moles}}{m^3 . hr}$. If the concentration is expressed in $\frac{\text{mole}}{\text{liter}}$ and time in minutes calculate the value and decide the unit of rate constant.

1.11. A reaction with stoichiometric equation $\frac{1}{2} A + B \longrightarrow R + \frac{1}{2} S$ has the following rate expression : $(-r_A) = 2C_A^{0.5} C_B$. Find out the rate expression for this reaction if stoichiometric equation is

$$A + 2B \rightarrow 2R + S.$$

Elements of Reaction Engineering

Chemical Reaction Engineering deals with that activities of engineering where something new is produced from old materials. Designing of a reactor and understanding fully in depth of reactions need more emphasis in reaction engineering.

There are number of questions such as how to attach a particular problem dealing with chemical reactions, how best to get optimum products and how to optimize the variables for best required design. The book aims at giving clue to find out the solutions of the problems in fastest and easiest way. Any question can be answered if qualitative analysis, simplest design techniques, comparison between reactors on quantitative and qualitative basis are taken up.

Attempts have been made to describe the theory in simple mathematical manner with the help of explanations wherever required. Most of the equations have been derived from the first principle and complicated part have been simplified.

Many solved problems from industrial environmental have been added. Few challenging problems will serve as brain-storming sessions for students.

First section takes care of fundamental approach to homogeneous reactions while second section to hetrogeneous reactions. The content matter is highlighted as follows :

Part—I

- Introduction
- Homogeneous Reactions
- Batch Reactor
- Reactor Design Concept
- Reactor Design
- Energy and Pressure
- Effects on Chemical Reactions
- Behaviour of Non-ideal Reactors
- Fluid Mixing

Part—II

- Introduction
- Catalysts and its Rate in a Reactor
- Multiphase Reactions (Fluid-Solid reactors)
- Multiphase Reactions (Fluid-Fluid reactors)
- Multiphase Reactions (Solid-Solid reactors)
- Catalysts
- Transport Processes
- Reactor Design for Hetrogeneous Reactions

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