Chemical Engineering

Chemical Reaction Engineering

Comprehensive Theory

with **Solved Examples** and **Practice Questions**

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Chemical Reaction Engineering

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CHAPTER 1

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.

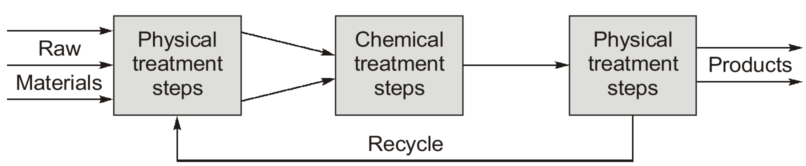


Figure : *Typical Chemical Process*

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.

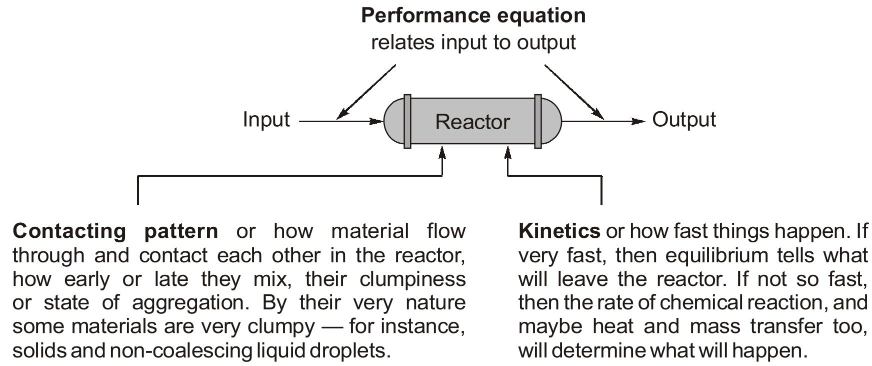


***Figure:** Information needed to predict what a reactor can do*

- 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

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

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. **Isomeration 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.

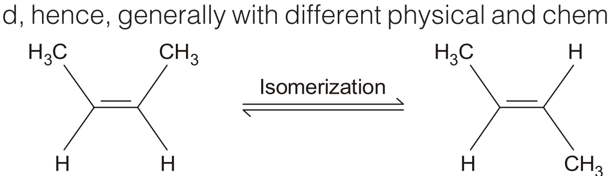


***Figure:** Number of carbon atoms and hydrogen are same but configuration is different.*

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.

   e.g. $2SO_2\,(g) + O_2 \rightleftharpoons 2SO_3\,(g)$

- 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.

e.g. $CaCO_3\,(s) \rightleftharpoons Cao\,(s) + CO_2\,(g)$

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

  e.g. $C_2H_4\,(g) + H_2\,(g) \xrightarrow{Ni\,(s)} C_2H_6\,(g)$

- 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 or 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 SO_2 to 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

$$aA + bB + \ldots.. \longrightarrow rR + sS + \ldots$$

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,

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

- 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,

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

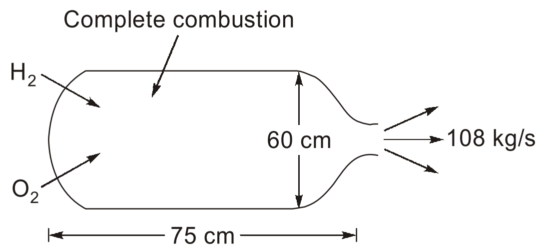
- In homogeneous systems, the volume of fluid in the reactor is often identical to the volume of reactor. In such a case V and V_r are identical.
- In heterogeneous systems all the above intensive definitions of reaction rate are related by

$$(\text{Volume of fluid})r_i = (\text{Mass of solid})r_i' = (\text{Surface of solid})r_i'' = (\text{Volume of solid})r_i''' = (\text{Volume of reactor})r_i''''$$

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

$$-r_{H2} = \frac{1}{V}\frac{dN_{H2}}{dt} \text{ and } -r_{O2} = \frac{1}{V}\frac{dN_{O2}}{dt}$$

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.

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \qquad \text{...(i)}$$

Molecular weight : 2 gm 16 gm 18 gm

Therefore, $$\text{H2O produced/s} = 108 \text{ kg/s}\left(\frac{1 \text{ kmol}}{18 \text{ kg}}\right) = 6 \text{ kmol/s}$$

So, from Eq. (i), H_2 used = 6 kmol/s

O_2 used = 3 kmol/s

$$-r_{H2} = \frac{1}{0.2121 \text{ m}^3} \times 6 \text{ kmol/s}$$
$$= 2.829 \times 10^4 \text{ mol used/(m}^3 \text{ of rocket)/s}$$

$$-r_{O2} = -\frac{1}{0.2121 \text{ m}^3} \times 3 \text{ kmol/s} = 1.415 \times 10^4 \text{ mol/m}^3\text{s}$$

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

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O, -\Delta H_r = 2816 \text{ kJ}$$

from air breathed out

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

Solution:

We want to find

$$-r'''_{O2} = -\frac{1}{V_{person}}\frac{dN_{O2}}{dt} = \frac{\text{mol } O_2 \text{ used}}{(\text{m}^3 \text{ of person})\text{s}} \qquad \text{...(i)}$$

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

$$\frac{dN_{O2}}{dt} = \left(\frac{6000 \text{ kJ/day}}{2816 \text{ kJ/mol glucose}}\right)\left(\frac{6 \text{ mol } O_2}{1 \text{ mol glucose}}\right) = 12.8 \text{ mol } O_2\text{/day}$$

Inserting into eq. (i)

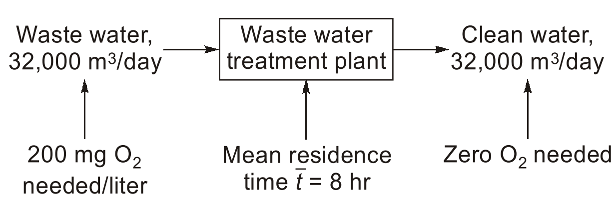
$$-r'''_{O2} = \frac{1}{0.075 \text{ m}^3} \times \frac{12.8 \text{ mol } O_2 \text{ used}}{\text{day}} \times \frac{1 \text{ day}}{24 \times 3600 \text{ s}}$$
$$= 0.002 \text{ mol } O_2 \text{ used/m}^3\text{.s}$$

Student's Assignments

Q.1 Consider a municipal water treatment plant for a small community (see fig.). Waste water, 32,000 m^3/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.

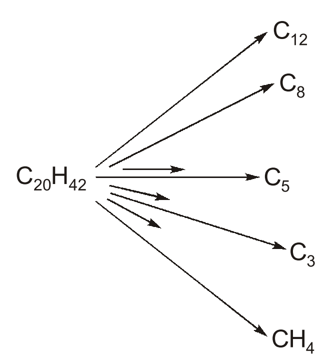
$$\text{Organic Waste} + O_2 \xrightarrow{\text{microbes}} CO_2 + H_2O$$

A typical entering feed has a BOD (biological oxygen demand) of 200 mg O_2/litre, while the effluent has a negligible BOD. Find the rate of reaction or decrease in BOD in the treatment tanks.

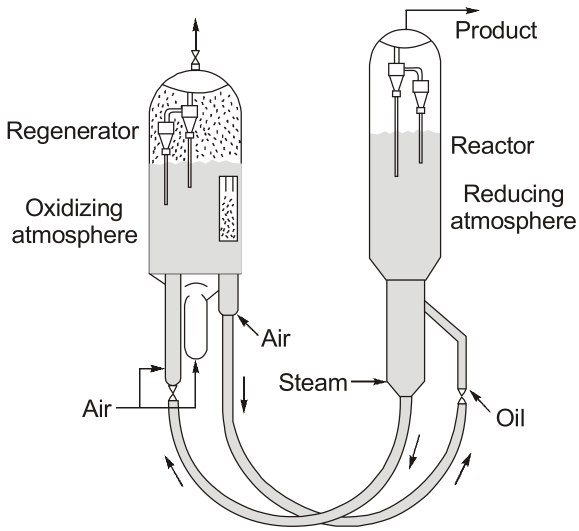


Q.2 FCC reactors are among the largest processing units used in the petroleum industry. Figure shows an example of such units. A typical unit is 4-10 m ID and 10-20 m high and contains about 50 tons of ρ = 800 kg/m^3 porous catalyst. It is fed about 38,000 barrels of crude oil per day (6000 m3/day at a density $\rho \cong 900$ 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 C20 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^3 catalyst)?



■ Explanation

1. Find the rate of reaction defined as

$$r_{O2} = \frac{\text{mol } O_2 \text{ used}}{s\ (m^3 \text{ of tank})}$$

Evaluate terms

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

or Volume of treatment tanks

$$= \left(\frac{1}{3}\text{ day}\right)(32000 \text{ m3/day}) = 10667 \text{ m}^3$$

O_2 used :

(200 mg/lit.)(1 gm/1000 mg)(mol/32 gm)(1000 lit/m^3)(32000 m3)(day) = 2×10^5 mol O_2/day

Thus, the rate of reaction

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

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

2. Find $-r'_{C20H42}$ and $-r'''_{C20H42}$ (evaluate terms)

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

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

$$mW_{C20H42} = [20(12) + 42(1)]\frac{1}{1000}$$

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

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

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

So, $-\dfrac{dN_{C20H42}}{dt}$

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

= 133 mol reacted/s

Thus, the rate of disappearance of $C_{20}H_{42}$

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

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

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

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

■■■■