

# Chapter 1

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## Overview of Chemical Reaction Engineering

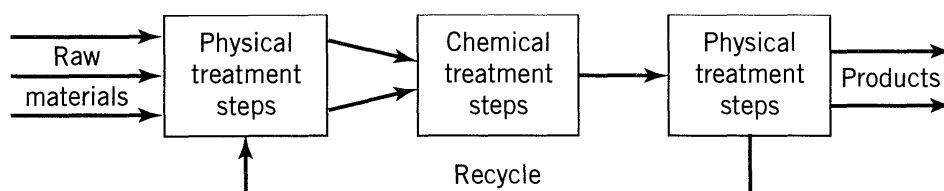
Every industrial chemical process is designed to produce economically a desired product from a variety of starting materials through a succession of treatment steps. Figure 1.1 shows a typical situation. The raw materials undergo a number of physical treatment steps to put them in the form in which they 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.

Design of equipment for the physical treatment steps is studied in the unit operations. In this book we are concerned with the chemical treatment step of a process. Economically this may be an inconsequential unit, perhaps a simple mixing tank. Frequently, however, the chemical treatment step is the heart of the process, the thing that makes or breaks the process economically.

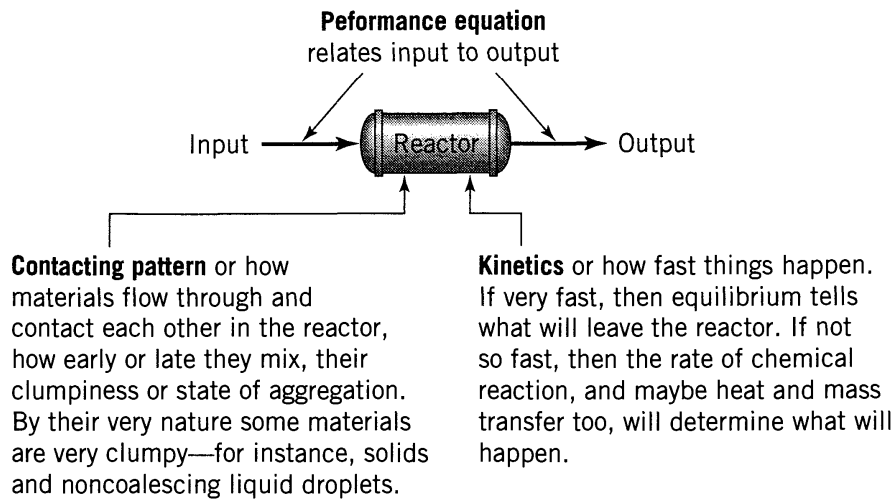
Design of the reactor is no routine matter, and many alternatives can be proposed for a process. In searching for the optimum it is not just the cost of the reactor that must be minimized. One design may have low reactor cost, but the materials leaving the unit may be such that their treatment requires a much higher cost than alternative designs. Hence, the economics of the overall process must be considered.

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 Fig. 1.2.



**Figure 1.1** Typical chemical process.



**Figure 1.2** Information needed to predict what a reactor can do.

Much of this book deals with finding the expression to relate input to output for various kinetics and various contacting patterns, or

$$\text{output} = f[\text{input, kinetics, contacting}] \quad (1)$$

This is called the *performance equation*. Why is this important? Because with this expression we can compare different designs and conditions, find which is best, and then scale up to larger units.

## Classification of Reactions

There are many ways of classifying chemical reactions. In chemical reaction engineering probably the most useful scheme is the breakdown according to the number and types of phases involved, the big division being between the *homogeneous* and *heterogeneous* systems. A reaction is homogeneous if it takes place in one phase alone. A reaction is heterogeneous if it requires the presence of at least two phases to proceed at the rate that it does. It is immaterial whether the reaction takes place in one, two, or more phases; at an interface; or whether the reactants and products are distributed among the phases or are all contained within a single phase. All that counts is that at least two phases are necessary for the reaction to proceed as it does.

Sometimes this classification is not clear-cut as with the large class of biological reactions, the enzyme-substrate reactions. Here the enzyme acts as a catalyst in the manufacture of proteins and other products. Since enzymes themselves are highly complicated large-molecular-weight proteins of colloidal size, 10–100 nm, enzyme-containing solutions represent a gray region between homogeneous and heterogeneous systems. Other examples for which the distinction between homogeneous and heterogeneous systems is not sharp are the very rapid chemical reactions, such as the burning gas flame. Here large nonhomogeneity in composition and temperature exist. Strictly speaking, then, we do not have a single phase, for a phase implies uniform temperature, pressure, and composition throughout. The answer to the question of how to classify these borderline cases is simple. It depends on how we *choose* to treat them, and this in turn depends on which

**Table 1.1** Classification of Chemical Reactions Useful in Reactor Design

	Noncatalytic	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 pro- duce nitric acid Cracking of crude oil Oxidation of SO <sub>2</sub> to SO <sub>3</sub>

description we think is more useful. Thus, only in the context of a given situation can we decide how best to treat these borderline cases.

Cutting across this classification is the catalytic reaction whose rate is altered by materials that are neither reactants nor products. These foreign materials, called *catalysts*, need not be present in large amounts. Catalysts act somehow as go-betweens, either hindering or accelerating the reaction process while being modified relatively slowly if at all.

Table 1.1 shows the classification of chemical reactions according to our scheme with a few examples of typical reactions for each type.

## Variables Affecting the Rate of Reaction

Many variables may affect the rate of a chemical reaction. In homogeneous systems the temperature, pressure, and composition are obvious variables. In heterogeneous systems more than one phase is involved; hence, the problem becomes more complex. Material may have to move from phase to phase during reaction; hence, the rate of mass transfer can become important. For example, in the burning of a coal briquette the diffusion of oxygen through the gas film surrounding the particle, and through the ash layer at the surface of the particle, can play an important role in limiting the rate of reaction. In addition, the rate of heat transfer may also become a factor. Consider, for example, an exothermic reaction taking place at the interior surfaces of a porous catalyst pellet. If the heat released by reaction is not removed fast enough, a severe nonuniform temperature distribution can occur within the pellet, which in turn will result in differing point rates of reaction. These heat and mass transfer effects become increasingly important the faster the rate of reaction, and in very fast reactions, such as burning flames, they become rate controlling. Thus, heat and mass transfer may play important roles in determining the rates of heterogeneous reactions.

## Definition of Reaction Rate

We next ask how to *define* the rate of reaction in meaningful and useful ways. To answer this, let us adopt a number of definitions of rate of reaction, all

interrelated and all intensive rather than extensive measures. But first we must select one reaction component for consideration and define the rate in terms of this component  $i$ . If the rate of change in number of moles of this component due to reaction is  $dN_i/dt$ , then the rate of reaction in its various forms is defined as follows. Based on unit volume of reacting fluid,

$$r_i = \frac{1}{V} \frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{volume of fluid}) (\text{time})} \quad (2)$$

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

$$r'_i = \frac{1}{W} \frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{mass of solid}) (\text{time})} \quad (3)$$

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

$$r''_i = \frac{1}{S} \frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{surface}) (\text{time})} \quad (4)$$

Based on unit volume of solid in gas-solid systems

$$r'''_i = \frac{1}{V_s} \frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{volume of solid}) (\text{time})} \quad (5)$$

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

$$r''''_i = \frac{1}{V_r} \frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{volume of reactor}) (\text{time})} \quad (6)$$

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 and Eqs. 2 and 6 are used interchangeably. In heterogeneous systems all the above definitions of reaction rate are encountered, the definition used in any particular situation often being a matter of convenience.

From Eqs. 2 to 6 these intensive definitions of reaction rate are related by

$$\left( \begin{array}{c} \text{volume} \\ \text{of fluid} \end{array} \right) r_i = \left( \begin{array}{c} \text{mass of} \\ \text{solid} \end{array} \right) r'_i = \left( \begin{array}{c} \text{surface} \\ \text{of solid} \end{array} \right) r''_i = \left( \begin{array}{c} \text{volume} \\ \text{of solid} \end{array} \right) r'''_i = \left( \begin{array}{c} \text{volume} \\ \text{of reactor} \end{array} \right) r''''_i$$

or

$$Vr_i = Wr'_i = Sr''_i = V_s r'''_i = V_r r''''_i \quad (7)$$

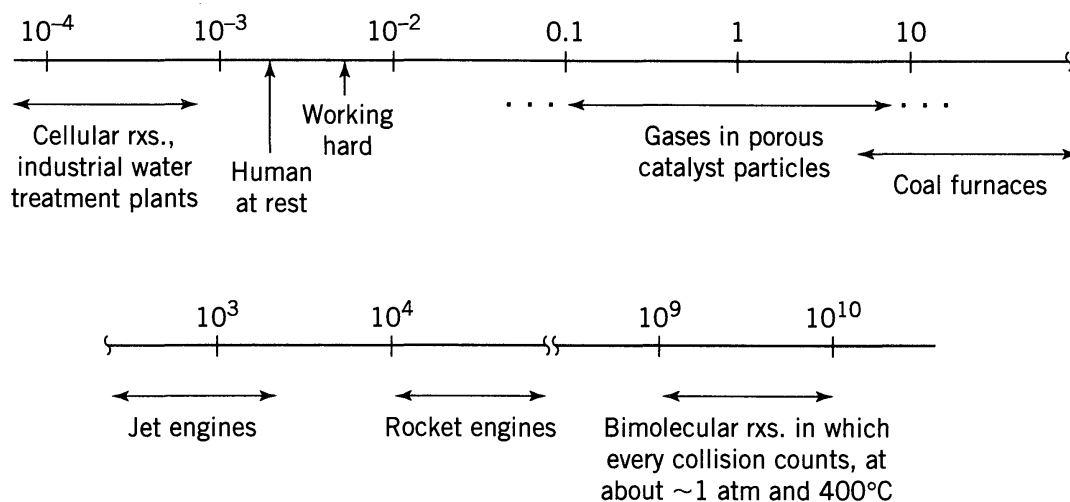
## Speed of Chemical Reactions

Some reactions occur very rapidly; others very, very slowly. For example, in the production of polyethylene, one of our most important plastics, or in the production of gasoline from crude petroleum, we want the reaction step to be complete in less than one second, while in waste water treatment, reaction may take days and days to do the job.

Figure 1.3 indicates the relative rates at which reactions occur. To give you an appreciation of the relative rates or relative values between what goes on in sewage treatment plants and in rocket engines, this is equivalent to

1 sec to 3 yr

With such a large ratio, of course the design of reactors will be quite different in these cases.



**Figure 1.3** Rate of reactions  $-r_A''' = \frac{\text{moles of A disappearing}}{\text{m}^3 \text{ of thing} \cdot \text{s}}$

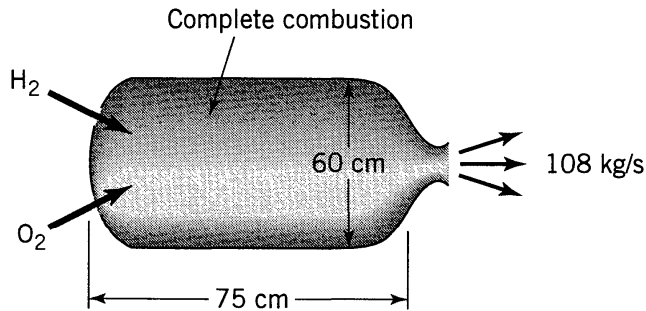
## Overall Plan

Reactors come in all colors, shapes, and sizes and are used for all sorts of reactions. As a brief sampling we have the giant cat crackers for oil refining; the monster blast furnaces for iron making; the crafty activated sludge ponds for sewage treatment; the amazing polymerization tanks for plastics, paints, and fibers; the critically important pharmaceutical vats for producing aspirin, penicillin, and birth control drugs; the happy-go-lucky fermentation jugs for moonshine; and, of course, the beastly cigarette.

Such reactions are so different in rates and types that it would be awkward to try to treat them all in one way. So we treat them by type in this book because each type requires developing the appropriate set of performance equations.

**EXAMPLE 1.1 THE ROCKET ENGINE**

A rocket engine, Fig. E1.1, 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 produces 108 kg/s of exhaust gases. If combustion is complete, find the rate of reaction of hydrogen and of oxygen.



**Figure E1.1**

**SOLUTION**

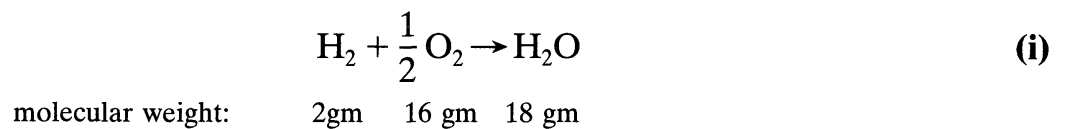
We want to evaluate

$$-r_{\text{H}_2} = \frac{1}{V} \frac{dN_{\text{H}_2}}{dt} \quad \text{and} \quad -r_{\text{O}_2} = \frac{1}{V} \frac{dN_{\text{O}_2}}{dt}$$

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

$$V = \frac{\pi}{4} (0.6)^2 (0.75) = 0.2121 \text{ m}^3$$

Next, let us look at the reaction occurring.



Therefore,

$$\text{H}_2\text{O produced/s} = 108 \text{ kg/s} \left( \frac{1 \text{ kmol}}{18 \text{ kg}} \right) = 6 \text{ kmol/s}$$

So from Eq. (i)

$$\text{H}_2 \text{ used} = 6 \text{ kmol/s}$$

$$\text{O}_2 \text{ used} = 3 \text{ kmol/s}$$

and the rate of reaction is

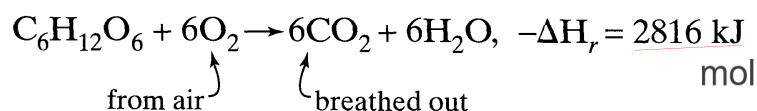
$$\underline{\underline{-r_{\text{H}_2}}} = -\frac{1}{0.2121 \text{ m}^3} \cdot \frac{6 \text{ kmol}}{\text{s}} = \underline{\underline{2.829 \times 10^4 \frac{\text{mol used}}{(\text{m}^3 \text{ of rocket}) \cdot \text{s}}}}$$

$$\underline{\underline{-r_{\text{O}_2}}} = -\frac{1}{0.2121 \text{ m}^3} \cdot 3 \frac{\text{kmol}}{\text{s}} = \underline{\underline{1.415 \times 10^4 \frac{\text{mol}}{\text{m}^3 \cdot \text{s}}}}$$

**Note:** Compare these rates with the values given in Figure 1.3. ■

### EXAMPLE 1.2 THE LIVING PERSON

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  $\text{m}^3$  of person per second.

#### SOLUTION

We want to find

$$-r''_{\text{O}_2} = -\frac{1}{V_{\text{person}}} \frac{dN_{\text{O}_2}}{dt} = \frac{\text{mol O}_2 \text{ used}}{(\text{m}^3 \text{ of person})\text{s}} \quad (\text{i})$$

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

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

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

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

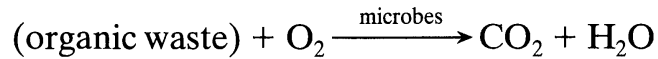
Inserting into Eq. (i)

$$-r'''_{O_2} = \frac{1}{0.075 \text{ m}^3} \cdot \frac{12.8 \text{ mol O}_2 \text{ used}}{\text{day}} \frac{1 \text{ day}}{24 \times 3600 \text{ s}} = \underline{\underline{0.002 \frac{\text{mol O}_2 \text{ used}}{\text{m}^3 \cdot \text{s}}}}$$

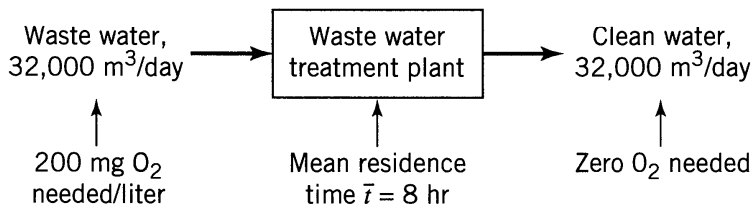
**Note:** Compare this value with those listed in Figure 1.3.

**PROBLEMS**

**1.1. Municipal waste water treatment plant.** Consider a municipal water treatment plant for a small community (Fig. P1.1). Waste water, 32 000 m<sup>3</sup>/day, flows through the treatment plant with a mean residence time of 8 hr, air is bubbled through the tanks, and microbes in the tank attack and break down the organic material

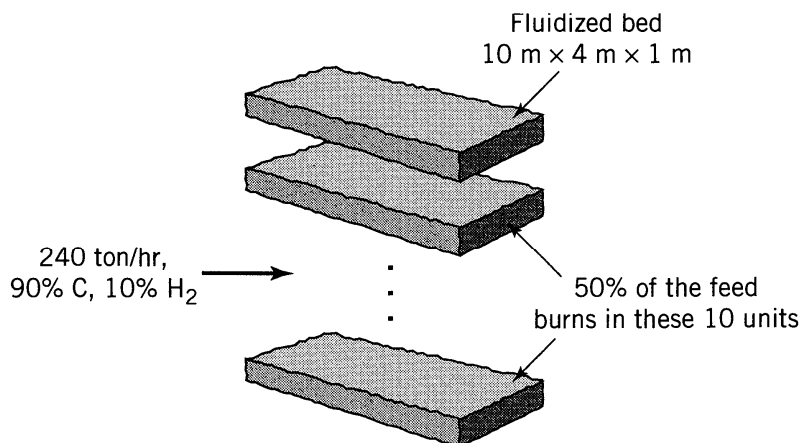


A typical entering feed has a BOD (biological oxygen demand) of 200 mg O<sub>2</sub>/liter, while the effluent has a negligible BOD. Find the rate of reaction, or decrease in BOD in the treatment tanks.



**Figure P1.1**

**1.2. Coal burning electrical power station.** Large central power stations (about 1000 MW electrical) using fluidized bed combustors may be built some day (see Fig. P1.2). These giants would be fed 240 tons of coal/hr (90% C, 10%



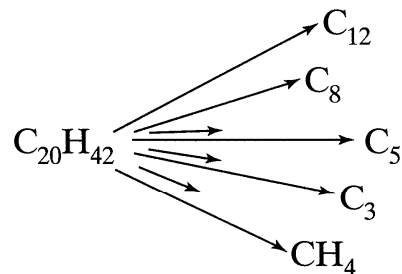
**Figure P1.2**



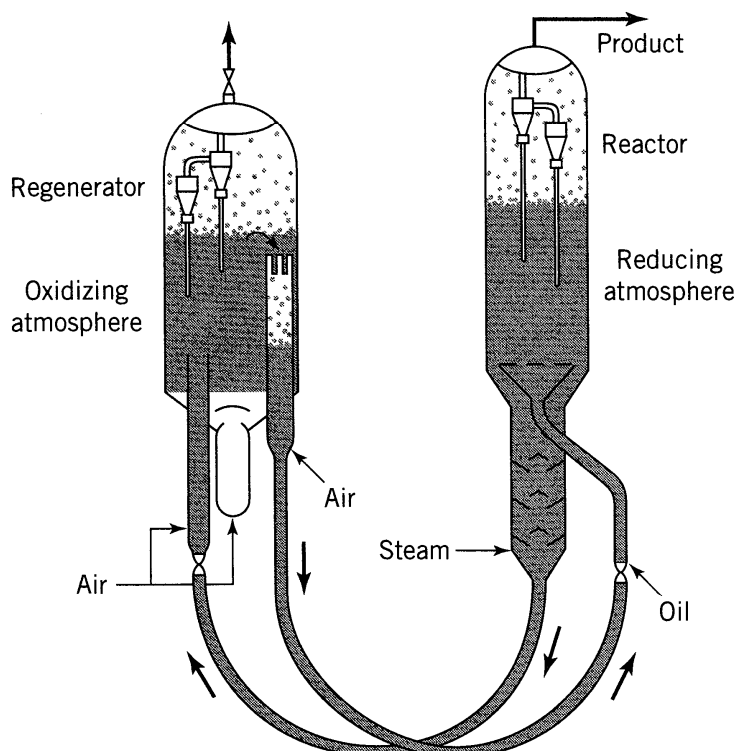
$H_2$ ), 50% of which would burn within the battery of primary fluidized beds, the other 50% elsewhere in the system. One suggested design would use a battery of 10 fluidized beds, each 20 m long, 4 m wide, and containing solids to a depth of 1 m. Find the rate of reaction within the beds, based on the oxygen used.

**1.3. Fluid cracking crackers (FCC).** FCC reactors are among the largest processing units used in the petroleum industry. Figure P1.3 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 ( $6000 \text{ m}^3/\text{day}$  at a density  $\rho \cong 900 \text{ kg/m}^3$ ), 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  $C_{20}$  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 cat · s) and as  $r'''$  (mols reacted/ $\text{m}^3 \text{ cat} \cdot \text{s}$ )?



**Figure P1.3** The Exxon Model IV FCC unit.