

# Chapter 17

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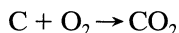
## Heterogeneous Reactions—Introduction

The second half of this book treats the kinetics and design of chemical reactors for heterogeneous systems of various kinds, each chapter considering a different system (see Chapter 1 for discussions of heterogeneous and homogeneous systems). For these systems there are two complicating factors that must be accounted for beyond what is normally considered in homogeneous systems. First, we have the complication of the rate expression, and second the complication of the contacting patterns for two-phase systems. Let us briefly discuss these in turn.

**The Complications of the Rate Equation.** Since more than one phase is present, the movement of material from phase to phase must be considered in the rate equation. Thus the rate expression in general will incorporate mass transfer terms in addition to the usual chemical kinetics term. These mass transfer terms are different in type and numbers in the different kinds of heterogeneous systems; hence, no single rate expression has general application. Here are some simple examples.

### **EXAMPLE 17.1**    *THE BURNING OF A CARBON PARTICLE IN AIR*

Tell how many rate steps are involved. The kinetics is given by



and ignore the possible formation of CO.

### **SOLUTION**

From Fig. E17.1 we see that two steps in series are involved—mass transfer of oxygen to the surface followed by reaction at the surface of the particle.

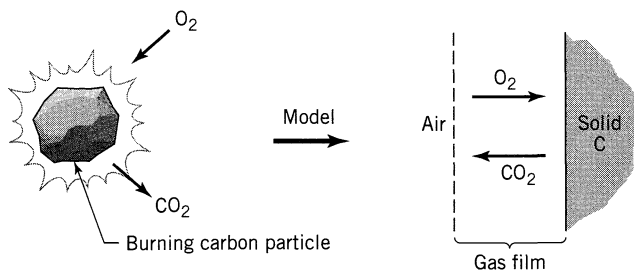


Fig. E17.1

**EXAMPLE 17.2 AEROBIC FERMENTATION**

Tell how many rate steps are involved when air bubbles through a tank of liquid which contains dispersed microbes and is taken up by the microbes to produce product material.

**SOLUTION**

From Fig. E17.2 we see that there are up to seven possible resistance steps, only one involving the reaction. How many you choose to consider depends on you and on the situation.

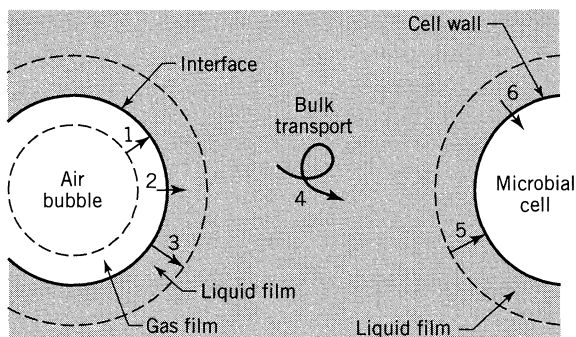


Fig. E17.2

To get an overall rate expression, write the individual rate steps on the same basis (unit surface of burning particle, unit volume of fermenter, unit volume of cells, etc.).

$$-r_A = -\frac{1}{V} \frac{dN_A}{dt} = \frac{\text{mol A reacted}}{\text{volume of reactor fluid} \cdot \text{time}}$$

or

$$-r'_A = -\frac{1}{W} \frac{dN_A}{dt} = \frac{\text{mol A reacted}}{\text{mass of solid} \cdot \text{time}}$$

or

$$-r''_A = -\frac{1}{S} \frac{dN_A}{dt} = \frac{\text{mol A reacted}}{\text{interfacial surface} \cdot \text{time}}$$

Now put all the mass transfer and reaction steps into the same rate form and then combine. Thus

$$\frac{\text{mol A reacted}}{\text{time}} = (-r_A)V = (-r'_A)W = (-r''_A)S$$

or

$$r_A = \frac{W}{V} r'_A, \quad r''_A = \frac{V}{S} r_A, \quad r'_A = \frac{S}{W} r''_A$$

and if the steps are in series, as in Examples 17.1 and 17.2

$$r_{\text{overall}} = r_1 = r_2 = r_3$$

If they are in parallel

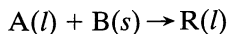
$$r_{\text{overall}} = r_1 + r_2$$

Consider steps in series. In general, if all the steps are linear in concentration, then it is easy to combine them. However, if any of the steps are nonlinear, then you will get a messy overall expression. Therefore, you may try to bypass this nonlinear step in one of various ways. Approximating the  $r_A$  versus  $C_A$  curve by a first-order expression is probably the most useful procedure.

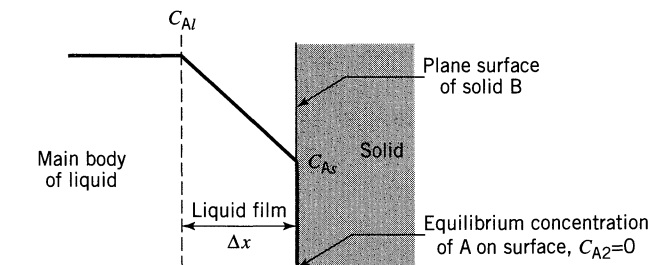
Another point: in combining rates we normally do not know the concentration of materials at intermediate conditions, so these are the concentrations that we eliminate in combining rates. Example 17.3 shows this.

**EXAMPLE 17.3** OVERALL RATE FOR A LINEAR PROCESS

Dilute A diffuses through a stagnant liquid film onto a plane surface consisting of B, reacts there to produce R which diffuses back into the mainstream. Develop the overall rate expression for the L/S reaction



which takes place on this flat surface, see Fig. E17.3.



**Figure E17.3.**

**SOLUTION**

By diffusion, the flux of A to the surface is

$$r''_{A1} = \frac{1}{S} \frac{dN_A}{dt} = -\frac{\mathcal{D}}{\Delta x} (C_{Al} - C_{As}) = k_l (C_{Al} - C_{As}) \quad (\text{i})$$

Reaction is first order with respect to A, so based on unit surface

$$r''_{A2} = \frac{1}{S} \frac{dN_A}{dt} = k'' C_A \quad (\text{ii})$$

At steady state the flow rate to the surface is equal to the reaction rate at the surface (steps in series). So

$$r''_{A1} = r''_{A2}$$

and from Eqs. (i) and (ii)

$$k_l (C_{Al} - C_{As}) = k'' C_{As}$$

from which

$$C_{As} = \frac{k_l}{k_l + k''} C_{Al} \quad (\text{iii})$$

Replacing Eq. (iii) into either Eq. (i) or Eq. (ii) then eliminates  $C_{As}$  which cannot be measured, giving

$$r''_{A1} = r''_{A2} = r''_A = -\frac{1}{\frac{1}{k_l} + \frac{1}{k''}} C_{Al} = -k_{\text{overall}} C_{Al}, \quad \left[ \frac{\text{mol}}{\text{m}^2 \cdot \text{s}} \right]$$

**Comment** This result shows that  $1/k_l$  and  $1/k''$  are additive resistances. It so happens that the addition of resistances to obtain an overall resistance is permissible only when the rate is a linear function of the driving force and when the processes occur in series.

#### EXAMPLE 17.4 OVERALL RATE FOR A NONLINEAR PROCESS

Repeat Example 17.3 with just one change: let the reaction step be second order with respect to A, or

$$r''_{A2} = -k'' C_A^2$$

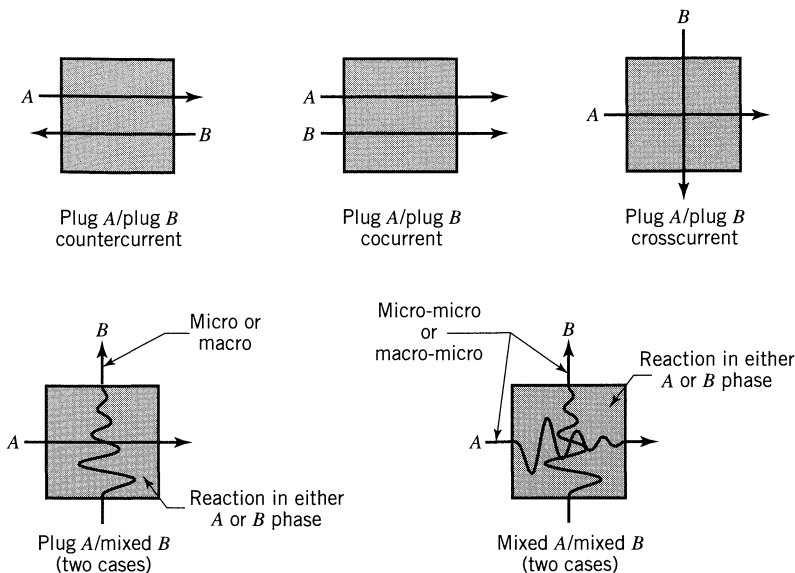
#### SOLUTION

Combining the reaction steps to eliminate  $C_{As}$ , as was done in Example 17.3, is now not so simple, and gives

$$-r''_A = -r''_{A1} = -r''_{A2} = \frac{k_l}{2k''} (2k'' C_{Al} + k_l - \sqrt{k_l^2 + 4k''k_l C_{Al}}), \quad \left[ \frac{\text{mol}}{\text{m}^2 \cdot \text{s}} \right]$$

### Contacting Patterns for Two-Phase Systems

There are many ways that two phases can be contacted, and for each the design equation will be unique. Design equations for these ideal flow patterns may be developed without too much difficulty. However, when real flow deviates considerably from these, we can do one of two things: we may develop models to mirror actual flow closely, or we may calculate performance with ideal patterns which “bracket” actual flow. Fortunately, most real reactors for heterogeneous systems can be satisfactorily approximated by one of the five ideal flow patterns of Fig. 17.1. Notable exceptions are the reactions which take place in fluidized beds. There special models must be developed.



**Figure 17.1.** Ideal contacting patterns for two flowing fluids.

## Final Thoughts on Flow Modeling

In reactor design and scale-up, it is essential to select a flow model which reasonably represents our setup. Too often we put too little thought here, carelessly picking a nonrepresentative model and then doing computer calculations to the  $n$ th degree of accuracy. And then we are surprised when design and scale-up do not agree with our predictions. A simple reasonable model is much better than a precise and detailed model which does not represent the contacting. Often the choice of a good flow model and the knowledge of how the flow pattern changes with scale-up spells the difference between success and failure.

The preceding thoughts guide us in our approach to heterogeneous reaction, which we will consider in the rest of the book.

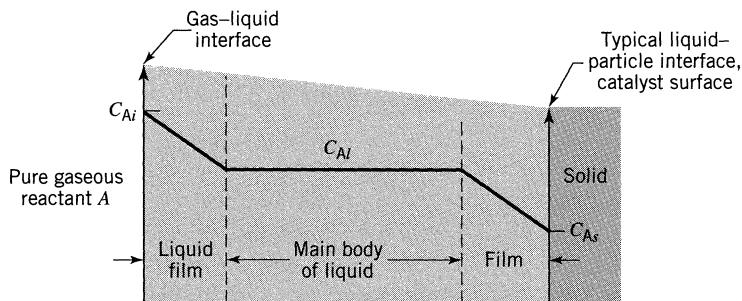
## PROBLEMS

- 17.1.** Gaseous reactant A diffuses through a gas film and reacts on the surface of a solid according to a reversible first-order rate,

$$-r_A'' = k''(C_{As} - C_{Ae})$$

where  $C_{Ae}$  is the concentration of A in equilibrium with the solid surface. Develop an expression for the rate of reaction of A accounting for both the mass transfer and reaction steps.

- 17.2. Example 17.4 gives the final rate expression for film mass transfer followed by a second-order rate expression for reaction on a plane surface. Please derive this expression and show that it is correct.
- 17.3. In slurry reactors, pure reactant gas is bubbled through liquid containing suspended catalyst particles. Let us view these kinetics in terms of the film theory, as shown in Fig. P17.3. Thus, to reach the surface of the solid, the



**Figure P17.3**

reactant which enters the liquid must diffuse through the liquid film into the main body of liquid, and then through the film surrounding the catalyst particle. At the surface of the particle, reactant yields product according to first-order kinetics. Derive an expression for the rate of reaction in terms of these resistances.

# Chapter 18

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## Solid Catalyzed Reactions

With many reactions, the rates are affected by materials which are neither reactants nor products. Such materials called *catalysts* can speed a reaction by a factor of a million or much more, or they may slow a reaction (negative catalyst).

There are two broad classes of catalysts: those that operate at close to ambient temperature with biochemical systems, and the man-made catalysts that operate at high temperature.

The biochemical catalysts, called *enzymes*, are found everywhere in the biochemical world and in living creatures, and without their action I doubt that life could exist at all. In addition, in our bodies hundreds of different enzymes and other catalysts are busily at work all the time, keeping us alive. We treat these catalysts in Chapter 27.

The man-made catalysts, mostly solids, usually aim to cause the high-temperature rupture or synthesis of materials. These reactions play an important role in many industrial processes, such as the production of methanol, sulfuric acid, ammonia, and various petrochemicals, polymers, paints, and plastics. It is estimated that well over 50% of all the chemical products produced today are made with the use of catalysts. These materials, their reaction rates, and the reactors that use them are the concern of this chapter and Chapters 19–22.

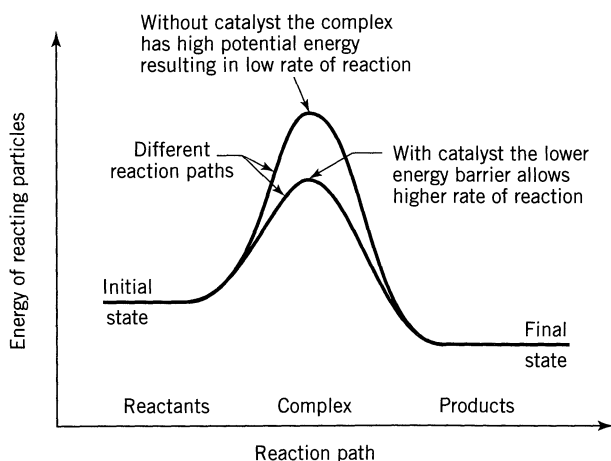
Consider petroleum. Since this consists of a mixture of many compounds, primarily hydrocarbons, its treatment under extreme conditions will cause a variety of changes to occur simultaneously, producing a spectrum of compounds, some desirable, others undesirable. Although a catalyst can easily speed the rate of reactions a thousandfold or a millionfold, still, when a variety of reactions are encountered, the most important characteristic of a catalyst is its *selectivity*. By this we mean that it only changes the rates of certain reactions, often a single reaction, leaving the rest unaffected. Thus, in the presence of an appropriate catalyst, products containing predominantly the materials desired can be obtained from a given feed.

The following are some general observations.

1. The selection of a catalyst to promote a reaction is not well understood; therefore, in practice extensive trial and error may be needed to produce a satisfactory catalyst.



2. Duplication of the chemical constitution of a good catalyst is no guarantee that the solid produced will have any catalytic activity. This observation suggests that it is the physical or crystalline structure which somehow imparts catalytic activity to a material. This view is strengthened by the fact that heating a catalyst above a certain critical temperature may cause it to lose its activity, often permanently. Thus present research on catalysts is strongly centered on the surface structure of solids.
3. To explain the action of catalysts, it is thought that reactant molecules are somehow changed, energized, or affected to form intermediates in the regions close to the catalyst surface. Various theories have been proposed to explain the details of this action. In one theory, the intermediate is viewed as an association of a reactant molecule with a region of the surface; in other words, the molecules are somehow attached to the surface. In another theory, molecules are thought to move down into the atmosphere close to the surface and be under the influence of surface forces. In this view the molecules are still mobile but are nevertheless modified. In still a third theory, it is thought that an active complex, a free radical, is formed at the surface of the catalyst. This free radical then moves back into the main gas stream, triggering a chain of reactions with fresh molecules before being finally destroyed. In contrast with the first two theories, which consider the reaction to occur in the vicinity of the surface, this theory views the catalyst surface simply as a generator of free radicals, with the reaction occurring in the main body of the gas.
4. In terms of the transition-state theory, the catalyst reduces the potential energy barrier over which the reactants must pass to form products. This lowering in energy barrier is shown in Fig. 18.1.
5. Though a catalyst may speed up a reaction, it never determines the equilibrium or endpoint of a reaction. This is governed by thermodynamics alone. Thus with or without a catalyst the equilibrium constant for the reaction is always the same.



**Figure 18.1** Representation of the action of a catalyst.

6. Since the solid surface is responsible for catalytic activity, a large readily accessible surface in easily handled materials is desirable. By a variety of methods, active surface areas the size of football fields can be obtained per cubic centimeter of catalyst.

Though there are many problems related to solid catalysts, we consider only those which are related to the development of kinetic rate equations needed in design. We simply assume that we have a catalyst available to promote a specific reaction. We wish to evaluate the kinetic behavior of reactants in the presence of this material and then use this information for design.

The Spectrum of Kinetic Regimes

Consider a porous catalyst particle bathed by reactant A. The rate of reaction of A for the particle as a whole may depend on:

- ① Surface kinetics, or what happens at the surfaces, interior or exterior of the particle. This may involve the adsorption of reactant A onto the surface, reaction on the surface, or desorption of product back into the gas stream.
- ② Pore diffusion resistance which may cause the interior of the particle to be starved for reactant.
- ③ Particle  $\Delta T$  or temperature gradients within the particle. This is caused by large heat release or absorption during reaction.
- ④ Film  $\Delta T$  between the outer surface of the particle and the main gas stream. For example, the particle may be uniform in temperature throughout but hotter than the surrounding gas.
- ⑤ Film diffusion resistance or concentration gradients across the gas film surrounding the particle.

For gas/porous catalyst systems slow reactions are influenced by ① alone, in faster reactions ② intrudes to slow the rate, then ③ and/or ④ enter the picture, ⑤ unlikely limits the overall rate. In liquid systems the order in which these effects intrude is ①, ②, ⑤, and rarely ③ and/or ④.

In different areas of application (outside of catalytic kinetics too) different combinations of these five factors enter the picture. Table 18.1 shows what we normally encounter.

Table 18.1 Factors which Influence the Rate of Reaction of Particles

Rate Influencing Factor	Porous Catalyst Particle	Catalyst Coated Surface	Burning of a Droplet of Fuel	Cells and Simple Living Creatures
① Surface reaction	Yes	Yes	No	Yes
② Pore diffusion	Yes	No	No	Maybe
③ Particle $\Delta T$	Not too likely	No	No	No
④ Film $\Delta T$	Sometimes	Rare	All important	No
⑤ Film mass transfer	No	Yes	All important	Could be

Although here we introduce all the phenomena which affect the rate, the real world is never so exciting that we have to concern ourselves with all five factors at any one time. In fact, in the majority of situations with porous catalyst particles we only have to consider factors ① and ②.

Here let us treat factors ① and ②; then ③ and ④ briefly.

## 18.1 THE RATE EQUATION FOR SURFACE KINETICS

Because of the great industrial importance of catalytic reactions, considerable effort has been spent in developing theories from which kinetic equations can rationally be developed. The most useful for our purposes supposes that the reaction takes place on an active site on the surface of the catalyst. Thus three steps are viewed to occur successively at the surface.

**Step 1.** A molecule is adsorbed onto the surface and is attached to an active site.

**Step 2.** It then reacts either with another molecule on an adjacent site (dual-site mechanism), with one coming from the main gas stream (single-site mechanism), or it simply decomposes while on the site (single-site mechanism).

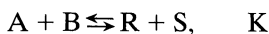
**Step 3.** Products are desorbed from the surface, which then frees the site.

In addition, all species of molecules, free reactants, and free products as well as site-attached reactants, intermediates, and products taking part in these three processes are assumed to be in equilibrium.

Rate expressions derived from various postulated mechanisms are all of the form

$$\text{rate of reaction} = \frac{(\text{kinetic term})(\text{driving force or displacement from equilibrium})}{(\text{resistance term})} \quad (1)$$

For example, for the reaction



occurring in the presence of inert carrier material U, the rate expression when adsorption of A controls is

$$-r_A'' = \frac{k(p_A - p_R p_S / K p_B)}{(1 + K_A p_R p_S / K p_B + K_B p_B + K_R p_R + K_S p_S + K_U p_U)^2}$$

When reaction between adjacent site-attached molecules of A and B controls, the rate expression is

$$-r_A'' = \frac{k(p_A p_B - p_R p_S / K)}{(1 + K_A p_A + K_B p_B + K_R p_R + K_S p_S + K_U p_U)^2}$$

whereas for desorption of R, controlling it becomes

$$-r_A'' = \frac{k(p_A p_B / p_S - p_R / K)}{1 + K_A p_A + K_B p_B + K K_R p_A p_B / p_S + K_S p_S + K_U p_U}$$

Each detailed mechanism of reaction with its controlling factor has its corresponding rate equation, involving anywhere from three to seven arbitrary constants, the  $K$  values. For reasons to be made clear, we do not intend to use equations such as these. Consequently, we do not go into their derivations. These are given by Hougen and Watson (1947), Corrigan (1954, 1955), Walas (1959), and elsewhere.

Now, in terms of the contact time or space time, most catalytic conversion data can be fitted adequately by relatively simple first- or  $n$ th-order rate expressions (see Prater and Lago, 1956). Since this is so, why should we concern ourselves with selecting one of a host of rather complicated rate expressions which satisfactorily fits the data?

The following discussion summarizes the arguments for and against the use of simple empirical kinetic equations.

**Truth and Predictability.** The strongest argument in favor of searching for the actual mechanism is that if we find one which we think represents what truly occurs, extrapolation to new and more favorable operating conditions is much more safely done. This is a powerful argument. Other arguments, such as augmenting knowledge of the mechanism of catalysis with the final goal of producing better catalysts in the future, do not concern a design engineer who has a specific catalyst at hand.

**Problems of Finding the Mechanism.** To prove that we have such a mechanism we must show that the family of curves representing the rate equation type of the favored mechanism fits the data *so much better than the other families that all the others can be rejected*. With the large number of parameters (three to seven) that can be chosen arbitrarily for each rate-controlling mechanism, a very extensive experimental program is required, using very precise and reproducible data, which in itself is quite a problem. We should bear in mind that it is not good enough to select the mechanism that well fits—or even best fits—the data. Difference in fit may be explainable entirely in terms of experimental error. In statistical terms these differences may not be “significant.” Unfortunately, if a number of alternative mechanisms fit the data equally well, we must recognize that the equation selected can only be considered to be one of good fit, not one that represents reality. With this admitted, there is no reason why we should not use the simplest and easiest-to-handle equation of satisfactory fit. In fact, unless there are good positive reasons for using the more complicated of two equations, we should always select the simpler of the two if both fit the data equally well. The statistical analyses and comments by Chou (1958) on the codimer example in Hougen and Watson (1947) in which 18 mechanisms were examined illustrate the difficulty in finding the correct mechanism from kinetic data, and show that even in the most carefully conducted programs of experimentation the magnitude of the experimental error will very likely mask the differences predicted by the various mechanisms.

Thus it is hardly ever possible to determine with reasonable confidence which is the correct mechanism.

**Problems of Combining Resistances.** Suppose that we have found the correct mechanism and resultant rate equation for the surface phenomenon. Combining this step with any of the other resistance steps, such as pore or film diffusion, becomes rather impractical. When this has to be done, it is best to replace the multiconstant rate equation by an equivalent first-order expression, which can then be combined with other reaction steps to yield an overall rate expression.

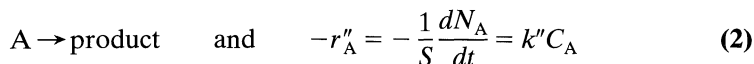
**Summary on Surface Kinetics.** From this discussion we conclude that it is good enough to use the simplest available correlating rate expression, hence first-order or  $n$ th-order kinetics, to represent the surface reaction.

For additional comments questioning the validity of the active-site approach, suggesting forms of kinetic equations to be used in reactor design, and suggesting what is the real utility of the active site theory, see the opposing points of view presented by Weller (1956) and Boudart (1956).

## 18.2 PORE DIFFUSION RESISTANCE COMBINED WITH SURFACE KINETICS

### Single Cylindrical Pore, First-Order Reaction

First consider a single cylindrical pore of length  $L$ , with reactant A diffusing into the pore, and reacting on the surface by a first-order reaction



taking place at the walls of the pore, and product diffusing out of the pore, as shown in Fig. 18.2. This simple model will later be extended.

The flow of materials into and out of any section of pore is shown in detail in Fig. 18.3. At steady state a material balance for reactant A for this elementary section gives

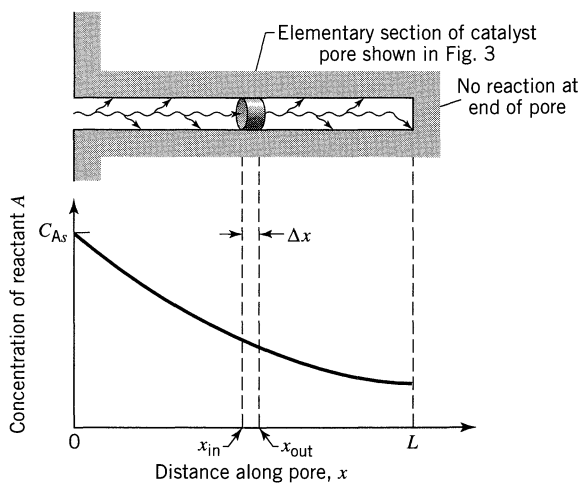
$$\text{output} - \text{input} + \text{disappearance by reaction} = 0 \quad (4.1)$$

or with the quantities shown in Fig. 18.3,

$$-\pi r^2 \mathcal{D} \left( \frac{dC_A}{dx} \right)_{\text{out}} + \pi r^2 \mathcal{D} \left( \frac{dC_A}{dx} \right)_{\text{in}} + k'' C_A (2\pi r \Delta x) = 0$$

Rearranging gives

$$\frac{\left( \frac{dC_A}{dx} \right)_{\text{out}} - \left( \frac{dC_A}{dx} \right)_{\text{in}}}{\Delta x} - \frac{2k''}{\mathcal{D}r} C_A = 0$$

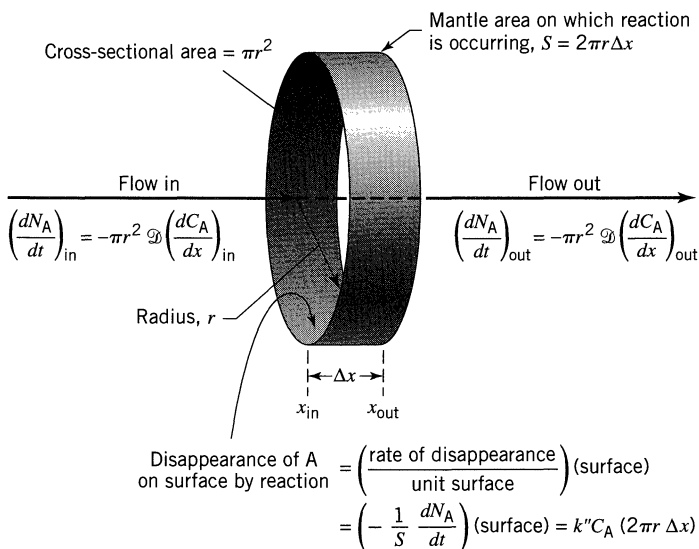


**Figure 18.2** Representation of a cylindrical catalyst pore.

and taking the limit as  $\Delta x$  approaches zero (see the equation above Eq. 13.18a), we obtain

$$\frac{d^2 C_A}{dx^2} - \frac{2k''}{\mathcal{D}r} C_A = 0 \quad (3)$$

Note that the first-order chemical reaction is expressed in terms of unit surface area of the wall of the catalyst pore; hence  $k''$  has unit of length per time (see



**Figure 18.3** Setting up the material balance for the elementary slice of catalyst pore.

Eq. 1.4). In general, the interrelation between rate constants on different bases is given by

$$kV = k'W = k''S \quad (4)$$

Hence for the cylindrical catalyst pore

$$k = k'' \left( \frac{\text{surface}}{\text{volume}} \right) = k'' \left( \frac{2\pi rL}{\pi r^2 L} \right) = \frac{2k''}{r} \quad (5)$$

Thus in terms of volumetric units Eq. 3 becomes

$$\frac{d^2 C_A}{dx^2} - \frac{k}{\mathcal{D}} C_A = 0 \quad (6)$$

This is a frequently met linear differential equation whose general solution is

$$C_A = M_1 e^{mx} + M_2 e^{-mx} \quad (7)$$

where

$$m = \sqrt{\frac{k}{\mathcal{D}}} = \sqrt{\frac{2k''}{\mathcal{D}r}}$$

and where  $M_1$  and  $M_2$  are constants. It is in the evaluation of these constants that we restrict the solution to this system alone. We do this by specifying what is particular about the model selected, a procedure which requires a clear picture of what the model is supposed to represent. These specifications are called the boundary conditions of the problem. Since two constants are to be evaluated, we must find and specify two boundary conditions. Examining the physical limits of the conceptual pore, we find that the following statements can always be made. First, at the pore entrance

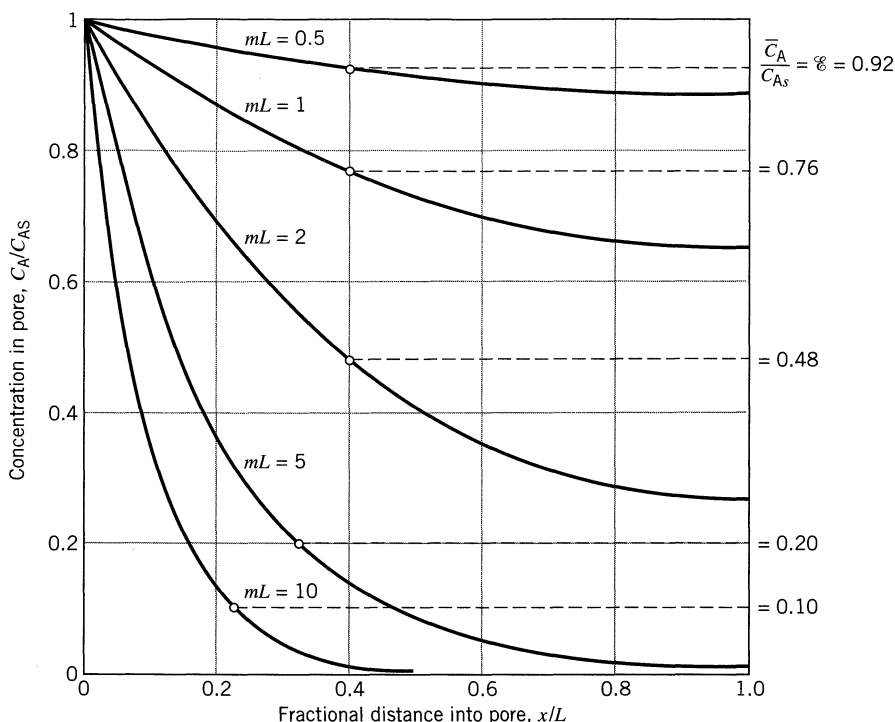
$$C_A = C_{As}, \quad \text{at} \quad x = 0 \quad (8a)$$

Second, because there is no flux or movement of material through the interior end of the pore

$$\frac{dC_A}{dx} = 0, \quad \text{at} \quad x = L \quad (8b)$$

With the appropriate mathematical manipulations of Eqs. 7 and 8 we then obtain

$$M_1 = \frac{C_{As} e^{-mL}}{e^{mL} + e^{-mL}}, \quad M_2 = \frac{C_{As} e^{mL}}{e^{mL} + e^{-mL}} \quad (9)$$



**Figure 18.4** Distribution and average value of reactant concentration within a catalyst pore as a function of the parameter  $mL = L\sqrt{k/\mathcal{D}}$

Hence the concentration of reactant within the pore is

$$\frac{C_A}{C_{A_s}} = \frac{e^{m(L-x)} + e^{-m(L-x)}}{e^{mL} + e^{-mL}} = \frac{\cosh m(L-x)}{\cosh mL} \quad (10)$$

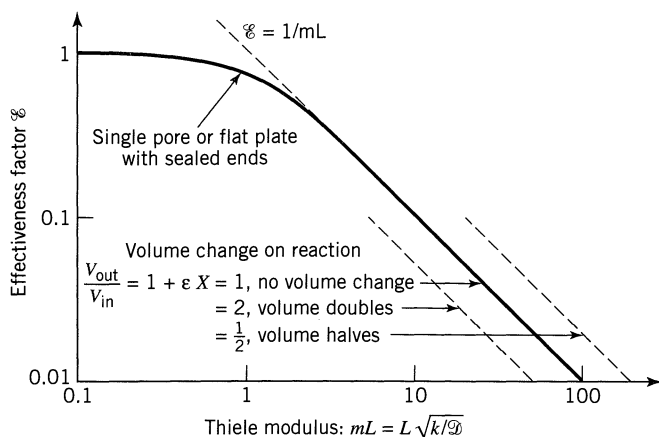
This progressive drop in concentration on moving into the pore is shown in Fig. 18.4, and this is seen to be dependent on the dimensionless quantity  $mL$ , or  $M_T$ , called the *Thiele modulus*.

To measure how much the reaction rate is lowered because of the resistance to pore diffusion, define the quantity  $\mathcal{E}$  called the effectiveness factor as follows:

$$\begin{aligned} \text{Effectiveness factor, } \mathcal{E} &= \frac{(\text{actual mean reaction rate within pore})}{(\text{rate if not slowed by pore diffusion})} \\ &= \frac{\bar{r}_A, \text{ with diffusion}}{r_A, \text{ without diffusion resistance}} \end{aligned} \quad (11)$$

In particular, for first-order reactions  $\mathcal{E} = C_A/C_{A_s}$  because the rate is proportional to the concentration. Evaluating the average rate in the pore from Eq. 10 gives





**Figure 18.5** The effectiveness factor as a function of the parameter  $mL$  or  $M_T$ , called the Thiele modulus, prepared from Aris (1957) and Thiele (1939).

the relationship

$$\mathcal{E}_{\text{first order}} = \frac{\bar{C}_A}{C_{As}} = \frac{\tanh mL}{mL} \quad (12)$$

which is shown by the solid line in Fig. 5. With this figure we can tell whether pore diffusion modifies the rate of reaction, and inspection shows that this depends on whether  $mL$  is large or small.

For small  $mL$ , or  $mL < 0.4$ , we see that  $\mathcal{E} \cong 1$ , the concentration of reactant does not drop appreciably within the pore; thus pore diffusion offers negligible resistance. This can also be verified by noting that a small value for  $mL = L\sqrt{k/D}$  means either a short pore, slow reaction, or rapid diffusion, all three factors tending to lower the resistance to diffusion.

For large  $mL$ , or  $mL > 4$ , we find that  $\mathcal{E} = 1/mL$ , the reactant concentration drops rapidly to zero on moving into the pore, hence diffusion strongly influences the rate of reaction. We call this the regime of *strong pore resistance*.

## 18.3 POROUS CATALYST PARTICLES

The results for a single pore can approximate the behavior of particles of various shapes—spheres, cylinders, etc. For these systems the following apply.

1. **Use of the proper diffusion coefficient.** Replace the molecular diffusion coefficient  $\mathcal{D}$  by the effective diffusion coefficient of fluid in the porous structure. Representative  $\mathcal{D}_e$  values for gases and liquids in porous solids are given by Weisz (1959).
2. **Proper measure of particle size.** To find the effective distance penetrated

by gas to get to all the interior surfaces we define a characteristic size of particle

$$L \left\{ \begin{array}{l} = \left( \frac{\text{volume of particle}}{\text{exterior surface available for reactant penetration}} \right), \text{ any particle shape} \\ = \frac{\text{thickness}}{2}, \text{ for flat plates} \\ = \frac{R}{2}, \text{ for cylinders} \\ = \frac{R}{3}, \text{ for spheres} \end{array} \right. \quad (13)$$

**3. Measures of reactions rates.** In catalytic systems the rate of reaction can be expressed in one of many equivalent ways. For example, for first-order kinetics

$$\text{Based on volume of voids in the reactor} \quad -r_A = -\frac{1}{V} \frac{dN_A}{dt} = kC_A, \left[ \frac{\text{mols reacted}}{\text{m}^3 \text{ voids} \cdot \text{s}} \right] \quad (14)$$

$$\text{Based on weight of catalyst pellets} \quad -r'_A = -\frac{1}{W} \frac{dN_A}{dt} = k'C_A, \left[ \frac{\text{mol reacted}}{\text{kg cat} \cdot \text{s}} \right] \quad (15)$$

$$\text{Based on catalyst surface} \quad -r''_A = -\frac{1}{S} \frac{dN_A}{dt} = k''C_A, \left[ \frac{\text{mol reacted}}{\text{m}^2 \text{ cat. surf.} \cdot \text{s}} \right] \quad (16)$$

$$\text{Based on volume of catalyst pellets} \quad -r'''_A = -\frac{1}{V_p} \frac{dN_A}{dt} = k'''C_A, \left[ \frac{\text{mol reacted}}{\text{m}^3 \text{ solid} \cdot \text{s}} \right] \quad (17)$$

$$\text{Based on total reactor volume} \quad -r'''_A = -\frac{1}{V_r} \frac{dN_A}{dt} = k'''C_A, \left[ \frac{\text{mol reacted}}{\text{m}^3 \text{ reactor} \cdot \text{s}} \right] \quad (18)$$


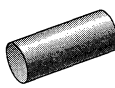

Use whichever definition is convenient. However, for porous catalyst particles rates based on unit mass and on unit volume of particles,  $r'$  and  $r'''$  are the useful measures. Hence for  $n$ th order reactions

$$\begin{aligned} -r'_A \left[ \frac{\text{mol A}}{(\text{kg cat}) \cdot \text{s}} \right] &= k' C_A^n \quad \text{where} \quad k' = \left[ \frac{(\text{m}^3 \text{ gas})^n}{(\text{mol A})^{n-1} (\text{kg cat}) \cdot \text{s}} \right] \\ -r'''_A \left[ \frac{\text{mol A}}{(\text{m}^3 \text{ cat}) \cdot \text{s}} \right] &= k''' C_A^n \quad \text{where} \quad k''' = \left[ \frac{(\text{m}^3 \text{ gas})^n}{(\text{mol A})^{n-1} (\text{m}^3 \text{ cat}) \cdot \text{s}} \right] \end{aligned} \quad (19)$$

**4.** In a manner similar to what was done for a single cylindrical pore, Thiele

(1939) and Aris (1957) related  $\mathcal{E}$  with  $M_T$  for the various particle shapes as follows:

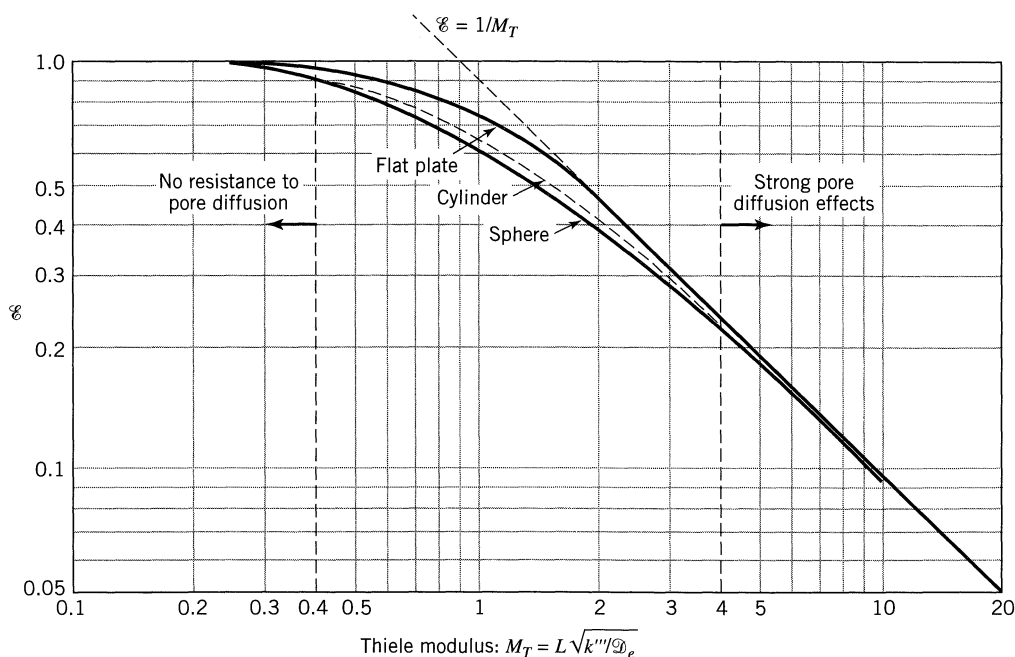
$$\begin{array}{lcl}
 \left. \begin{array}{l} A \rightarrow R \\ -r_A''' = k''' C_A \mathcal{E} \\ \text{mol/m}^3 \text{ cat} \cdot \text{s} \end{array} \right\} \dots \text{where } \mathcal{E} = \begin{cases} = \frac{1}{M_T} \cdot \tanh M_T & \text{(20)} \\ = \frac{1}{M_T} \cdot \frac{I_1(2M_T)}{I_0(2M_T)} & \text{(21)} \\ = \frac{1}{M_T} \cdot \left( \frac{1}{\tanh 3M_T} - \frac{1}{3M_T} \right) & \text{(22)} \end{cases}
 \end{array}$$

 (20)  
 (21)  
 (22)

where

$$M_T = L \sqrt{k''' / \mathcal{D}_e} \quad (23)$$

These relationships are shown in Fig. 18.6. If you know  $\mathcal{D}_e$ ,  $k'''$ , and  $L$  you can find the reaction rate from  $M_T$  and Fig. 18.6. However, what if you want to evaluate  $k'''$  from an experiment in which you measure a rate which could have been slowed by diffusional resistance, but which you are unsure of?



**Figure 18.6** Effectiveness factor versus  $M_T$  for porous particles of various shapes.

5. **Finding pore resistance effects from experiment.** Here we have a simple trick to help us. Define another modulus which only includes observable and measurable quantities. This is known as the Wagner-Weisz-Wheeler modulus  $M_W$  (lucky for us that the three researchers who first dealt with this problem had last names all starting with the same letter).

$$M_W = M_T^2 \mathcal{E} = L^2 \frac{(-r_A'''/C_A)_{\text{obs}}}{\mathcal{D}_e} \quad (24)$$

We shall call this the Wagner modulus.

6. **Pore resistance limits.** When reactant fully penetrates the particle and bathes all its surfaces, then the particle is in the diffusion free regime. This occurs when  $M_T < 0.4$  or  $M_W < 0.15$ .

At the other extreme when the center of the particle is starved for reactant and is unused then the particle is in the strong pore resistance regime. This occurs when  $M_T > 4$  or  $M_W > 4$ .

Figures 18.6 and 18.7 show these limits.

7. **Particles of Different Sizes.** Comparing the behavior of particles of size  $R_1$  and  $R_2$  we find in the diffusion-free regime

$$\frac{r'_{A1}}{r'_{A2}} = \frac{\mathcal{E}_1 k' C_A}{\mathcal{E}_2 k' C_A} = \frac{\mathcal{E}_1}{\mathcal{E}_2} = 1$$

In the regime of strong diffusion resistance

$$\frac{r'_{A1}}{r'_{A2}} = \frac{\mathcal{E}_1}{\mathcal{E}_2} = \frac{M_{T2}}{M_{T1}} = \frac{R_2}{R_1} \quad (25)$$

Thus the rate varies inversely proportional to the particle size.

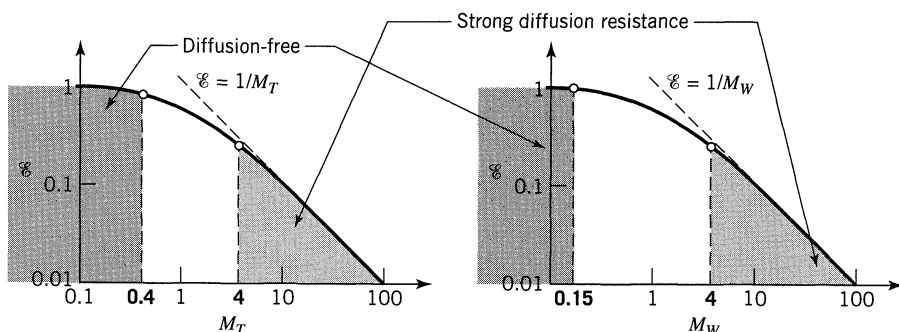


Figure 18.7 Shows the limits for negligible and for strong pore diffusion resistance.

## Extensions

There are many extensions to this basic treatment. Here we just mention a few.

**Mixture of Particles of Various Shapes and Sizes.** For a catalyst bed consisting of a mixture of particles of various shapes and sizes Aris (1957) showed that the correct mean effectiveness factor is

$$\bar{\mathcal{E}} = \mathcal{E}_1 f'_1 + \mathcal{E}_2 f'_2 + \dots$$

where  $f'_1, f'_2, \dots$  are the volume fractions of particles of sizes 1, 2,  $\dots$  in the mixture.

**Molar Volume Change.** With decrease in fluid density (expansion) during reaction the increased outflow of molecules from the pores makes it harder for reactants to diffuse into the pore, hence lowering  $\mathcal{E}$ . On the other hand, volumetric contraction results in a net molar flow into the pore, hence increasing  $\mathcal{E}$ . For a first-order reaction Thiele (1939) found that this flow simply shifted the  $\mathcal{E}$  versus  $M_T$  curve as shown in Fig. 18.5.

**Arbitrary Reaction Kinetics.** If the Thiele modulus is generalized as follows [see Froment and Bischoff (1962)]

$$M_T = \frac{(-r'''_{As})L}{\left[2\mathcal{D}_e \int_{C_{Ae}}^{C_{As}} (-r'''_A) dC_A\right]^{1/2}}, \quad C_{Ae} = \left(\begin{array}{c} \text{equilibrium} \\ \text{concentration} \end{array}\right) \quad (26)$$

then the  $\mathcal{E}$  versus  $M_T$  curves for all forms of rate equation closely follow the curve for the first-order reaction. This generalized modulus becomes

for first-order reversible reactions

$$M_T = L \sqrt{\frac{k'''}{\mathcal{D}_e X_{Ae}}} \quad (27)$$

for  $n$ th-order irreversible reactions

$$M_T = L \sqrt{\frac{(n+1)k'''C_{As}^{n-1}}{2\mathcal{D}_e}} \quad (28)$$

$n$ th-order reactions behave in an unexpected way in the region of strong pore resistance. Combining the  $n$ th-order rate with the generalized modulus of Eq.

28 we obtain

$$\begin{aligned} -r_A''' &= k''' C_{As}^n \mathcal{C} = k''' C_{As}^n \cdot \frac{1}{M_T} = k''' C_{As}^n \cdot \frac{1}{L} \sqrt{\frac{2\mathcal{D}_e}{(n+1)k''' C_{As}^{n-1}}} \\ &= \left( \frac{2}{n+1} \cdot \frac{k''' \mathcal{D}_e}{L^2} \right)^{1/2} C_{As}^{(n+1)/2} \end{aligned} \quad (29)$$

Thus, in the regime of strong pore diffusion, an  $n$ th-order reaction behaves like a reaction of order  $(n+1)/2$  or

0 order becomes  $1/2$  order

1st order remains 1st order

2nd order becomes 1.5 order

3rd order becomes 2nd order

(30)

In addition the temperature dependency of reactions is affected by strong pore resistance. From Eq. 29 the observed rate constant for  $n$ th-order reactions is

$$k_{\text{obs}}''' = \left( \frac{2}{n+1} \cdot \frac{k''' \mathcal{D}_e}{L^2} \right)^{1/2}$$

Taking logarithms and differentiating with respect to temperature and noting that both the reaction rate and to a lesser extent the diffusional process are temperature-dependent gives

$$\frac{d(\ln k_{\text{obs}}''')}{dT} = \frac{1}{2} \left[ \frac{d(\ln k''')}{dT} + \frac{d(\ln \mathcal{D}_e)}{dT} \right] \quad (31)$$

With Arrhenius temperature dependencies for both reaction and diffusion we have

$$k''' = k_0''' e^{-E_{\text{true}}/RT} \quad \text{and} \quad \mathcal{D}_e = \mathcal{D}_{e0} e^{-E_{\text{diff}}/RT}$$

and replacing in Eq. 31 gives

$$\mathbf{E}_{\text{obs}} = \frac{\mathbf{E}_{\text{true}} + \mathbf{E}_{\text{diff}}}{2} \quad (32)$$

Since the activation energy for gas-phase reactions is normally rather high, say  $80 \sim 240$  kJ, while that for diffusion is small (about 5 kJ at room temperature or 15 kJ at  $1000^\circ\text{C}$ ), we can write approximately

$$\mathbf{E}_{\text{obs}} \cong \frac{\mathbf{E}_{\text{true}}}{2} \quad (33)$$

These results show that the observed activation energy for reactions influenced by strong pore resistance is approximately one-half the true activation energy.

### Summary—Diffusion Resistance in Pores

For first-order surface reaction we summarize our finding in compact form in Eq. 34.

$$\begin{array}{l}
 \text{rate without any diffusion effects} \quad = 1 \text{ for no diffusion resistance} \\
 \text{this flat plate expression is a good approximation for all particle shapes} \\
 \text{... with ...} \quad \mathcal{E} = \frac{\tanh M_T}{M_T} \\
 -r_A''' = k_A''' C_{As} \mathcal{E} \\
 \text{characteristic length} \quad M_T = L \sqrt{\frac{k_A'''}{\mathcal{D}_e}} \\
 \text{effective diffusion coefficient in porous solids; m}^2 \text{ gas/m solid-s} \\
 \text{where} \quad \mathcal{E} = \text{effectiveness factor, a fudge factor which varies between 0 and 1, and which accounts for the resistance to pore diffusion} \\
 \text{... and also ...} \quad M_W = M_T^2 \mathcal{E} = \frac{L^2 (-r_{A, \text{obs}}''')}{C_{A, \text{obs}} \mathcal{D}_e} \\
 M_T = \text{Thiele modulus, useful for predicting reactor behavior from known kinetic information, thus known } k_A''' \\
 M_W = \text{Weisz modulus, useful for interpreting experiments since it only includes observables}
 \end{array} \quad (34)$$

To find how pore resistance influences the rate evaluate  $M_T$  or  $M_W$ , then find  $\mathcal{E}$  from the above equations or figures, and insert  $\mathcal{E}$  into the rate equation.

Desirable processing range: Fine solids are free of pore diffusion resistance but are difficult to use (imagine the pressure drop of a packed bed of face powder). On the other hand a bed of large particles have a small  $\Delta p$  but are liable to be in the regime of strong pore diffusion where much of the pellets' interior is unused.

For most effective operations what we want is to use the largest particle size which is still free of diffusional resistance or

$$M_T \cong 0.4 \quad \text{or} \quad M_W \cong 0.15 \quad (35)$$

## 18.4 HEAT EFFECTS DURING REACTION

When reaction is so fast that the heat released (or absorbed) in the pellet cannot be removed rapidly enough to keep the pellet close to the temperature of the fluid, then nonisothermal effects intrude. In such a situation two different kinds of temperature effects may be encountered:

Within-particle  $\Delta T$ . There may be a temperature variation within the pellet.

Film  $\Delta T$ . The pellet may be hotter (or colder) than the surrounding fluid.

For exothermic reaction, heat is released and particles are hotter than the surrounding fluid, hence the nonisothermal rate is always higher than the isothermal rate as measured by the bulk stream conditions. However, for endothermic reactions the nonisothermal rate is lower than the isothermal rate because the particle is cooler than the surrounding fluid.

Thus our first conclusion: if the harmful effects of thermal shock, or sintering of the catalyst surface, or drop in selectivity, do not occur with hot particles, then we would encourage nonisothermal behavior in exothermic reactions. On the other hand, we would like to depress such behavior for endothermic reactions.

We next ask which form of nonisothermal effect, if any, may be present. The following simple calculations tell.

For *film*  $\Delta T$  we equate the rate of heat removal through the film with the rate of heat generation by reaction within the pellet. Thus

$$\begin{aligned} Q_{\text{generated}} &= (V_{\text{pellet}})(-r''_{A,\text{obs}})(-\Delta H_r) \\ Q_{\text{removed}} &= hS_{\text{pellet}}(T_g - T_s) \end{aligned}$$

and on combining we find

$$\Delta T_{\text{film}} = (T_g - T_s) = \frac{L(-r''_{A,\text{obs}})(-\Delta H_r)}{h} \quad (36)$$

where  $L$  is the characteristic size of the pellet.

For *within-particle*  $\Delta T$  the simple analysis by Prater (1958) for any particle geometry and kinetics gives the desired expression. Since the temperature and concentration within the particle are represented by the same form of differential equation (Laplace equation) Prater showed that the  $T$  and  $C_A$  distributions must have the same shape; thus at any point in the pellet  $x$

$$-k_{\text{eff}} \frac{dT}{dx} = \mathcal{D}_e \frac{dC_A}{dx} (-\Delta H_r) \quad (37)$$

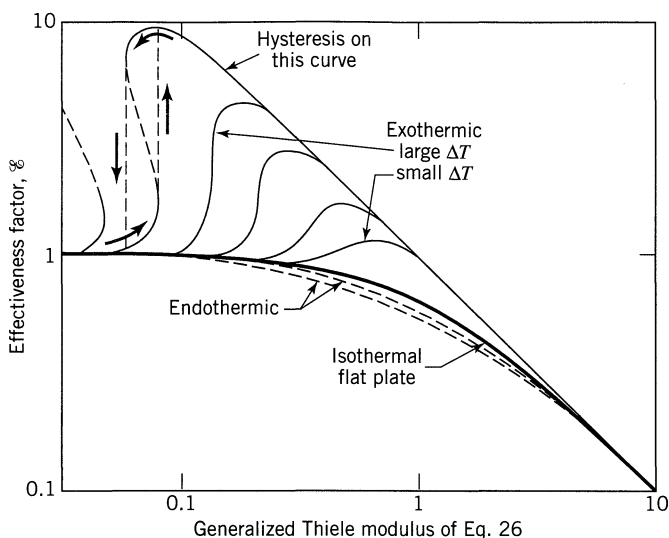
and for the pellet as a whole

$$\Delta T_{\text{particle}} = (T_{\text{center}} - T_s) = \frac{\mathcal{D}_e(C_{A_s} - C_{A,\text{center}})(-\Delta H_r)}{k_{\text{eff}}} \quad (38)$$

where  $k_{\text{eff}}$  is the effective thermal conductivity within the pellet.

For temperature gradients within particles the corresponding nonisothermal effective factor curves have been calculated by Carberry (1961), Weisz and Hicks (1962), and others [see Bischoff (1967) for references]. Figure 18.8 illustrates these curves in dimensionless form, and shows that the shape is very similar to the isothermal curve of Fig. 18.6 with the following exception. For exothermic reactions only, where pore resistance just begins to intrude, the effectiveness factor can become greater than unity. This finding is not unexpected in light of the above discussion.





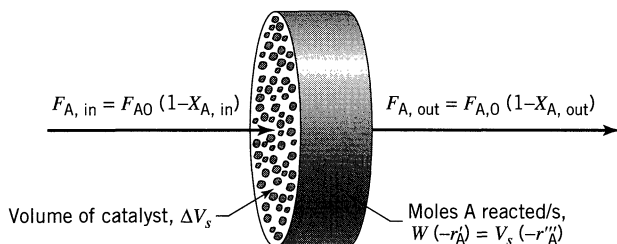
**Figure 18.8** Nonisothermal effectiveness factor curve for temperature variation within the particle. Adapted from Bischoff (1967).

However, for gas-solid systems Hutchings and Carberry (1966) and McGreavy and coworkers (1969, 1970) show that if reaction is fast enough to introduce nonisothermal effects, then the temperature gradient occurs primarily across the gas film, not within the particle. Thus we may expect to find a significant film  $\Delta T$ , before any within-particle  $\Delta T$  becomes evident.

For detailed versions of Fig. 18.8 which show  $\mathcal{E}$  versus  $M_T$  and  $\mathcal{E}$  versus  $M_W$  plus discussion and problems dealing with nonisothermal reactors, see Chapter 22 in Levenspiel (1996).

## 18.5 PERFORMANCE EQUATIONS FOR REACTORS CONTAINING POROUS CATALYST PARTICLES

**For Plug Flow.** Take a thin slice of the PFR. Then following the analysis of Chapter 5 for homogeneous reactions we have the situation shown in Fig. 18.9.



**Figure 18.9** Elementary slice of solid catalyzed plug flow reactor.

At steady state a material balance for reactant A gives

$$\text{input} = \text{output} + \text{accumulation} \cdots \left[ \frac{\text{mol A}}{\text{s}} \right] \quad (39)$$

in symbols

$$F_{A0} - F_{A0} X_{A\text{in}} = F_{A0} - F_{A0} X_{A\text{out}} + (-r'_A) \Delta W$$

In differential form

$$F_{A0} dX_A = (-r'_A) dW = (-r''_A) dV_s \quad (40)$$

Integrating over the whole reactor gives

$$\boxed{\frac{W}{F_{A0}} = \int_0^{X_{A\text{out}}} \frac{dX_A}{-r'_A} \quad \text{or} \quad \frac{V_s}{F_{A0}} = \int_0^{X_{A\text{out}}} \frac{dX_A}{-r''_A}} \quad (41)$$

Note the similarity of this equation with Eq. 5.13 for homogeneous reactions. To bring this analogy closer let

$$\frac{WC_{A0}}{F_{A0}} = \tau' \quad \left[ \frac{\text{kg} \cdot \text{s}}{\text{m}^3} \right] \quad (42)$$

$$\frac{V_s C_{A0}}{F_{A0}} = \tau'' \quad \left[ \frac{\text{m}^3 \cdot \text{s}}{\text{m}^3} \right] \quad (43)$$

We have no name for these two measures but if we wanted to we could call them by the ugly terms *weight-time*, and *volume-time*, respectively. So for first-order catalytic reactions Eq. 41 becomes

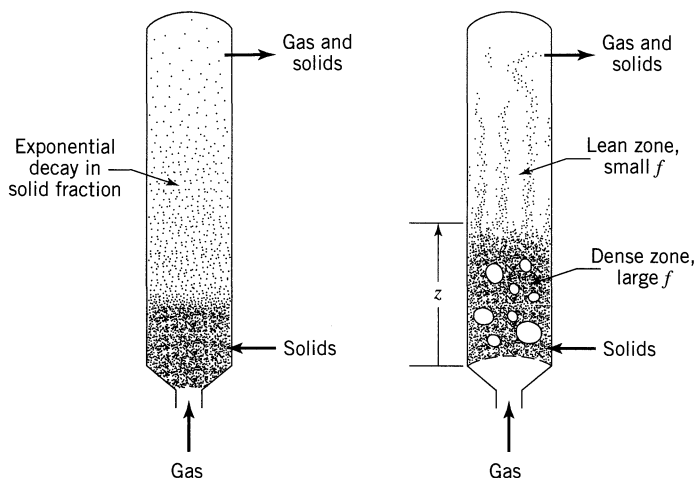
$$k' \tau' = k'' \tau'' = (1 + \varepsilon_A) \ln \frac{1}{1 - X_{A\text{out}}} - \varepsilon_A X_{A\text{out}} \quad [-] \quad (44)$$

**For Mixed Flow.** Here we have, following the analysis of Chapter 5, for any  $\varepsilon_A$  value

$$\boxed{\frac{W}{F_{A0}} = \frac{X_{A\text{out}} - X_{A\text{in}}}{(-r'_{A\text{out}})} \quad \text{or} \quad \frac{V_s}{F_{A0}} = \frac{X_{A\text{out}} - X_{A\text{in}}}{(-r''_{A\text{out}})}} \quad (45)$$

For first-order reactions with  $C_{A\text{in}} = C_{A0}$ , and  $\varepsilon_A \neq 0$

$$k' \tau' = k'' \tau'' = \frac{X_{A\text{out}}(1 + \varepsilon_A X_{A\text{out}})}{1 - X_{A\text{out}}} \quad (46)$$



**Figure 18.10** Catalytic reactors where solid fraction  $f$  varies with height.

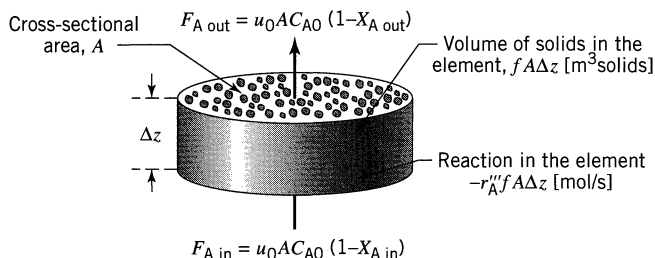
### For a Reactor Containing a Batch of Catalyst and a Batch of Gas

$$\frac{t}{C_{A0}} = \frac{V}{W_s} \int \frac{dX_A}{-r'_A} \quad \text{or} \quad \frac{t}{C_{A0}} = \frac{V}{V_s} \int \frac{dX_A}{-r'''_A} \quad \left[ \frac{\text{m}^3 \cdot \text{s}}{\text{mol}} \right] \quad (47)$$

**Extensions of the Simple Performance Equations.** There are numerous applications of catalytic reactions where the fraction of solids  $f$  varies with height  $z$  in the reactor (see Fig. 18.10).

For these situations the performance equations could more usefully be written differently. With  $u_0$  as the superficial gas velocity (velocity if solids are absent) through the vertical reactor, Fig. 18.11 shows what happens in a thin slice through the reactor. A steady-state material balance gives

$$\text{Input of A} = \text{output of A} + \text{disappearance of A}$$



**Figure 18.11** Section of catalytic reactor which has a solid fraction  $f$ .

In symbols

$$u_0 A C_{A0} (1 - X_{Ain}) = u_0 A C_{A0} (1 - X_{Aout}) + (-r_A''') f A \Delta z$$

In differential form

$$\frac{C_{A0} dX_A}{-r_A'''} = \frac{f dz}{u_0} \quad (48)$$

Integrating

$$\boxed{C_{A0} \int_0^{X_A} \frac{dX_A}{(-r_A''')} = \frac{1}{u_0} \int_0^H f dz} \quad (49)$$

For first-order reactions this expression reduces to

$$(1 + \varepsilon_A) \ln \frac{1}{1 - X_A} - \varepsilon_A X_A = \frac{k'''}{u_0} \int_0^H f dz \quad (50)$$

For the special case where  $\varepsilon_A = 0$ ,  $f$  is constant, and the height of catalyst bed is  $H$ , we have

$$-\frac{dC_A}{dz} = f \frac{k''' C_A}{u_0} \quad \text{or} \quad \ln \frac{C_{A0}}{C_A} = \frac{k''' f H}{u_0} \quad (51)$$

The original derivation leading to Eqs. 40 to 47 is used in the next chapter on packed beds. The extension leading to Eqs. 48 to 51 is used in Chapter 20, when dealing with suspended solids reactors.

## 18.6 EXPERIMENTAL METHODS FOR FINDING RATES

Any type of reactor with known contacting pattern may be used to explore the kinetics of catalytic reactions. Since only one fluid phase is present in these reactions, the rates can be found as with homogeneous reactions. The only special precaution to observe is to make sure that the performance equation used is dimensionally correct and that its terms are carefully and precisely defined.

The experimental strategy in studying catalytic kinetics usually involves measuring the extent of conversion of gas passing in steady flow through a batch of solids. Any flow pattern can be used, as long as the pattern selected is known; if it is not known then the kinetics *cannot be found*. A batch reactor can also be used. In turn we discuss the following experimental devices:

Differential (flow) reactor

Integral (plug flow) reactor

Mixed flow reactor

Batch reactor for both gas and solid

**Differential Reactor.** We have a differential flow reactor when we choose to consider the rate to be constant at all points within the reactor. Since rates are concentration-dependent this assumption is usually reasonable only for small conversions or for shallow small reactors. But this is not necessarily so, e.g., for slow reactions where the reactor can be large, or for zero-order kinetics where the composition change can be large.

For each run in a differential reactor the plug flow performance equation becomes

$$\frac{W}{F_{A0}} = \int_{X_{Ain}}^{X_{Aout}} \frac{dX_A}{-r'_A} = \frac{1}{(-r'_{A})_{ave}} \int_{X_{Ain}}^{X_{Aout}} dX_A = \frac{X_{Aout} - X_{Ain}}{(-r'_{A})_{ave}} \quad (52)$$

from which the average rate for each run is found. Thus each run gives directly a value for the rate at the average concentration in the reactor, and a series of runs gives a set of rate-concentration data which can then be analyzed for a rate equation.

Example 18.2 illustrates the suggested procedure.

**Integral Reactor.** When the variation in reaction rate within a reactor is so large that we choose to account for these variations in the method of analysis, then we have an integral reactor. Since rates are concentration-dependent, such large variations in rate may be expected to occur when the composition of reactant fluid changes significantly in passing through the reactor. We may follow one of two procedures in searching for a rate equation.

**Integral Analysis.** Here a specific mechanism with its corresponding rate equation is put to the test by integrating the basic performance equation to give, similar to Eq. 5.17,

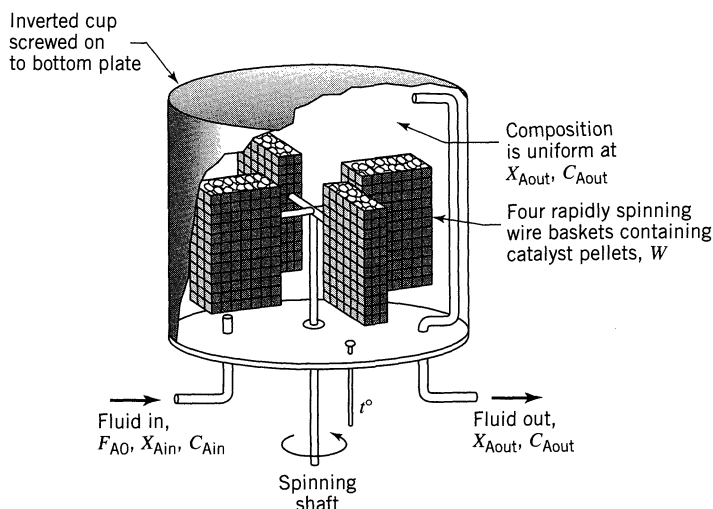
$$\frac{W}{F_{A0}} = \int_0^{X_A} \frac{dX_A}{-r'_A} \quad (53)$$

Equations 5.20 and 5.23 are the integrated forms of Eq. 5.17 for simple kinetic equations, and Example 18.3a illustrates this procedure.

**Differential Analysis.** Integral analysis provides a straightforward rapid procedure for testing some of the simpler rate expressions. However, the integrated forms of these expressions become unwieldy with more complicated rate expressions. In these situations, the differential method of analysis becomes more convenient. The procedure is closely analogous to the differential method described in Chapter 3. So, by differentiating Eq. 53 we obtain

$$-r'_A = \frac{dX_A}{dW/F_{A0}} = \frac{dX_A}{d(W/F_{A0})} \quad (54)$$

Example 18.3b illustrates this procedure.

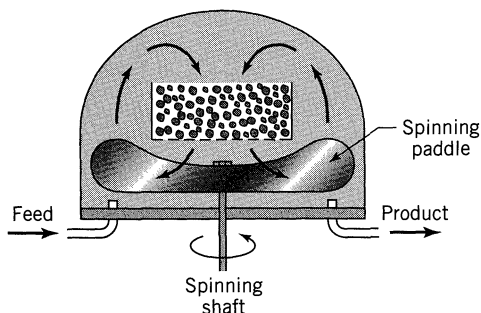


**Figure 18.12** Sketch of a Carberry basket-type experimental mixed flow reactor.

**Mixed Flow Reactor.** A mixed flow reactor requires a uniform composition of fluid throughout, and although it may seem difficult at first thought to approach this ideal with gas-solid systems (except for differential contacting), such contacting is in fact practical. One simple experimental device which closely approaches this ideal has been devised by Carberry (1964). It is called the *basket-type mixed flow reactor*, and it is illustrated in Fig. 18.12. References to design variations and uses of basket reactors are given by Carberry (1969). Another device for approaching mixed flow is the design developed by Berty (1974), and illustrated in Fig. 18.13. Still another design is that of a recycle reactor with  $R = \infty$ . This is considered in the next section.

For the mixed flow reactor the performance equation becomes

$$\frac{W}{F_{A0}} = \frac{X_{Aout}}{-r'_{Aout}}$$



**Figure 18.13** Principle of the Berty experimental mixed flow reactor.

from which the rate is

$$-r'_{Aout} = \frac{F_{A0} X_{Aout}}{W} \quad (55)$$

Thus each run gives directly a value for the rate at the composition of the exit fluid.

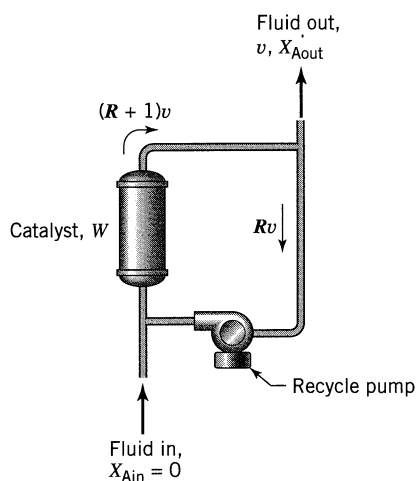
Examples 5.1, 5.2, and 5.3 and 18.6 show how to treat such data.

**Recycle Reactor.** As with integral analysis of an integral reactor, when we use a recycle reactor we must put a specific kinetic equation to the test. The procedure requires inserting the kinetic equation into the performance equation for recycle reactors

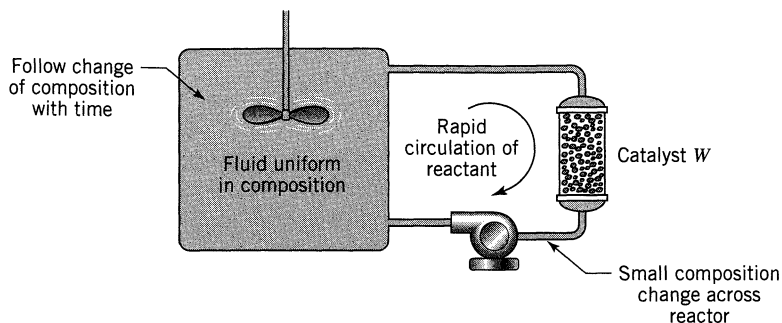
$$\frac{W}{F_{A0}} = (R + 1) \int_{X_{Af}}^{X_{A0}} \frac{dX_A}{(R/R+1)X_{Af} - r'_A} \quad (6.21)$$

and integrating. Then a plot of the left- versus right-hand side of the equation tests for linearity. Figure 18.14 sketches an experimental recycle reactor.

Unfortunately such data would be difficult to interpret when done using a low or intermediate recycle ratio. So we ignore this regime. But with a large enough recycle ratio mixed flow is approached, in which case the methods of the mixed flow reactor (direct evaluation of rate from each run) can be used. Thus a high recycle ratio provides a way of approximating mixed flow with what is essentially a plug flow device. But be warned, the problems of deciding how large a recycle ratio is large enough can be serious. Wedel and Villadsen (1983) and Broucek (1983) discuss the limitation of this reactor.



**Figure 18.14** Experimental recycle reactor. When the recycle ratio is large enough mixed flow is closely approximated.



**Figure 18.15** Batch reactor (batch of catalyst and batch of fluid) for catalytic reactions.

**Batch Reactor.** Figure 18.15 sketches the main features of an experimental reactor which uses a batch of catalyst and a batch of fluid. In this system we follow the changing composition with time and interpret the results with the batch reactor performance equation.

$$\frac{t}{C_{A0}} = \int_0^{X_A} \frac{dX_A}{-r_A} = \frac{V}{W} \int \frac{dX_A}{-r'_A} \quad V = \left( \begin{array}{l} \text{volume} \\ \text{of gas} \end{array} \right) \quad (56)$$

The procedure is analogous with the homogeneous batch reactor. To ensure meaningful results, the composition of fluid must be uniform throughout the system at any instant. This requires that the conversion per pass across the catalyst be small.

A recycle reactor without through-flow becomes a batch reactor. This type of batch reactor was used by Butt et al. (1962).

### Comparison of Experimental Reactors

1. The integral reactor can have significant temperature variations from point to point, especially with gas-solid systems, even with cooling at the walls. This could well make kinetic measurements from such a reactor completely worthless when searching for rate expressions. The basket reactor is best in this respect.
2. The integral reactor is useful for modeling the operations of larger packed bed units with all their heat and mass transfer effects, particularly for systems where the feed and product consist of a variety of materials.
3. Since the differential and mixed flow reactors give the rate directly they are more useful in analyzing complex reacting systems. The test for anything but a simple kinetic form can become awkward and impractical with the integral reactor.
4. The small conversions needed in differential reactors require more accurate measurements of composition than the other reactor types.
5. The recycle reactor with large recycle acts as a mixed flow reactor and shares its advantages. Actually, to minimize heat effects the catalyst need not be all at one location, but can be distributed throughout the recycle loop.



6. In exploring the physical factors of heat and mass transfer, the integral reactor most closely models the larger fixed bed; however, the basket, recycle, and batch  $G/S$  reactors are more suited for finding the limits for such heat effects, for avoiding the regime where these effects intrude, and for studying the kinetics of the reaction unhindered by these phenomena.
7. The batch  $G/S$  reactor, like the integral reactor, gives cumulative effects, thus is useful for following the progress of multiple reactions. In these reactors it is easier to study reactions free from heat and mass transfer resistances (simply increase the circulation rate), and it is also simple to slow down the progress of reactions (use a larger batch of fluid, or less catalyst); however, direct modeling of the packed bed with all its complexities is best done with the integral flow reactor.
8. Because of the ease in interpreting its results the mixed flow reactor is probably the most attractive device for studying the kinetics of solid catalyzed reactions.

### Determining Controlling Resistances and the Rate Equation

Interpretation of experiments becomes difficult when more than one resistance affects the rate. To avoid this problem we should like, with preliminary runs, to first find the limits of operations where the various resistances become important. This will allow us to select conditions of operations in which the resistances can be studied separately.

**Film Resistance.** First of all, it is best to see whether film resistance of any kind (for mass or heat transfer) need be considered. This can be done in a number of ways.

1. Experiments can be devised to see whether the conversion changes at different gas velocities but at identical weight-time. This is done by using different amounts of catalyst in integral or differential reactors for identical values for weight-time, by changing the spinning rate in basket reactors, or by changing the circulation rate in recycle or batch reactors.
2. If data are available we can calculate whether film resistance to heat transfer is important by the estimate of Eq. 36., and whether film resistance to mass transport is important by comparing the observed first-order rate constant based on the volume of particle with the mass transfer coefficient for that type of flow.

For fluid moving past a single particle at relative velocity  $u$  Froessling (1938) gives

$$\frac{k_g d_p}{\mathcal{D}} = 2 + 0.6 \text{Re}^{1/2} \text{Sc}^{1/3} = 2 + 0.6 \left( \frac{d_p u \rho}{\mu} \right)^{1/2} \left( \frac{\mu}{\rho \mathcal{D}} \right)^{1/3}$$

while for fluid passing through a packed bed of particles Ranz (1952) gives

$$\frac{k_g d_p}{\mathcal{D}} = 2 + 1.8 \text{Re}^{1/2} \text{Sc}^{1/3}, \quad \text{Re} > 80$$

Thus we have roughly

$$\left. \begin{aligned} k_g &\sim \frac{1}{d_p} && \text{for small } d_p \text{ and } u \\ k_g &\sim \frac{u^{1/2}}{d_p^{1/2}} && \text{for large } d_p \text{ and } u \end{aligned} \right\} \quad (57)$$

Thus to see whether film mass transfer resistance is important compare

$$k''_{\text{obs}} V_p \text{ versus } k_g S_{\text{ex}} \quad (58)$$

If the two terms are of the same order of magnitude we may suspect that the gas film resistance affects the rate. On the other hand, if  $k_{\text{obs}} V_p$  is much smaller than  $k_g S_{\text{ex}}$  we may ignore the resistance to mass transport through the film. Example 18.1 illustrate this type of calculation. The results of that example confirm our earlier statement that film mass transfer resistance is unlikely to play a role with porous catalyst.

**Nonisothermal Effects.** We may expect temperature gradients to occur either across the gas film or within the particle. However, the previous discussion indicates that for gas-solid systems the most likely effect to intrude on the rate will be the temperature gradient across the gas film. Consequently, if experiment shows that gas film resistance is absent then we may expect the particle to be at the temperature of its surrounding fluid; hence, isothermal conditions may be assumed to prevail. Again see Example 18.1.

**Pore Resistance.** The effectiveness factor accounts for this resistance. Thus, based on unit mass of catalyst we have

$$-r'_A = k''_A C_A^n \mathcal{E} \quad \text{where} \quad \mathcal{E} = \frac{1}{M_T}$$

The existence of pore resistance can be determined by

1. Calculation if  $\mathcal{D}_e$  is known.
2. Comparing rates for different pellet sizes.
3. Noting the drop in activation energy of the reaction with rise in temperature, coupled with a possible change in reaction order.

## 18.7 PRODUCT DISTRIBUTION IN MULTIPLE REACTIONS

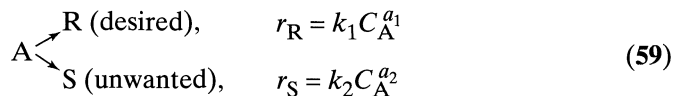
More often than not, solid-catalyzed reactions are multiple reactions. Of the variety of products formed, usually only one is desired, and it is the yield of this material which is to be maximized. In cases such as these the question of product distribution is of primary importance.

Here we examine how strong pore diffusion modifies the true instantaneous fractional yield for various types of reactions; however, we leave to Chapter 7

the calculation of the overall fractional yield in reactors with their particular flow patterns of fluid. In addition, we will not consider film resistance to mass transfer since this effect is unlikely to influence the rate.

### Decomposition of a Single Reactant by Two Paths

*No resistance to pore diffusion.* Consider the parallel-path decomposition



Here the instantaneous fractional yield at any element of catalyst surface is given by

$$\varphi_{\text{true}} \left( \frac{\text{R}}{\text{R} + \text{S}} \right) = \frac{r_{\text{R}}}{r_{\text{R}} + r_{\text{S}}} = \frac{1}{1 + (k_2/k_1) C_{\text{A}}^{a_2 - a_1}} \quad (60)$$

or for first-order reactions

$$\varphi_{\text{true}} = \frac{1}{1 + (k_2/k_1)} \quad (61)$$

*Strong resistance to pore diffusion.* Under these conditions we have

$$r_{\text{R}} = k_1 C_{\text{A}_g}^{a_1} \cdot \mathcal{E}_1 = k_1 C_{\text{A}_g}^{a_1} \cdot \frac{1}{M_T}$$

and with Eq. 29

$$r_{\text{R}} \cong k_1 C_{\text{A}_g}^{a_1} \cdot \frac{1}{L} \left[ \frac{4\mathcal{D}_e}{(a_1 + a_2 + 2)(k_1 + k_2) C_{\text{A}_g}^{a_1 - 1}} \right]^{1/2}$$

Using a similar expression for  $r_{\text{S}}$  and replacing both of these into the defining equation for  $\varphi$  gives

$$\varphi_{\text{obs}} = \frac{r_{\text{R}}}{r_{\text{R}} + r_{\text{S}}} \cong \frac{1}{1 + (k_2/k_1) C_{\text{A}_g}^{(a_2 - a_1)/2}} \quad (62)$$

and for equal-order or for first-order reactions

$$\varphi_{\text{obs}} = \frac{1}{1 + (k_2/k_1)} \quad (63)$$

This result is expected since the rules in Chapter 7 suggest that the product distribution for competing reactions of same order should be unaffected by changing concentration of A in the pores or in the reactor.

## Reactions in Series

As characteristic of reactions in which the desired product can decompose further, consider the successive first-order decompositions



When  $C_A$  does not drop in the interior of catalyst particles, true rates are observed, thus

$$\varphi_{\text{obs}} = \varphi_{\text{true}} \quad \text{or} \quad \left(\frac{k_2}{k_1}\right)_{\text{obs}} = \left(\frac{k_2}{k_1}\right)_{\text{true}} \quad (64)$$

*Strong resistance to pore diffusion.* An analysis similar to that starting with Eq. 2 using the appropriate kinetic rate expressions gives the concentration ratio of materials in the main gas stream (or pore mouths) at any point in the reactor. Thus the differential expression (see Wheeler, 1951 for details) is

$$\frac{dC_{Rg}}{dC_{Ag}} = -\frac{1}{1+\gamma} + \gamma \frac{C_{Rg}}{C_{Ag}}, \quad \gamma = \left(\frac{k_2}{k_1}\right)^{1/2} \quad (65)$$

For mixed flow with  $C_A$  going from  $C_{A0}$  to  $C_{Ag}$  Eq. 65 with  $C_{R0} = 0$  gives

$$C_{Rg} = \frac{1}{1+\gamma} \cdot \frac{C_{Ag}(C_{A0} - C_{Ag})}{C_{Ag} + \gamma(C_{A0} - C_{Ag})} \quad (66)$$

For plug flow, integration with  $C_{R0} = 0$  gives

$$\frac{C_{Rg}}{C_{A0}} = \frac{1}{1+\gamma} \cdot \frac{1}{1-\gamma} \left[ \left(\frac{C_{Ag}}{C_{A0}}\right)^\gamma - \frac{C_{Ag}}{C_{A0}} \right] \quad (67)$$

Comparing Eqs. 66 and 67 with the corresponding expressions for no resistance in pores, Eqs. 8.41 and 8.37, shows that here the distributions of A and R are given by a reaction having the square root of the true  $k$  ratio, with the added modification that  $C_{Rg}$  is divided by  $1 + \gamma$ . The maximum yield of R is likewise affected. Thus for plug flow Eq. 8.8 or 8.38 is modified to give

$$\frac{C_{Rg, \text{max}}}{C_{A0}} = \frac{\gamma^{\gamma/(1-\gamma)}}{1+\gamma}, \quad \gamma = \left(\frac{k_2}{k_1}\right)^{1/2} \quad (68)$$

and for mixed flow Eq. 8.15 or 8.41 is modified to give

$$\frac{C_{Rg, \text{max}}}{C_{A0}} = \frac{1}{(1+\gamma)(\gamma^{1/2} + 1)^2} \quad (69)$$

Table 18.2 shows that the yield of R is about halved in the presence of strong resistance to diffusion in the pores.

**Table 18.2** The Role of Diffusion in Pores for First-Order Reactions in Series

$k_2/k_1$	$C_{Rg, \max}/C_{A0}$ for Plug Flow			$C_{Rg, \max}/C_{A0}$ for Mixed Flow		
	No Resistance	Strong Resistance	Percent Decrease	No Resistance	Strong Resistance	Percent Decrease
1/64	0.936	0.650	30.6	0.790	0.486	38.5
1/16	0.831	0.504	39.3	0.640	0.356	44.5
1/4	0.630	0.333	47.6	0.444	0.229	48.5
1	0.368	0.184	50.0	0.250	0.125	50.0
4	0.157	0.083	47.2	0.111	0.057	48.5
16	0.051	0.031	38.2	0.040	0.022	44.5

For more on the whole subject of the shift in product distribution caused by diffusional effects, see Wheeler (1951).

### Extensions to Real Catalysts

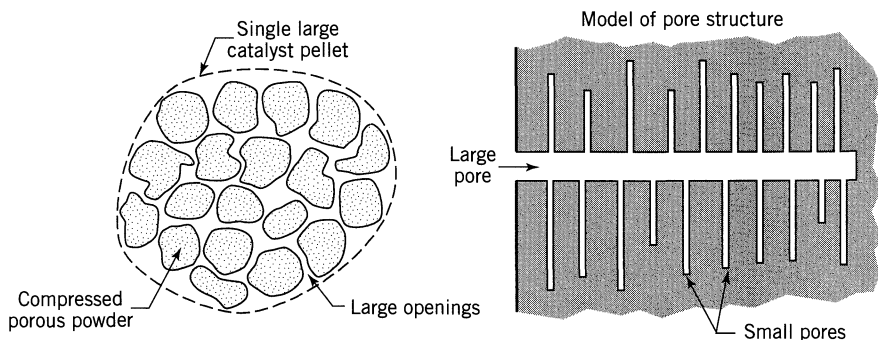
So far we have considered catalyst pellets having only one size of pore. Real catalysts, however, have pores of various sizes. A good example of this are the pellets prepared by compressing a porous powder. Here there are large openings between the agglomerated particles and small pores within each particle. As a first approximation we may represent this structure by two pore sizes as shown in Fig. 18.16. If we define the degree of branching of a porous structure by  $\alpha$  where

$\alpha = 0$  represents a nonporous particle

$\alpha = 1$  represents a particle with one size of pore

$\alpha = 2$  represents a particle with two pore sizes

then every real porous pellet can be characterized by some value of  $\alpha$ .



**Figure 18.16** Porous structure with two sizes of pores as a model for a pellet of compressed porous powder.

Now for strong pore diffusion in one size of pore we already know that the observed order of reaction, activation energy, and  $k$  ratio for multiple reactions will differ from the true value. Thus from Eqs. 30 and 32

$$\text{for } \alpha = 1 \left\{ \begin{array}{l} E_{\text{obs}} = \frac{1}{2} E_{\text{diff}} + \frac{1}{2} E \\ n_{\text{obs}} = 1 + \frac{n-1}{2} \\ \left( \frac{k_2}{k_1} \right)_{\text{obs}} = \left( \frac{k_2}{k_1} \right)^{1/2} \cdots \text{for side-by-side reactions} \end{array} \right. \quad (70)$$

Carberry (1962a, b), Tartarelli (1968), and others have extended this type of analysis to other values of  $\alpha$  and to reversible reactions. Thus for two sizes of pores, where reaction occurs primarily in the smaller pores (because of much more area there), while both sizes of pores offer strong pore diffusional resistance, we find

$$\text{for } \alpha = 2 \left\{ \begin{array}{l} E_{\text{obs}} = \frac{3}{4} E_{\text{diff}} + \frac{1}{4} E \\ n_{\text{obs}} = 1 + \frac{n-1}{4} \\ \left( \frac{k_2}{k_1} \right)_{\text{obs}} = \left( \frac{k_2}{k_1} \right)^{1/4} \cdots \text{for side-by-side reactions} \end{array} \right. \quad (71)$$

More generally for an arbitrary porous structure

$$\text{for any } \alpha \left\{ \begin{array}{l} E_{\text{obs}} = \left( 1 - \frac{1}{2^\alpha} \right) E_{\text{diff}} + \frac{1}{2^\alpha} E \\ n_{\text{obs}} = 1 + \frac{n-1}{2^\alpha} \\ \left( \frac{k_2}{k_1} \right)_{\text{obs}} = \left( \frac{k_2}{k_1} \right)^{1/2^\alpha} \cdots \text{for side-by-side reactions} \end{array} \right. \quad (72)$$

These findings show that for large  $\alpha$ , diffusion plays an increasingly important role, in that the observed activation energy decreases to that of diffusion, and the reaction order approaches unity. So, for a given porous structure with unknown  $\alpha$ , the only reliable estimate of the true  $k$  ratio would be from experiments under conditions where pore diffusion is unimportant. On the other hand, finding the experimental ratio of  $k$  values under both strong and negligible pore resistance should yield the value of  $\alpha$ . This in turn should shed light on the pore structure geometry of the catalyst.

**EXAMPLE 18.1 SEARCH OF THE RATE-CONTROLLING MECHANISM**

An experimental rate measurement on the decomposition of A is made with a particular catalyst (see pertinent data listed below).

- (a) Is it likely that film resistance to mass transfer influences the rate?
- (b) Could this run have been made in the regime of strong pore diffusion?
- (c) Would you expect to have temperature variations within the pellet or across the gas film?

*Data*

For the spherical particle:

$$d_p = 2.4 \text{ mm or } L = R/3 = 0.4 \text{ mm} = 4 \times 10^{-4} \text{ m cat}$$

$$\mathcal{D}_e = 5 \times 10^{-5} \text{ m}^2/\text{hr} \cdot \text{m cat (effective mass conductivity)}$$

$$k_{\text{eff}} = 1.6 \text{ kJ/hr} \cdot \text{m cat} \cdot \text{K (effective thermal conductivity)}$$

For the gas film surrounding the pellet (from correlations in the literature):

$$h = 160 \text{ kJ/hr} \cdot \text{m}^2 \text{ cat} \cdot \text{K (heat transfer coefficient)}$$

$$k_g = 300 \text{ m}^3/\text{hr} \cdot \text{m}^2 \text{ cat (mass transfer coefficient)}$$

For the reaction:

$$\Delta H_r = -160 \text{ kJ/mol A (exothermic)}$$

$$C_{A_g} = 20 \text{ mol/m}^3 \text{ (at 1 atm and 336}^\circ\text{C)}$$

$$-r'''_{A, \text{obs}} = 10^5 \text{ mol/hr} \cdot \text{m}^3 \text{ cat}$$

Assume that the reaction is first order.

**SOLUTION**

- (a) **Film mass transfer.** From Eq. 58, and introducing numerical values, we obtain

$$\begin{aligned} \frac{\text{observed rate}}{\text{rate if film resistance controls}} &= \frac{k'''_{\text{obs}} V_p}{k_g S_{\text{ex}}} = \frac{(-r'''_{A, \text{obs}}/C_{A_g})(\pi d_p^3/6)}{k_g(\pi d_p^2)} = \frac{-r'''_{A, \text{obs}}}{C_{A_g} k_g} \cdot \frac{d_p}{6} \\ &= \frac{10^5 \text{ mol/hr} \cdot \text{m}^3 \text{ cat}}{(20 \text{ mol/m}^3)(300 \text{ m}^3/\text{hr} \cdot \text{m}^2 \text{ cat})} \cdot \frac{2.4 \times 10^{-3} \text{ m cat}}{6} \\ &= \frac{1}{150} \end{aligned}$$

The observed rate is very much lower than the limiting film mass transfer rate.

Thus the resistance to film mass transfer certainly should not influence the rate of reaction.

(b) **Strong pore diffusion.** Equations 24 and Fig. 18.7 test for strong pore diffusion. Thus

$$M_W = \frac{(-r_A''')_{\text{obs}} L^2}{\mathcal{D}_e C_{A_g}} = \frac{(10^5 \text{ mol/hr} \cdot \text{m}^3 \text{ cat})(4 \times 10^{-4} \text{ m cat})^2}{(5 \times 10^{-5} \text{ m}^3/\text{hr} \cdot \text{m cat})(20 \text{ mol/m}^3)} = 16$$

This quantity  $M_W$  is greater than 4, hence pore diffusion is influencing and slowing the rate of reaction.

(c) **Nonisothermal operations.** The estimate for the upper limit to temperature variations is given by Eqs. 38 and 36. Thus within the pellet

$$\begin{aligned} \Delta T_{\text{max, pellet}} &= \frac{\mathcal{D}_e (C_{A_g} - 0)(-\Delta H_r)}{k_{\text{eff}}} \\ &= \frac{(5 \times 10^{-5} \text{ m}^3/\text{hr} \cdot \text{m cat})(20 \text{ mol/m}^3)(160 \text{ kJ/mol})}{(1.6 \text{ kJ/hr} \cdot \text{m cat} \cdot \text{K})} \\ &= 0.1^\circ\text{C} \end{aligned}$$

Across the gas film

$$\begin{aligned} \Delta T_{\text{max, film}} &= \frac{L(-r_A''')_{\text{obs}}(-\Delta H_r)}{h} \\ &= \frac{(4 \times 10^{-4} \text{ m})(10^5 \text{ mol/hr} \cdot \text{m}^3)(160 \text{ kJ/mol})}{(160 \text{ kJ/hr} \cdot \text{m}^2 \cdot \text{K})} \\ &= 40^\circ\text{C} \end{aligned}$$

These estimates show that the pellet is close to uniform in temperature, but could well be hotter than the surrounding fluid.

The findings of this example use coefficients close to those observed in real gas-solid systems (see the appendix), and the conclusions verify the discussion of this chapter.

### EXAMPLE 18.2 THE RATE EQUATION FROM A DIFFERENTIAL REACTOR

The catalytic reaction



is run at 3.2 atm and 117°C in a plug flow reactor which contains 0.01 kg of catalyst and uses a feed consisting of the partially converted product of 20 liters/hr of pure unreacted A. The results are as follows:



Run	1	2	3	4
$C_{Ain}$ , mol/liter	0.100	0.080	0.060	0.040
$C_{Aout}$ , mol/liter	0.084	0.070	0.055	0.038

Find a rate equation to represent this reaction.

**SOLUTION**

Since the maximum variation about the mean concentration is 8% (run 1), we may consider this to be a differential reactor and we may apply Eq. 52 to find the reaction rate.

Basing conversion for all runs on pure A at 3.2 atm and 117°C, we have

$$C_{A0} = \frac{N_{A0}}{V} = \frac{p_{A0}}{RT} = \frac{3.2 \text{ atm}}{(0.082 \text{ liter} \cdot \text{atm/mol} \cdot \text{K})(390 \text{ K})} = 0.1 \frac{\text{mol}}{\text{liter}}$$

and

$$F_{A0} = C_{A0} v = \left(0.1 \frac{\text{mol A}}{\text{liter}}\right) \left(20 \frac{\text{liters}}{\text{hr}}\right) = 2 \frac{\text{mol}}{\text{hr}}$$

Because the density changes during reaction, concentrations and conversions are related by

$$\frac{C_A}{C_{A0}} = \frac{1 - X_A}{1 + \varepsilon_A X_A} \quad \text{or} \quad X_A = \frac{1 - C_A/C_{A0}}{1 + \varepsilon_A (C_A/C_{A0})}$$

where  $\varepsilon_A = 3$  for the basis selected (pure A).

Table E18.2 shows the details of the calculations. Plotting  $-r'_A$  versus  $C_A$  as shown in Fig. E18.2 gives a straight line through the origin, indicating a first-

**Table E18.2**

$\frac{C_{Ain}}{C_{A0}}$	$\frac{C_{Aout}}{C_{A0}}$	$C_{Aav}$ mol/liter	$X_{Ain} =$	$X_{Aout} =$	$\frac{\Delta X_A}{X_{Aout} - X_{Ain}}$	$-r'_A = \frac{\Delta X_A}{W/F_{A0}}$
			$1 - \frac{C_{Ain}}{C_{A0}}$ $1 + \varepsilon_A \frac{C_{Ain}}{C_{A0}}$	$1 - \frac{C_{Aout}}{C_{A0}}$ $1 + \varepsilon_A \frac{C_{Aout}}{C_{A0}}$		
1	0.84	0.092	$\frac{1-1}{1+3} = 0$	$\frac{1-0.84}{1+3(0.84)} = 0.0455$	0.0455	$\frac{0.0455}{0.01/2} = 9.1$
0.8	0.70	0.075	0.0588	0.0968	0.0380	7.6
0.6	0.55	0.0575	0.1429	0.1698	0.0269	5.4
0.4	0.38	0.039	0.2727	0.2897	0.0171	3.4

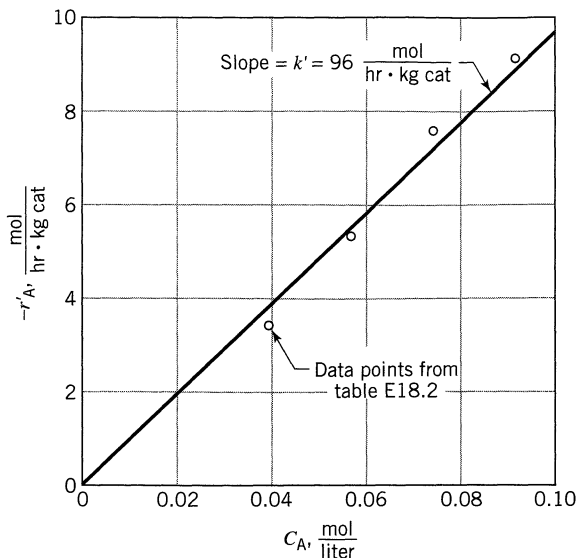


Figure E18.2

order decomposition. The rate in terms of moles A reacted/hr·kg cat is then found from this figure to be

$$\underline{\underline{-r'_A}} = -\frac{1}{W} \frac{dN_A}{dt} = \left( 96 \frac{\text{liters}}{\text{hr} \cdot \text{kg cat}} \right) \left( C_A \frac{\text{mol}}{\text{liter}} \right)$$

### EXAMPLE 18.3 THE RATE EQUATION FROM AN INTEGRAL REACTOR

The catalytic reaction



is studied in a plug flow reactor using various amounts of catalyst and 20 liters/hr of pure A feed at 3.2 atm and 117°C. The concentrations of A in the effluent stream is recorded for the various runs as follows.

Run	1	2	3	4
Catalyst used, kg	0.020	0.040	0.080	0.160
$C_{Aout}$ , mol/liter	0.074	0.060	0.044	0.029

- Find the rate equation for this reaction, using the integral method of analysis
- Repeat part (a), using the differential method of analysis.

**SOLUTION**

(a) **Integral Analysis.** From Example 18.2 we have for all experimental runs

$$C_{A0} = 0.1 \text{ mol/liter}, \quad F_{A0} = 2 \text{ mol/hr}, \quad \varepsilon_A = 3$$

Since the concentration varies significantly during the runs, the experimental reactor should be considered to be an integral reactor.

As a first guess try a first-order rate expression. Then for plug flow Eq. 44 gives

$$k' \frac{C_{A0} W}{F_{A0}} = (1 + \varepsilon_A) \ln \frac{1}{1 - X_A} - \varepsilon_A X_A$$

and with  $\varepsilon_A$ ,  $C_{A0}$ , and  $F_{A0}$  replaced by numerical values this becomes

$$\left( 4 \ln \frac{1}{1 - X_A} - 3X_A \right) = k' \left( \frac{W}{20} \right) \quad (\text{i})$$

The two terms in parentheses should be proportional to each other with  $k'$  as the constant of proportionality. Evaluating these terms in Table E18.3a for

**Table E18.3a** Calculations Needed to Test the Fit of Eq. (i); Integral Analysis

$X_A = \frac{C_{A0} - C_A}{C_{A0} + 3C_A}$	$4 \ln \frac{1}{1 - X_A}$	$3X_A$	$\left( 4 \ln \frac{1}{1 - X_A} - 3X_A \right)$	$W, \text{ kg}$	$\frac{W}{20}$
0.0808	0.3372	0.2424	0.0748	0.02	0.001
0.1429	0.6160	0.4287	0.1873	0.04	0.002
0.2415	1.1080	0.7245	0.3835	0.08	0.004
0.379	1.908	1.137	0.771	0.16	0.008

the data points and plotting as in Fig. 18.3a, we see that there is no reason to suspect that we do not have a linear relationship. Hence we may conclude that the first-order rate equation satisfactorily fits the data. With  $k'$  evaluated from Fig. 18.3a, we then have

$$\underline{\underline{-r'_A = \left( 95 \frac{\text{liters}}{\text{hr} \cdot \text{kg cat}} \right) \left( C_A, \frac{\text{mol}}{\text{liter}} \right)}}$$

(b) **Differential Analysis.** Equation 54 shows that the rate of reaction is given by the slope of the  $X_A$  versus  $W/F_{A0}$  curve. The tabulation (Table E18.3b) based on the measured slopes in Fig. E18.3b shows how the rate of reaction

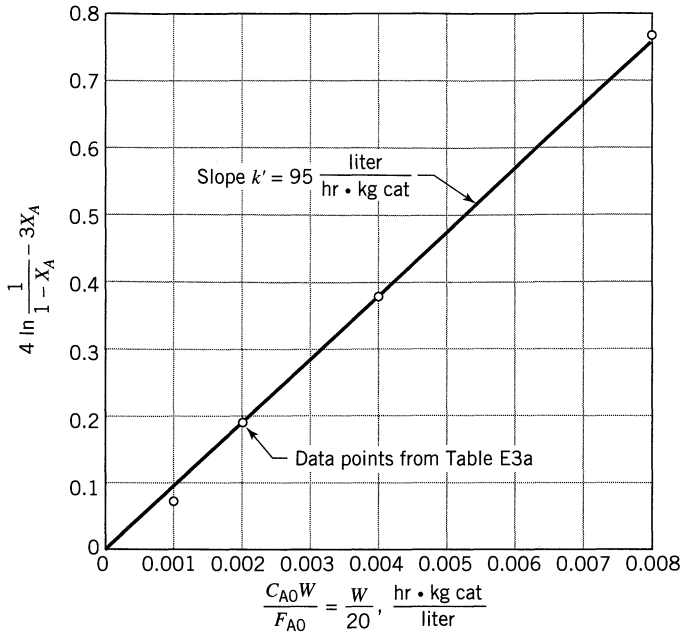


Figure E18.3a

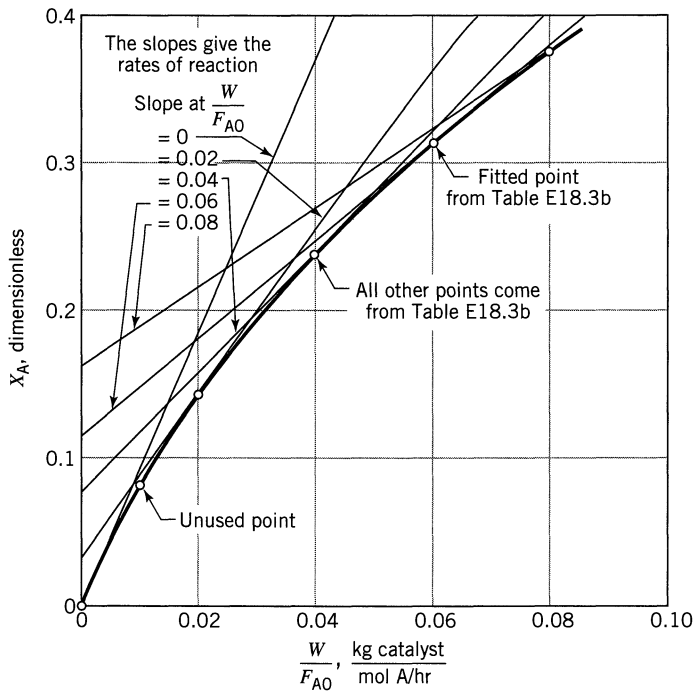
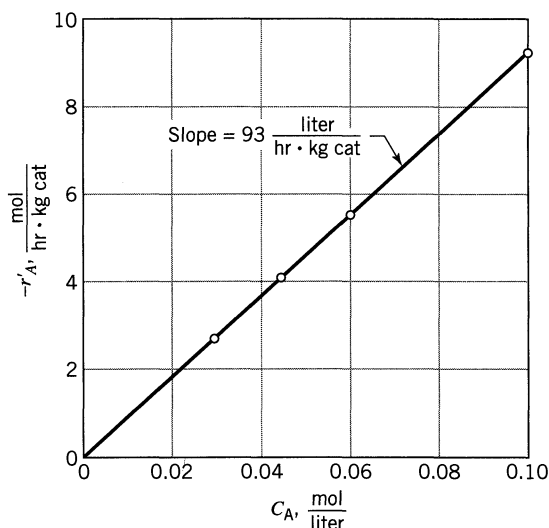


Figure E18.3b

**Table E18.3b** Calculations Used for the Differential Analysis

$W$	$\frac{W}{F_{A0}}$	$\frac{C_{Aout}}{C_{A0}}$	$X_A = \frac{1 - \frac{C_A}{C_{A0}}}{1 + \varepsilon_A \frac{C_A}{C_{A0}}}$	$-r'_A = \frac{dX_A}{d\left(\frac{W}{F_{A0}}\right)}$ (from Fig. E18.3b)
0	0	1	0	$\frac{0.4}{0.043} = 9.3$
0.02	0.01	0.74	0.0808	unused
0.04	0.02	0.60	0.1429	5.62
0.08	0.04	0.44	0.2415	4.13
0.16	0.08	0.29	0.379	2.715

**Figure E18.3c**

is found at various  $C_A$ . The linear relation between  $-r'_A$  and  $C_A$  in Fig. E18.3c then gives for the rate equation:

$$\underline{\underline{-r'_A = \left(93 \frac{\text{liters}}{\text{hr} \cdot \text{kg cat}}\right) \left(C_A, \frac{\text{mol}}{\text{liter}}\right)}}$$

#### EXAMPLE 18.4 PLUG FLOW REACTOR SIZE FROM A RATE EQUATION

Consider the catalytic reaction of Example 18.2. Using the rate equation found for this reaction determine the amount of catalyst needed in a packed bed reactor (assume plug flow) for 35% conversion of A to R for a feed of 2000 mol/hr of pure A at 3.2 atm and 117°C.

**SOLUTION**

The amount of catalyst needed is given by the first-order rate expression for plug flow, Eq. 44. Thus

$$W = \frac{F_{A0}}{kC_{A0}} \left[ (1 + \varepsilon_A) \ln \frac{1}{1 - X_A} - \varepsilon_A X_A \right]$$

Replacing all the known values from Example 18.2 into this expression gives the final result, or

$$\begin{aligned} W &= \frac{2000 \frac{\text{mol A}}{\text{hr}}}{\left(96 \frac{\text{liter}}{\text{hr} \cdot \text{kg cat}}\right) \left(0.1 \frac{\text{mol A}}{\text{liter}}\right)} \left(4 \ln \frac{1}{0.65} - 1.05\right) \\ &= \underline{\underline{140 \text{ kg catalyst}}} \end{aligned}$$

**EXAMPLE 18.5 PLUG FLOW REACTOR SIZE FROM RATE CONCENTRATION DATA**

For the reaction of Example 18.2 suppose the following rate concentration data are available:

$C_A$ , mol/liter	0.039	0.0575	0.075	0.092
$-r'_A$ , mol A/hr · kg cat	3.4	5.4	7.6	9.1

Directly from this data, and without using a rate equation, find the size of packed bed needed to treat 2000 mol/hr of pure A at 117°C (or  $C_{A0} = 0.1$  mol/liter,  $\varepsilon_A = 3$ ) to 35% conversion, all at 3.2 atm.

**Note:** Rate information such as this can be obtained from a differential reactor (see Table E18.2), or from other types of experimental reactors.

**SOLUTION**

To find the amount of catalyst needed without using an analytic expression for the rate concentration relationship requires graphical integration of the plug flow performance equation, or

$$\frac{W}{F_{A0}} = \int_0^{0.35} \frac{dX_A}{-r'_A}$$

Table E18.5

$-r'_A$ (given)	$\frac{1}{-r'_A}$	$C_A$ (given)	$X_A = \frac{1 - C_A/0.1}{1 + 3C_A/0.1}$
3.4	0.294	0.039	0.2812
5.4	0.186	0.0575	0.1563
7.6	0.1316	0.075	0.0778
9.1	0.110	0.092	0.02275

The needed  $1/-r'_A$  versus  $X_A$  data are determined in Table E18.5 and are plotted in Fig. E18.5. Integrating graphically then gives

$$\int_0^{0.35} \frac{dX_A}{-r'_A} = 0.0735$$

Hence

$$\underline{W} = \left( 2000 \frac{\text{mol A}}{\text{hr}} \right) \left( 0.0735 \frac{\text{hr} \cdot \text{kg cat}}{\text{mol A}} \right) = \underline{\underline{147 \text{ kg cat}}}$$

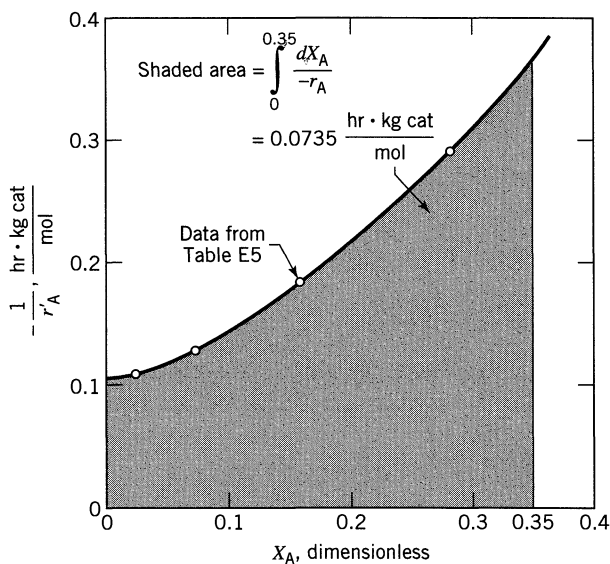
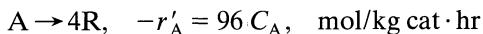


Figure E18.5

**EXAMPLE 18.6 MIXED FLOW REACTOR SIZE**

For the reaction of Example 18.2 determine the amount of catalyst needed in a packed bed reactor with a very large recycle rate (assume mixed flow) for 35% conversion of A to R for a feed rate of 2000 mol/hr of pure A at 3.2 atm and 117°C. For the reaction at this temperature



From Example 18.2,  $C_{A0} = 0.1$  mol/liter and  $\varepsilon_A = 3$ .

**SOLUTION**

At 35% conversion the concentration of reactant is

$$C_A = C_{A0} \left( \frac{1 - X_A}{1 + \varepsilon_A X_A} \right) = 0.1 \left( \frac{1 - 0.35}{1 + 3(0.35)} \right) = 0.0317$$

Now for mixed flow Eq. 45 gives

$$\frac{W}{F_{A0}} = \frac{X_{A\text{out}} - X_{A\text{in}}}{-r'_{A\text{out}}} = \frac{X_{A\text{out}} - X_{A\text{in}}}{k' C_{A\text{out}}}$$

or

$$\underline{W} = 2000 \left( \frac{0.35 - 0}{96(0.0317)} \right) = \underline{\underline{230 \text{ kg}}}$$

**Note:** A mixed flow reactor requires more catalyst than does a plug flow reactor, as expected.

**EXAMPLE 18.7 MASS TRANSFER RESISTANCES**

What is the most reasonable interpretation, in terms of controlling resistances, of the kinetic data of Table E18.7 obtained in a basket type mixed flow reactor if we know that the catalyst is porous? Assume isothermal behavior.

**Table E18.7**

Pellet Diameter	Leaving Concentration of Reactant	Spinning Rate of Baskets	Measured Reaction Rate, $-r'_A$
1	1	high	3
3	1	low	1
3	1	high	1



**SOLUTION**

Let us see whether film resistance or pore resistance could be slowing the rate of reaction.

Runs 2 and 3 use different spinning rates but have the same reaction rate. Therefore film diffusion is ruled out for the larger pellets. But Eq. 57 shows that if film resistance is not important for large pellets it will not be important for small pellets. Therefore film resistance does not influence the rate.

Next, comparing run 1 and either run 2 or 3 shows that

$$-r'_A \propto \frac{1}{R}$$

Eq. 25 then tells us that we are in the regime of strong pore resistance. Thus our final conclusion is

- negligible film resistance
- strong pore diffusion resistance

**REFERENCES**

- Aris, R., *Chem. Eng. Sci.*, **6**, 262 (1957).  
 Berty, J., *Chem. Eng. Prog.*, **70** (5), 78 (1974).  
 Bischoff, K. B., *Chem. Eng. Sci.*, **22**, 525 (1967).  
 Boudart, M., *AIChE J.*, **2**, 62 (1956).  
 Broucek, R., *Chem. Eng. Sci.*, **38**, 1349 (1983).  
 Butt, J. B., Bliss, H., and Walker, C. A., *AIChE J.*, **8**, 42 (1962).  
 Carberry, J. J., *AIChE J.*, **7**, 350 (1961).  
 ———, *AIChE J.*, **8**, 557 (1962a).  
 ———, *Chem. Eng. Sci.*, **17**, 675 (1962b).  
 ———, *Ind. Eng. Chem.*, **56**, 39 (Nov. 1964).  
 ———, *Catalysis Reviews*, **3**, 61 (1969).  
 Chou, C. H., *Ind. Eng. Chem.*, **50**, 799 (1958).  
 Corrigan, T. E., *Chem. Eng.*, **61**, 236 (November 1954); **61**, 198 (December 1954); **62**, 199 (January 1955); **62**, 195 (February 1955); **62**, 203 (May 1955); **62**, 227 (July 1955).  
 Froessling, N., *Gerland Beitr. Geophys.*, **52**, 170 (1938).  
 Froment, G. F., and Bischoff, K. B., *Chemical Reactor Analysis and Design*, p. 162, John Wiley and Sons, New York, 1990.  
 Hougen, O. A., and Watson, K. M., *Chemical Process Principles*, Part III, John Wiley & Sons, New York, 1947.  
 Hutchings, J., and Carberry, J. J., *AIChE J.*, **12**, 20 (1966).  
 Levenspiel, O., *Chemical Reactor Omnibook*, Chap. 22, OSU Bookstore, Corvallis, OR, 1996.  
 McGreavy, C., and Cresswell, D. L., *Can. J. Ch.E.*, **47**, 583 (1969a).  
 ———, and ———, *Chem. Eng. Sci.*, **24**, 608 (1969b).  
 McGreavy, C., and Thornton, J. M., *Can. J. Ch. E.*, **48**, 187 (1970a).  
 ———, *Chem. Eng. Sci.*, **25**, 303 (1970b).  
 Prater, C. C., *Chem. Eng. Sci.*, **8**, 284 (1958).  
 ———, and Lago, R. M., *Advances in Catalysis*, **8**, 293 (1956).

- Ranz, W. E., *Chem. Eng. Prog.*, **48**, 247 (1952).  
 Satterfield, C. N., *Mass Transfer in Heterogeneous Catalysis*, M.I.T. Press, 1970.  
 Tartarelli, R., *Chim. Ind. (Milan)*, **50**, 556 (1968).  
 Thiele, E. W., *Ind. Eng. Chem.*, **31**, 916 (1939).  
 Walas, S., *Reaction Kinetics for Chemical Engineers*, McGraw-Hill, New York, 1959.  
 Wedel, S., and Villadsen, J., *Chem. Eng. Sci.*, **38**, 1346 (1983).  
 Weisz, P. B., *Chem. Eng. Prog. Symp. Series*, No. 25, **55**, 29 (1959).  
 ———, and Hicks, J. S., *Chem. Eng. Sci.*, **17**, 265 (1962).  
 Weller, S., *AIChE J.*, **2**, 59 (1956).  
 Wheeler, A., *Advances in Catalysis*, **3**, 250 (1951).

## PROBLEMS

These problems are loosely grouped as follows:

*Problems 1–19:* Direct application of performance equations. These problems should be tried first.

*Problems 20–30:* Pore diffusion kinetics.

*Problems 31–40:* Reactor size + pore diffusion

- 18.1.** While being shown around Lumphead Laboratories, you stop to view a reactor used to obtain kinetic data. It consists of a 5-cm ID glass column packed with a 30-cm height of active catalyst. Is this a differential or integral reactor?
- 18.2.** A solid catalyzed first-order reaction,  $\varepsilon = 0$ , takes place with 50% conversion in a basket type mixed reactor. What will be the conversion if the reactor size is trebled and all else—temperature, amount of catalyst, feed composition, and flow rate—remains unchanged?
- 18.3.** The following kinetic data on the reaction  $A \rightarrow R$  are obtained in an experimental packed bed reactor using various amounts of catalyst and a fixed feed rate  $F_{A0} = 10$  kmol/hr.

$W, \text{ kg cat}$	1	2	3	4	5	6	7
$X_A$	0.12	0.20	0.27	0.33	0.37	0.41	0.44

- (a) Find the reaction rate at 40% conversion.  
 (b) In designing a large packed bed reactor with feed rate  $F_{A0} = 400$  kmol/hr how much catalyst would be needed for 40% conversion.  
 (c) How much catalyst would be needed in part (b) if the reactor employed a very large recycle of product stream.

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A gas containing A ( $2 \text{ mol/m}^3$ ) is fed ( $1 \text{ m}^3/\text{hr}$ ) to a plug flow reactor with recycle loop ( $0.02 \text{ m}^3$  loop volume, 3 kg of catalyst), and the output composition from the reactor system is measured ( $0.5 \text{ mol A/m}^3$ ). Find the rate equation for the decomposition of A for the following cases. Be sure to give the units of  $-r'_A$ ,  $C_A$ , and  $k'$  in your final expression.

**18.4.** Very large recycle,  $A \rightarrow R$ ,  $n = 1/2$

**18.5.** Very large recycle,  $A \rightarrow 3R$ ,  $n = 1$ , 50% A–50% inerts in feed

**18.6.** No recycle,  $A \rightarrow 3R$ ,  $n = 2$ , 25% A–75% inerts in feed

Gaseous A reacts ( $A \rightarrow R$ ) in an experimental reactor. From the following conversion data at various conditions find a rate equation to represent the reaction

<b>18.7.</b>	$v_0, \text{m}^3/\text{hr}$	3	2	1.2	Mixed flow $C_{A0} = 10 \text{ mol/m}^3$ $W = 4 \text{ gm}$
	$X_A$	0.2	0.3	0.5	

<b>18.8.</b>	$W, \text{gm}$	0.5	1.0	2.5	Plug flow $C_{A0} = 60 \text{ mol/m}^3$ $v = 3 \text{ liter/min}$
	$C_A$	30	20	10	

The following kinetic data are obtained in an experimental Carberry type basket reactor using 100 gm of catalyst in the paddles and different flow rates from run to run:

$A \rightarrow R$ $C_{A0} = 10 \text{ mol/m}^3$	$F_{A0}, \text{mol/min}$	0.14	0.42	1.67	2.5	1.25
	$C_A, \text{mol/m}^3$	8	6	4	2	1

**18.9.** Determine the amount of catalyst needed in a packed bed reactor for 75% conversion of 1000 mol A/min of a  $C_{A0} = 8 \text{ mol/m}^3$  feed.

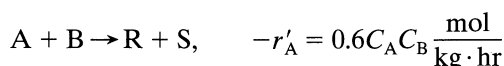
**18.10.** Find  $W$  for mixed flow,  $X_A = 0.90$ ,  $C_{A0} = 10 \text{ mol/m}^3$ ,  $F_{A0} = 1000 \text{ mol/min}$ .

How much catalyst is needed in a packed bed reactor for 80% conversion of 1000  $\text{m}^3/\text{hr}$  of pure gaseous A ( $C_{A0} = 100 \text{ mol/m}^3$ ) if the stoichiometry and rate are given by

**18.11.**  $A \rightarrow R, -r'_A = \frac{50C_A}{1 + 0.02C_A} \frac{\text{mol}}{\text{kg} \cdot \text{hr}}$

**18.12.**  $A \rightarrow R, -r'_A = 8C_A^2 \frac{\text{mol}}{\text{kg} \cdot \text{hr}}$

**18.13.** Gaseous feed with A and B ( $v_0 = 10 \text{ m}^3/\text{hr}$ ) pass through an experimental reactor packed with catalyst ( $W = 4 \text{ kg}$ ). Reaction occurs as follows:



Find the conversion of reactants if the feed contains  $C_{A0} = 0.1 \text{ mol/m}^3$  and  $C_{B0} = 10 \text{ mol/m}^3$ .

- 18.14.** A West Texas gas oil is cracked in a tubular reactor packed with silica-alumina cracking catalyst. The liquid feed ( $mw = 0.255$ ) is vaporized, heated, enters the reactor at  $630^\circ\text{C}$  and 1 atm, and with adequate temperature control stays close to this temperature within the reactor. The cracking reaction follows first-order kinetics and gives a variety of products with mean molecular weight  $mw = 0.070$ . Half the feed is cracked for a feed rate of  $60 \text{ m}^3 \text{ liquid/m}^3 \text{ reactor} \cdot \text{hr}$ . In the industry this measure of feed rate is called the *liquid hourly space velocity*. Thus  $\text{LHSV} = 60 \text{ hr}^{-1}$ . Find the first-order rate constants  $k'$  and  $k''$  for this cracking reaction.

*Data:* Density of liquid feed:  $\rho_l = 869 \text{ kg/m}^3$   
 Bulk density of packed bed:  $\rho_b = 700 \text{ kg/m}^3$   
 Density of catalyst particles:  $\rho_s = 950 \text{ kg/m}^3$

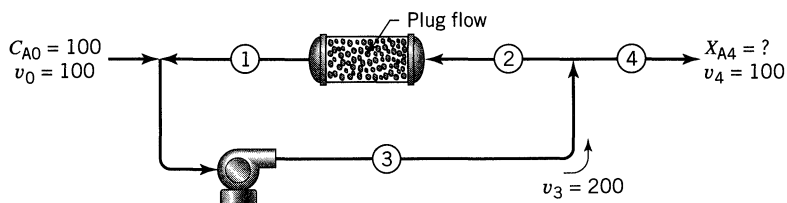
This problem is prepared from Satterfield (1970).

- 18.15.** Kinetic experiments on the solid catalyzed reaction  $A \rightarrow 3R$  are conducted at 8 atm and  $700^\circ\text{C}$  in a basket type mixed reactor  $960 \text{ cm}^3$  in volume and containing 1 gm of catalyst of diameter  $d_p = 3 \text{ mm}$ . Feed consisting of pure A is introduced at various rates into the reactor and the partial pressure of A in the exit stream is measured for each feed rate. The results are as follows:

Feed rate, liters/hr	100	22	4	1	0.6
$p_{A\text{out}}/p_{A\text{in}}$	0.8	0.5	0.2	0.1	0.05

Find a rate equation to represent the rate of reaction on catalyst of this size.

- 18.16.** “El jefe” (the chief) decided to do something to improve the low conversion ( $X_A = 0.80$ ) of our first-order solid-catalyzed liquid-phase reaction. Instead of ordering more of the expensive catalyst to fill the half-empty reactor, he decided to save money by adding some tricky piping to the present vertical packed bed reactor. When I saw what the mechanics were putting together for him, (see Fig. P18.16), I told “el jefe” that it didn’t seem right. I could sense right away that my saying this annoyed him, but all he said was, “All right, young lady. Why don’t you tell me what conversion to expect with this arrangement?” Please do this.



**Figure P18.16**

- 18.17.** The second-order reaction  $A \rightarrow R$  is studied in a recycle reactor with very large recycle ratio, and the following data are recorded:

Void volume of reactor: 1 liter

Weight of catalyst used: 3 gm

Feed to the reactor:  $C_{A0} = 2$  mol/liter

$v_0 = 1$  liter/hr

Exit stream condition:  $C_{Aout} = 0.5$  mol/liter

- Find the rate constant for this reaction (give units).
- How much catalyst is needed in a packed bed reactor for 80% conversion of 1000 liter/hr of feed of concentration  $C_{A0} = 1$  mol/liter. No recycle.
- Repeat part (b) if the reactor is packed with 1 part catalyst to 4 parts inert solid. This addition of inerts helps maintain isothermal conditions and reduce possible hot spots.

**Note:** Assume isothermal conditions throughout.

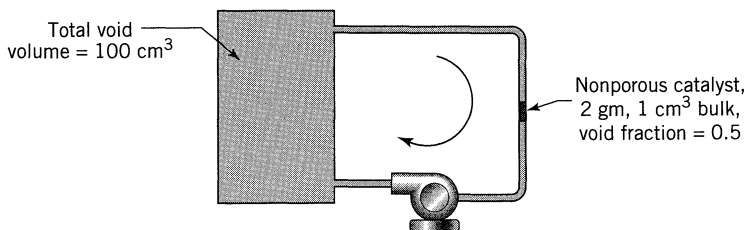
- 18.18.** A small experimental packed bed reactor ( $W = 1$  kg) using very large recycle of product stream gives the following kinetic data:

$A \rightarrow R,$		$C_A, \text{mol/m}^3$	1	2	3	6	9
$C_{A0} = 10 \text{ mol/m}^3$		$v_0, \text{liter/hr}$	5	20	65	133	540

Find the amount of catalyst needed for 75% conversion for a flow rate of 1000 mol A/hr of a  $C_{A0} = 8 \text{ mol/m}^3$  feed stream

- in a packed bed reactor with no recycle of exit fluid
  - in a packed bed reactor with very high recycle
- 18.19.** A closed loop batch G/S reactor (see Fig. P18.19) is used for catalytic rate studies. For this purpose feed gas with reactant is introduced into the system and is rapidly circulated through the catalyst loop. From the following composition-time data find a kinetic equation in units of mol/gm · min to represent this reaction.

$t, \text{min}$	0	4	8	16	36	Pure A at 609 K
$\pi_0 \text{ atm}$	1	0.75	0.67	0.6	0.55	$2A \rightarrow R$



**Figure P18.19**

- 18.20.** Our packed bed reactor runs the gas phase reaction  $A \rightarrow R$  at 10 atm and  $336^\circ\text{C}$ , and gives 90% conversion of a pure A feed. However, the catalyst salesman guarantees that in the absence of any pore diffusion resistance our reaction will proceed on his new improved porous catalyst ( $\mathcal{D}_e = 2 \times 10^{-6} \text{ m}^3/\text{m cat} \cdot \text{s}$ ) with a rate given by

$$-r_A''' = 0.88 C_A \frac{\text{mol}}{\text{m}^3 \text{ cat} \cdot \text{s}}$$

which is much better than what we now can do. The catalyst is rather expensive, since it is formulated of compressed kookaburra droppings and it is sold by weight. Still, we'll try it when we next replace our catalyst. What diameter of catalyst balls should we order?

- 18.21.** A reaction  $A \rightarrow R$  is to take place on a porous catalyst pellet ( $d_p = 6 \text{ mm}$ ,  $\mathcal{D}_e = 10^{-6} \text{ m}^3/\text{m cat} \cdot \text{s}$ ). How much is the rate slowed by pore diffusional resistance if the concentration of reactant bathing the particle is  $100 \text{ mol}/\text{m}^3$  and the diffusion-free kinetics are given by

$$-r_A''' = 0.1 C_A^2 \frac{\text{mol}}{\text{m}^3 \text{ cat} \cdot \text{s}}$$

- 18.22.** In the absence of pore diffusion resistance a particular first-order gas-phase reaction proceeds as reported below.

$$-r_A''' = 10^{-6} \text{ mol}/\text{cm}^3 \text{ cat} \cdot \text{s}$$

at

$$C_A = 10^{-5} \text{ mol}/\text{cm}^3, \quad \text{at 1 atm and } 400^\circ\text{C}$$

What size of spherical catalyst pellets ( $\mathcal{D}_e = 10^{-3} \text{ cm}^3/\text{cm cat} \cdot \text{s}$ ) would ensure that pore resistance effects do not intrude to slow the rate of reaction?

The first-order decomposition of A is run in an experimental mixed flow reactor. Find the role played by pore diffusion in these runs; in effect determine whether the runs were made under diffusion-free, strong resistance, or intermediate conditions.

<b>18.23.</b>	$d_p$	$W$	$C_{A0}$	$v$	$X_A$	$A \rightarrow R$
	3	1	100	9	0.4	
	12	4	300	8	0.6	

<b>18.24.</b>	$d_p$	$W$	$C_{A0}$	$v$	$X_A$	$A \rightarrow R$
	4	1	300	60	0.8	
	8	3	100	160	0.6	

18.25.

$d_p$	$W$	$C_{A0}$	$v$	$X_A$	
2	4	75	10	0.2	$A \rightarrow R$
1	6	100	5	0.6	

18.26. Find the activation energy of the first-order reaction from the following data:

$d_p$	$C_A$	$-r'_A$	$T, K$	
1	20	1	480	$A \rightarrow R$ $C_{A0} = 50$
2	40	1	480	
2	40	3	500	

18.27. What can you tell about the influencing resistances for the porous catalyst from the data of Table P18.27 obtained in a recycle type mixed flow reactor. In all runs the leaving stream has the same composition, and conditions are isothermal throughout.

Table P18.27

Quantity of Catalyst	Pellet Diameter	Flow Rate of Given Feed	Recycle Rate	Measured Reaction Rate, $-r'_A$
1	1	1	High	4
4	1	4	Higher still	4
1	2	1	Higher still	3
4	2	4	High	3

18.28. Experiments at 300°C in a packed bed reactor with very large recycle stream give the results shown below for the first order catalytic decomposition  $A \rightarrow R \rightarrow S$ . Under the best possible conditions (always at 300°C) what  $C_{R, \max}/C_{A0}$  may we expect, and how do you suggest we get this (what flow pattern and particle size, large or small)?

$d_p$	$W/F_{A0}$	$C_{R, \max}/C_{A0}$	
4	1	0.5	No recycle
8	2	0.5	

18.29. Experiments with a basket type mixed flow reactor on the solid catalyzed decomposition  $A \rightarrow R \rightarrow S$  give the results of Table P18.29. Under the best possible reaction conditions (always at 300°C) what is the maximum concentration of R we may expect? How do you suggest that this be obtained?

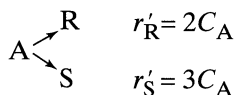
Table P18.29

Size of Porous Pellets	Temperature	$W/F_{A0}$	$C_{Rmax}/C_{A0}$
6 mm	300°C	25	23%
12 mm	300°C	50	23%

**18.30.** Reactant A at  $C_{A0} = 10 \text{ mol/m}^3$  is to be passed through a packed bed catalytic reactor where it will decompose into either R or S. To maximize the formation of R and for 90% decomposition of A determine

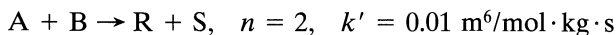
- whether to operate in the strong pore diffusion regime or in the diffusion-free regime
- whether to use plug flow or mixed flow (high recycle)
- $C_R$  expected in the exit stream.

The kinetics of the decomposition, when free of pore diffusion resistance, is given by



**18.31.** A packed bed reactor converts A to R by a first-order catalytic reaction,  $A \rightarrow R$ . With 9-mm pellets the reactor operates in the strong pore diffusion resistance regime and gives 63.2% conversion. If these pellets were replaced by 18-mm pellets (to reduce pressure drop) how would this affect the conversion?

**18.32.** We want to build a packed bed reactor filled with 1.2-cm porous catalyst particles ( $\rho_s = 2000 \text{ kg/m}^3$ ,  $\mathcal{D}_e = 2 \times 10^{-6} \text{ m}^2/\text{s}$ ) to treat  $1 \text{ m}^3/\text{s}$  of feed gas (1/3 A, 1/3 B, 1/3 inert) at 336°C and 1 atm to 80% conversion of A. Experiments with fine catalyst particles which are free from diffusional resistance show that



How much catalyst must we use?

**18.33.** In an experimental mixed flow reactor with 10 gm of 1.2-mm catalyst particles and a feed of  $4 \text{ cm}^3/\text{s}$  of pure A at 1 atm and 336°C we get 80% conversion for the first-order reaction



We want to design a commercial-sized reactor to treat large amounts of feed to 80% conversion at the above temperature and pressure. Our choice



is between a fluidized bed of 1-mm particles (assume mixed flow of gas) and a packed bed of 1.5-cm particles. Which should we choose so as to minimize the amount of catalyst needed? How much advantage is there in this choice?

*Additional Data:* For the catalyst particles:

$$\rho_s = 2000 \text{ kg/m}^3 \quad \mathcal{D}_e = 10^{-6} \text{ m}^2/\text{s}$$

In aqueous solution, and in contact with the right catalyst, reactant A is converted to product R by the elementary reaction  $A \rightarrow 2R$ . Find the mass of catalyst needed in a packed bed reactor for 90% conversion of  $10^4 \text{ mol A/hr}$  of feed having  $C_{A0} = 10^3 \text{ mol/m}^3$ . For this reaction

**18.34.**  $k''' = 8 \times 10^{-4} \text{ m}^3/\text{m}^3 \text{ bed} \cdot \text{s}$

**18.35.**  $k''' = 2 \text{ m}^3/\text{m}^3 \text{ bed} \cdot \text{s}$

*Additional data:*

Diameter of porous catalyst pellets = 6 mm

Effective diffusion coefficient of A in the pellet =  $4 \times 10^{-8} \text{ m}^2/\text{s}$

Voidage of packed bed = 0.5

Bulk density of packed bed =  $2000 \text{ kg/m}^3$  of bed

**18.36.** A first-order catalytic reaction  $A(l) \rightarrow R(l)$  is run in a long, narrow vertical reactor with upflow of liquid through a fluidized bed of catalyst particles. Conversion is 95% at the start of operations when the catalyst particles are 5 mm in diameter. The catalyst is friable and slowly wears away, particles shrink and the fine powder produced washes out of the reactor. After a few months each of the 5-mm spheres has shrunk to 3-mm spheres. What should be the conversion at this time? Assume plug flow of liquid.

- (a) Particles are porous and allow easy access for reactants (no resistance to pore diffusion).
- (b) Particles are porous and at all sizes provide a strong resistance to pore diffusion.

**18.37.** At present we are running our catalytic first-order reaction in the strong pore diffusion regime in a packed bed reactor filled with platinum impregnated 6-mm particles of uniform size. A catalyst manufacturer suggests that we replace our catalyst with 6-mm pellets consisting of fused 0.06-mm grains. The voidage between grains in the pellet would be about 25%. If these new pellets were free of pore diffusion resistance in their large voids (between grains), but if the grains were still in the strong diffusional resistance regime, how would this change affect the weight of catalyst needed and the reactor volume?

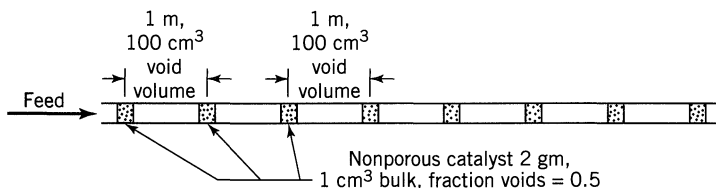
**18.38.** Instead of impregnating the whole porous particle uniformly with platinum (see Problem 18.37), suppose we only impregnate the outer layer of the

spherical particle to a thickness of 0.3 mm. How much platinum do we save by this change? Assume that we are in the strong pore diffusion regime throughout.

- 18.39.** Because the catalytic reaction  $A \rightarrow R$  is highly exothermic with rate highly temperature-dependent, a long tubular flow reactor immersed in a trough of water, as shown in Fig. P18.39, is used to obtain essentially isothermal kinetic data. Pure A at  $0^\circ\text{C}$  and 1 atm flows through this tube at  $10\text{ cm}^3/\text{sec}$ , and the stream composition is analyzed at various locations.

Distance from feed input, meters	0	12	24	36	48	60	72	84	( $\infty$ )
Partial pressure of A, mm Hg	760	600	475	390	320	275	240	215	150

Determine what size of plug flow reactor operating at  $0^\circ\text{C}$  and 1 atm would give 50% conversion of A to R for a feed rate of  $100\text{ kmol/hr}$  of pure A.



**Figure P18.39**

- 18.40.** A closed-loop experimental  $G/S$  batch system as sketched in Fig. P18.19 is used to study the kinetics of a catalytic reaction  $A \rightarrow 2R$ . Pure A is introduced into the systems and is circulated at  $0^\circ\text{C}$  and 1 atm at  $10\text{ cm}^3/\text{sec}$ . The stream is analyzed from time to time with the following results:

Time, min	0	2	4	6	8	10	12	14	( $\infty$ )
Partial pressure of A, mm Hg	760	600	475	290	320	275	240	215	150

- Determine the size of a plug flow reactor operating at  $0^\circ\text{C}$  and 1 atm required to effect a 50% conversion of A to R for a feed rate of  $100\text{ kmol A/hr}$ .
- Repeat part a with the modification that an inert at a partial pressure of 1 atm is present in the closed loop so that the total pressure at the start is 2 atm.

## The Packed Bed Catalytic Reactor

Reactant gas can be made to contact solid catalyst in many ways, and each has its specific advantages and disadvantages. Figure 19.1 illustrates a number of these contacting patterns. These may be divided into two broad types, the fixed-bed reactors of Fig. 19.1*a*, *b*, and *c* and the fluidized-bed reactors of Figs. 19.1*d*, *e*, and *f*. The moving-bed reactor of Fig. 19.1*g* is an intermediate case which embodies some of the advantages and some of the disadvantages of fixed-bed and fluidized-bed reactors. Let us compare the merits of these reactor types.

1. In passing through fixed beds, gases approximate plug flow. It is quite different with bubbling fluidized beds where the flow is complex and not well known, but certainly far from plug flow, and with considerable bypassing. This behavior is unsatisfactory from the standpoint of effective contacting and requires much more catalyst for high gas conversion, and greatly depresses the amount of intermediate which can be formed in series reactions. Hence, if efficient contacting in a reactor is of primary importance, then the fixed bed is favored.
2. Effective temperature control of large fixed beds can be difficult because such systems are characterized by a low heat conductivity. Thus in highly exothermic reactions hot spots or moving hot fronts are likely to develop which may ruin the catalyst. In contrast with this, the rapid mixing of solids in fluidized beds allows easily and reliably controlled, practically isothermal, operations. So if operations are to be restricted within a narrow temperature range, either because of the explosive nature of the reaction or because of product distribution considerations, then the fluidized bed is favored.
3. Fixed beds cannot use very small sizes of catalyst because of plugging and high-pressure drop, whereas fluidized beds are well able to use small-size particles. Thus for very fast reactions in which pore and film diffusion may influence the rate, the fluidized bed with its vigorous gas-solid contacting and small particles will allow a much more effective use of the catalyst.
4. If the catalyst has to be treated (regenerated) frequently because it deactivates rapidly, then the liquid-like fluidized state allows it to be pumped easily from unit to unit. This feature of fluidized contacting offers overwhelming advantages over fixed bed operations for such solids.

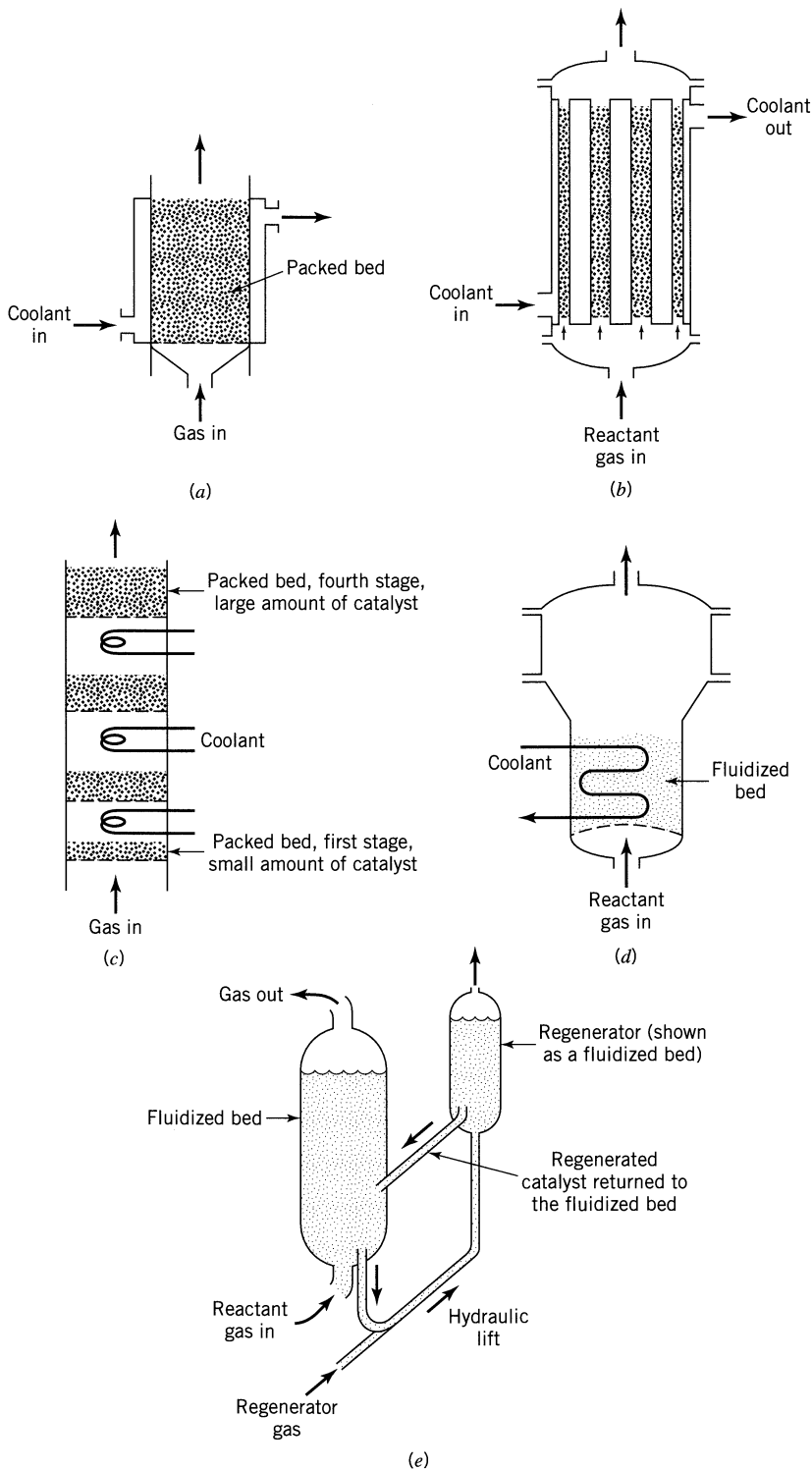
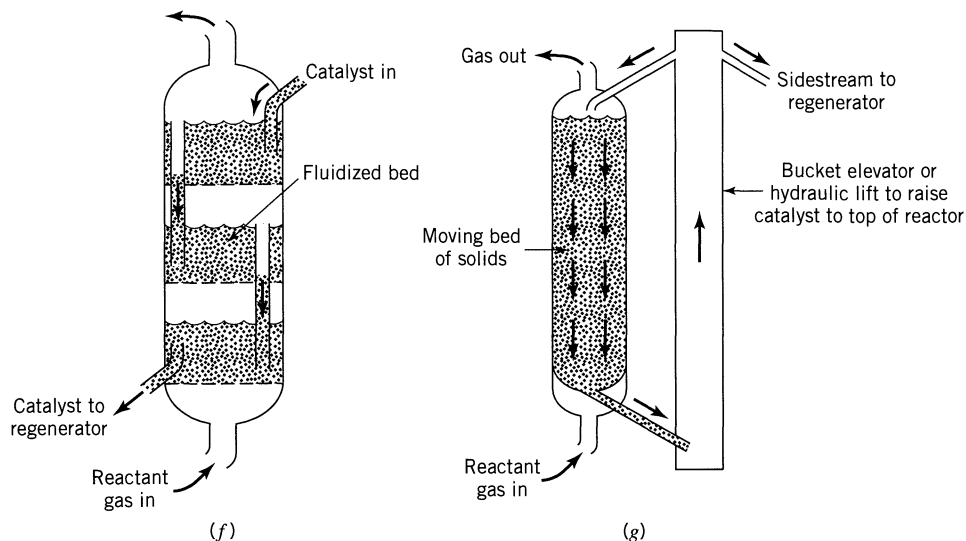


Figure 19.1 Various types of catalytic reactors.



**Figure 19.1** (Continued.)

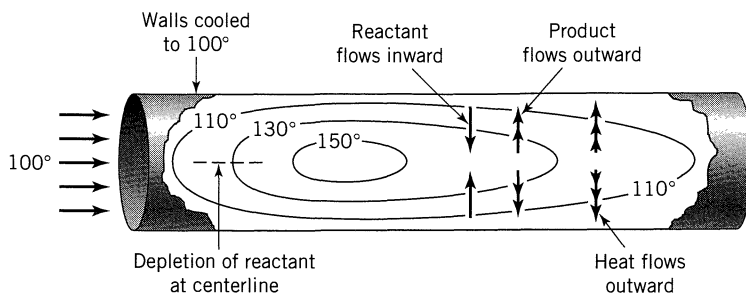
With these points in mind, let us proceed to Fig. 19.1. Figure 19.1*a* is a typical packed bed reactor embodying all its advantages and disadvantages. Figure 19.1*b* shows how the problem of hot spots can be substantially reduced by increasing the cooling surface. Figure 19.1*c* shows how intercooling can still further control the temperature. Note that in the first stage where reaction is fastest, conversion is kept low by having less catalyst present than in the other stages. Units such as these can all be incorporated in a single shell or can be kept separate with heat exchanges between stages.

Figure 19.1*d* shows a fluidized reactor for a stable catalyst which need not be regenerated. The heat exchanger tubes are immersed in the bed to remove or add heat and to control the temperature. Figure 19.1*e* shows operations with a deactivating catalyst which must be continually removed and regenerated. Figure 19.1*f* shows a three-stage countercurrent unit which is designed to overcome the shortcomings of fluidized beds with regard to poor contacting. Figure 19.1*g* shows a moving-bed reactor. Such units share with fixed beds the advantages of plug flow and disadvantages of large particle size, but they also share with fluidized beds the advantages of low catalyst-handling costs.

Many factors must be weighed to obtain optimum design, and it may be that the best design is one that uses two different reactor types in series. For example, for high conversion of a very exothermic reaction we may well look into the use of a fluidized bed followed by a fixed bed.

The main difficulties of design of catalytic reactors reduce to the following two questions: (1) How do we account for the nonisothermal behavior of packed beds? and (2) How do we account for the nonideal flow of gas in fluidized beds.

Consider a packed bed with heat exchange (Figs. 19.1*a* and 19.1*b*). For an exothermic reaction Fig. 19.2 shows the types of heat and mass movement that will occur when the packed bed is cooled at the walls. The centerline will be hotter than the walls, reaction will be faster, and reactants will be more rapidly consumed there; hence, radial gradients of all sorts will be set up.



**Figure 19.2** The temperature field in a packed bed reactor for an exothermic reaction creates radial movement of heat and matter.

The detailed analysis of this situation should include the simultaneous radial dispersion of heat and matter, and maybe axial dispersion too. In setting up the mathematical model, what simplifications are reasonable, would the results properly model the real situation, would the solution indicate unstable behavior and hot spots? These questions have been considered by scores of researchers, numerous precise solutions have been claimed; however, from the point of view of prediction and design the situation today still is not as we would wish. The treatment of this problem is quite difficult, and we will not consider it here. A good review of the state-of-the-art is given by Froment (1970), and Froment and Bischoff (1990).

The staged adiabatic packed bed reactor of Fig. 19.1c presents a different situation. Since there is no heat transfer in the zone of reaction the temperature and conversion are related simply, hence the methods of Chapter 9 can be applied directly. We will examine numerous variations of staging and heat transfer to show that this is a versatile setup which can closely approximate the optimum.

The fluidized bed and other suspended solid reactor types are considered in the next chapter.

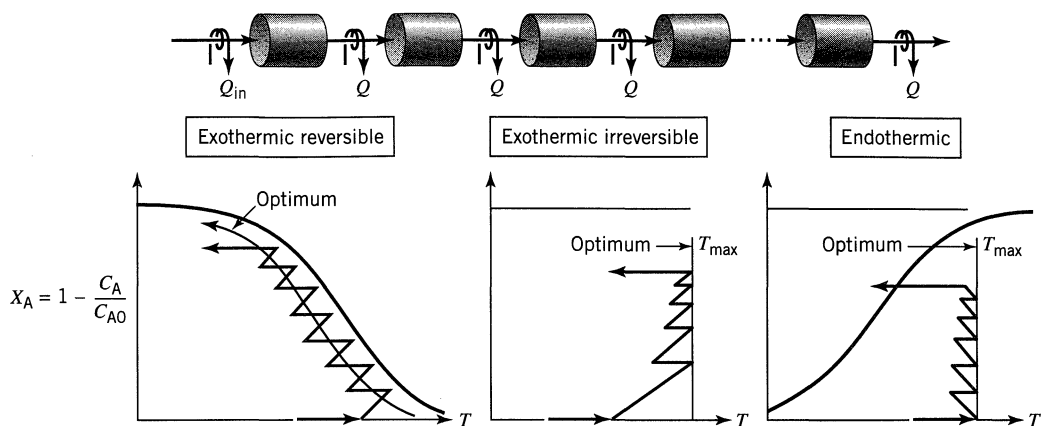
## Staged Adiabatic Packed Bed Reactors

With proper interchange of heat and proper gas flow, staged adiabatic packed beds become a versatile system, which is able to approximate practically any desired temperature progression. Calculation and design of such a system is simple, and we can expect that real operations will closely follow these predictions.

We illustrate the design procedure with the single reaction  $A \rightarrow R$  with any kinetics. This procedure can be extended to other reaction types without difficulty. We first consider different ways of operating these reactors, and then compare these and point out when one or other is favored.

**Staged Packed Beds (Plug Flow) with Intercooling.<sup>1</sup>** The reasoning in Chapter 9 shows that we would like the reacting conditions to follow the optimal tempera-

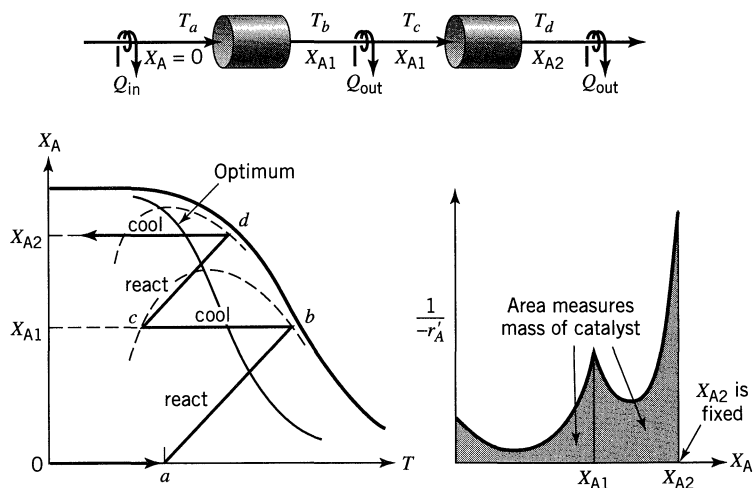
<sup>1</sup> This section follows directly from pp. 215–235 of Chapter 9. Hence it is suggested that the reader familiarize himself with that section before proceeding here.



**Figure 19.3** Sketch showing how staged packed beds can closely approach the optimal temperature progression.

ture progression. With many stages available this can be closely approximated, as shown in Fig. 19.3.

For any preset number of stages the optimization of operations reduces to minimizing the total amount of catalyst needed to achieve a given conversion. Let us illustrate the procedure for two-stage operations with *reversible exothermic reactions*. The method of attack is shown in Fig. 19.4. In this figure we wish to minimize the total area under the  $1/-r'_A$  versus  $X_A$  curve in going from  $X_A = 0$  to  $X_{A2} =$  some fixed or required conversion. In searching for this optimum we have three variables which we can set at will: the incoming temperature (point  $T_a$ ), the amount of catalyst used in the first stage (locates point  $b$  along the adiabatic), and the amount of intercooling (locates point  $c$  along the  $bc$  line). Fortunately, we are able to reduce this 3-dimensional search (5-dimensional for



**Figure 19.4** Optimum two-stage packed bed reactor.

three stages, etc.) to a one-dimensional search where  $T_a$  alone is guessed. The procedure is as follows:

1. Guess  $T_a$ .
2. Move along the adiabatic line until the following condition is satisfied:

$$\int_{\text{in}}^{\text{out}} \frac{\partial}{\partial T} \left( \frac{1}{-r'_A} \right) dX_A = 0 \quad (1)$$

This gives point  $b$  in Fig. 19.4, thus the amount of catalyst needed in the first stage as well as the outlet temperature from that stage. Especially in preliminary design it may not be convenient to use the criterion of Eq. 1. A simple alternative is a trial-and-error search. Usually two or three carefully chosen trials keeping away from low rate conditions will yield a good design, close to the optimum.

3. Cool to point  $c$  which has the same rate of reaction as point  $b$ ; thus

$$(-r'_A)_{\text{leaving a reactor}} = (-r'_A)_{\text{entering the next reactor}} \quad (2)$$

4. Move along the adiabatic from point  $c$  until the criterion of Eq. 1 is satisfied, giving point  $d$ .
- 5a. If point  $d$  is at the desired final conversion then we have guessed  $T_a$  correctly.
- 5b. If point  $d$  is not at the desired final conversion try a different incoming temperature  $T_a$ . Usually three trials will very closely approach the optimum.

For three or more stages the procedure is a direct extension of that presented here, and it still remains a one-dimensional search. This procedure was first developed by Konoki (1956a) and later, independently, by Horn (1961a).

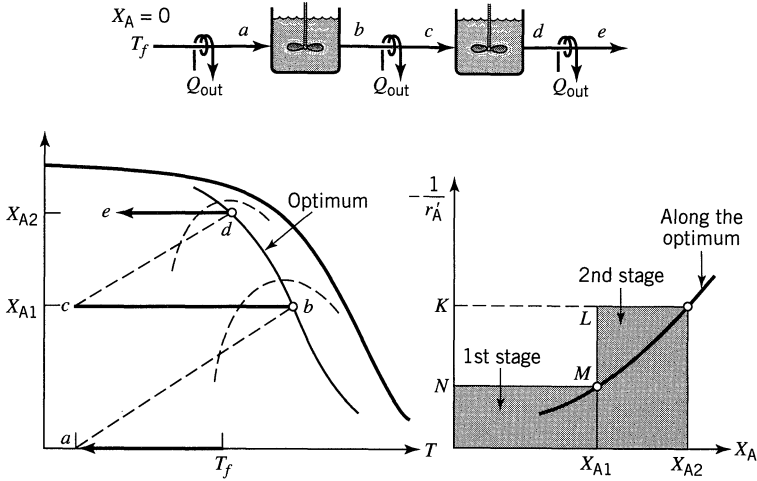
Overall cost considerations will determine the number of stages to be used, so in practice we examine 1, then 2, etc., stages until a minimum cost is obtained.

Let us next consider the two other cases of Fig. 19.3. For *irreversible exothermic reactions* the criterion for optimal operations has also been presented by Konoki (1956b). For *endothermic reactions* the optimal criterion has yet to be developed. In all these cases a trial-and-error search keeping far from the regions of low rates is recommended.

**Staged Mixed Flow Reactors.** For very high recycle the staged recycle reactors approach mixed flow. As shown in Fig. 19.5, in this case the reactors should operate on the line of optimum temperature progression, the best distribution of catalyst among the stages being found by the maximization of rectangles (see Figs. 6.9–6.11). In effect we need to choose the distribution of catalyst so as to maximize area KLMN which then minimizes the shaded area in Fig. 19.5.

**Staged Packed Beds with Recycle.** Here we have a flexible system which can approach mixed flow and as such is able to avoid regions of low rates. Figure



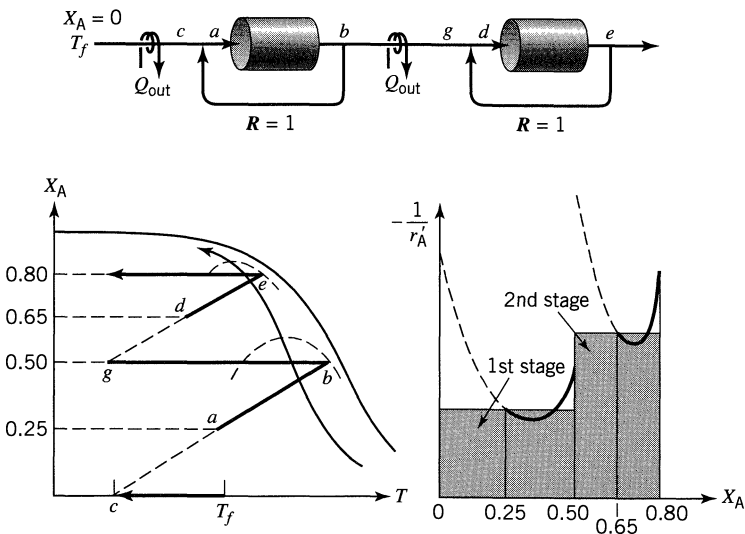


**Figure 19.5** Optimum two-stage mixed flow reactor set up (infinite recycle for staged packed beds).

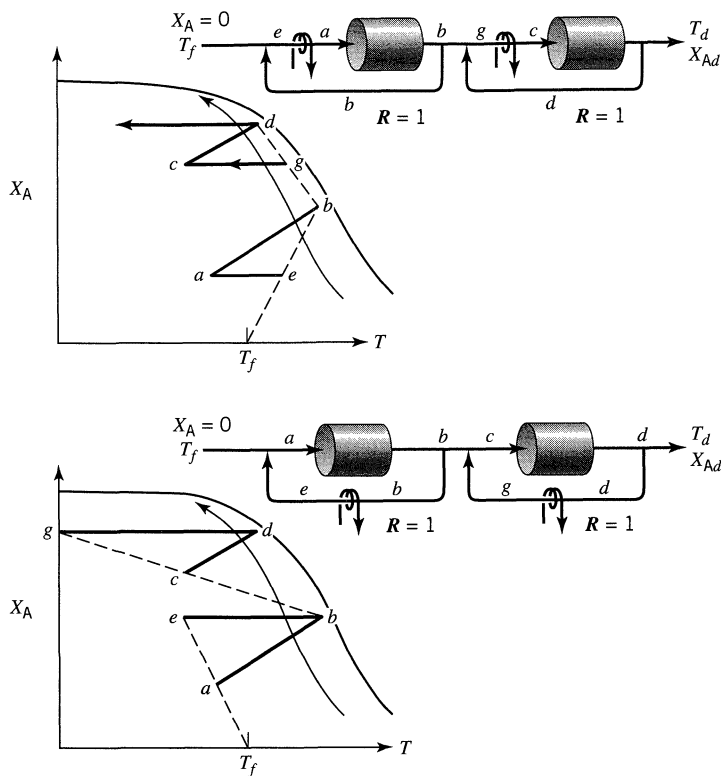
19.6 illustrates two-stage operations with a recycle ratio  $R = 1$ , and a feed temperature  $T_f$ . Extension to three or more stages follows directly.

Konoki (1961) presents the criterion for optimal operations; however, in preliminary design a few good guesses will suffice to closely approach optimal operations.

In recycle operations the heat exchangers can be located in a number of places without affecting what goes on in the reactor. Figure 19.6 illustrates one of these; other alternatives are shown in Fig. 19.7. The best location will depend on



**Figure 19.6** Optimum two-stage packed bed reactor with recycle. The conversions shown represent a recycle ratio  $R = 1$  in both stages.



**Figure 19.7** Different location for the heat exchangers while keeping the same reactor conditions as in Fig. 19.6.

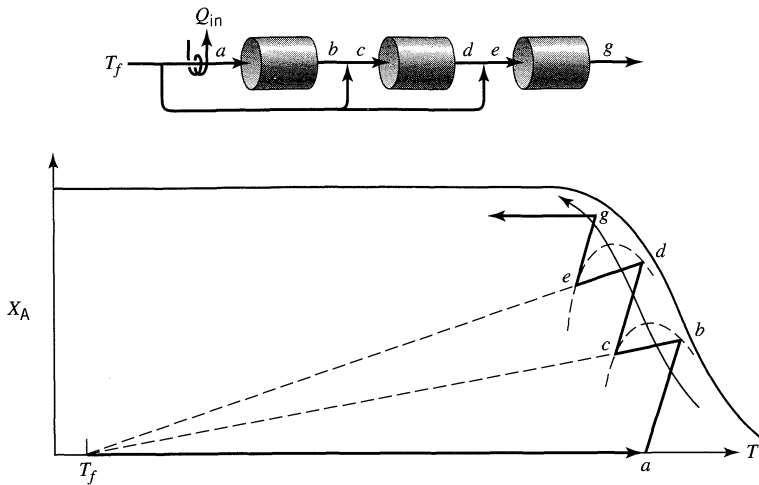
convenience for startup, and on which location gives a higher heat transfer coefficient (note that the exchanger arrangement of Fig. 19.7a has a higher through-flow of fluid than the arrangement of Fig. 19.7b).

**Cold Shot Cooling.** One way of eliminating the interstage heat exchangers is by properly adding cold feed directly into the second and succeeding stages of the reactor. The procedure is shown in Fig. 19.8. The criterion for optimal operations of such an arrangement is given by Konoki (1960), and, in somewhat different form, by Horn (1961b). They found that the extent of interstage cooling is given by Eq. 2, and this is shown in Fig. 19.8.

With cold shot cooling the calculation of reactor volumes by the  $1/-r'_A$  versus  $X_A$  curve becomes more complicated because different amounts of feed are involved in each stage. We can also cold shot cool with inert fluid. This will affect both the  $1/-r'_A$  versus  $X_A$  and  $T$  versus  $X_A$  curves.

**Choice of Contacting System.** With so many contacting alternatives let us suggest when one or other is favored.

1. For endothermic reactions the rate always decreases with conversion; hence we should always use plug flow with no recycle (see Chapter 9). For exother-



**Figure 19.8** Cold shot cooling eliminates interstage heat exchangers.

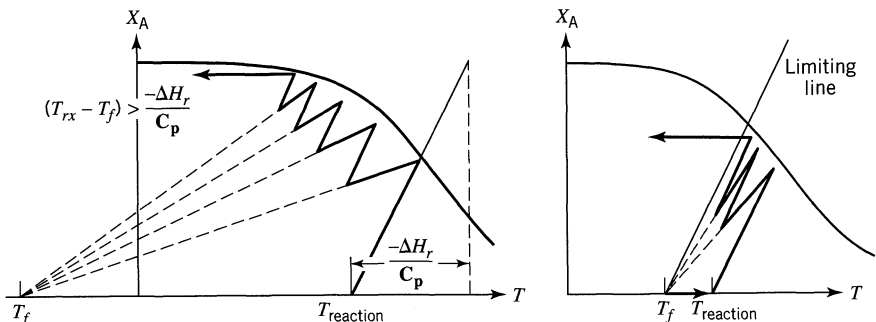
mic reactions the slope of the adiabatic line determines which contacting scheme is best. The rest of these comments concern this case of exothermic reactions.

2. All else being equal, cold shot cooling has the advantage of lower cost because interstage heat exchangers are not needed. However, cold shot cooling is only practical when the feed temperature is very much below the reaction temperature, and, in addition, when the temperature does not change much during reaction. These conditions can be summarized as follows:

Cold shot cooling is practical when

$$T_{\text{reaction}} - T_f > \frac{-\Delta H_r}{C_p}$$

Two situations, one when cold shot cooling is practical, the other when it is not, are shown in Fig. 19.9.



**Figure 19.9** Situations where cold shot cooling could be helpful and where it should not be used.

3. For exothermic reactions if the slope of the adiabatic line is low (large temperature rise during reaction) it is advantageous to avoid the low temperature regime where the rate is very low. Thus use high recycle approaching mixed flow. On the other hand, if the slope is high (small temperature rise during reaction) the rate decreases with conversion and plug flow is to be used. Typically, for pure gaseous reactant the slope of the adiabatic is small; for a dilute gas or for a liquid it is large. As an example, consider a reactant having  $C_p = 40 \text{ J/mol} \cdot \text{K}$  and  $\Delta H_r = -120\,000 \text{ J/mol}$  and inerts with  $C_p = 40 \text{ J/mol} \cdot \text{K}$ :

For a pure reactant gas stream

$$\text{slope} = \frac{C_p}{-\Delta H_r} = \frac{40}{120\,000} = \frac{1}{3000}$$

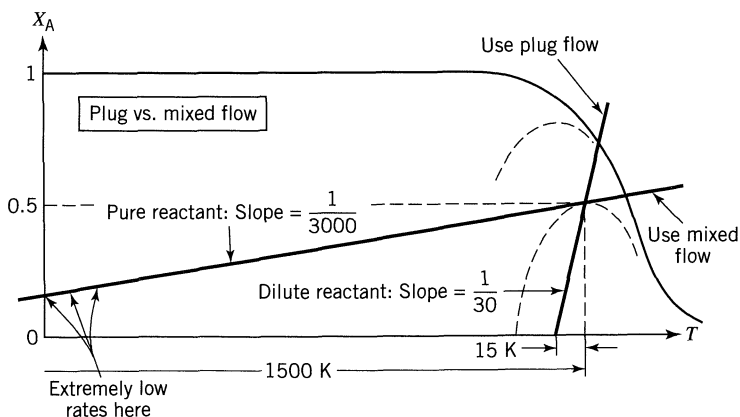
For a dilute 1% reactant gas stream

$$\text{slope} = \frac{C_p}{-\Delta H_r} = \frac{4000}{120\,000} = \frac{1}{30}$$

For a 1-molar liquid solution

$$\text{slope} = \frac{C_p}{-\Delta H_r} = \frac{4000}{120\,000} = \frac{1}{30}$$

The adiabatic lines for these cases are sketched in Fig. 19.10 and illustrate this point.



**Figure 19.10** Sketch showing why plug flow is used for steep adiabatic lines, and mixed flow (packed beds with large recycle) for lines with small slope.

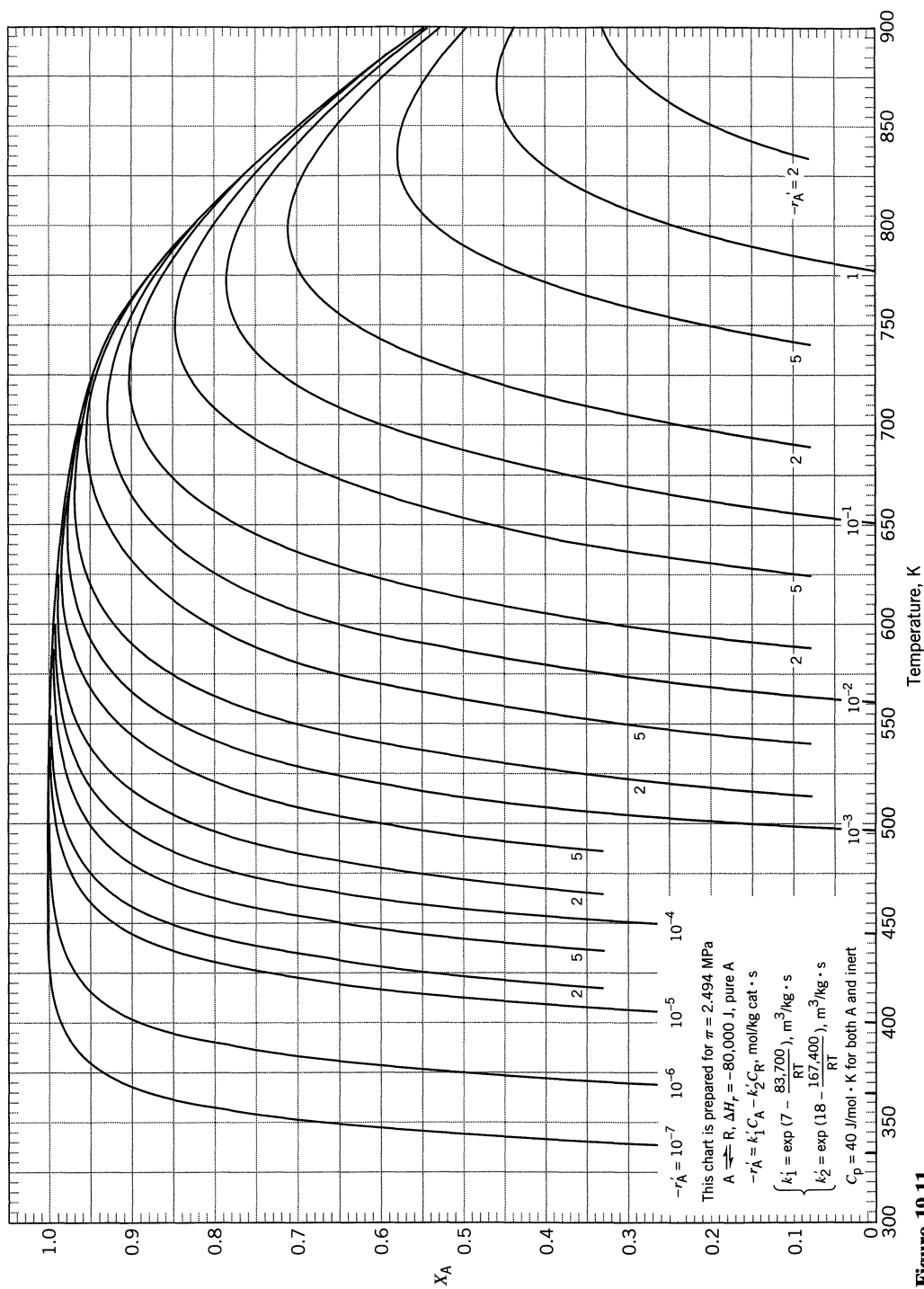


Figure 19.11

4. For exothermic reactions in staged reactors the above discussion can be summarized as follows:

For pure gas use high recycle approaching mixed flow.  
 For dilute gas (or a liquid) requiring no large preheating of feed use plug flow.  
 For a dilute gas (or a solution) requiring large preheating to bring the stream up to reaction temperature use cold shot operations.

(3)

### Preliminaries for a Set of Problems Dealing with a Single Packed Bed Reactor

A single catalytic packed bed reactor is to be designed to treat 100 mol/s of reactant A and produce product R. Feed gas enters at 2.49 MPa and 300 K, the maximum allowable temperature is 900 K unless otherwise noted, the product stream is wanted at 300 K, and the thermodynamics and kinetics of the exothermic reaction are given to us in Fig. 19.11. Prepare a sketch showing the details of the system you plan to use:

- type of reactor: plug, recycle, or mixed ( $\infty$  recycle)
- amount of catalyst needed
- heat duty ahead of the reactor, at the reactor itself, and after the reactor
- the temperature of all flowing streams

Example 19.1 treats one case, Problems 19.13 to 19.16 treat four other cases. In all these problems assume that

- we are dealing with ideal gases.
- $C_p = 40 \text{ J/mol} \cdot \text{K}$  for all materials, and at all temperatures. This means (from Example 9.1) that  $\Delta H_r$  has the same value at all temperatures.

#### EXAMPLE 19.1 DESIGN OF A SINGLE ADIABATIC PACKED BED SYSTEM

Work out a good design for 80% conversion of a feed consisting of 1 mol A and 7 mol inert.

#### SOLUTION

First determine the slope of the adiabatic line. For this note that 8 moles enter/mole of A. Thus

$$C_p = (40 \text{ J/mol} \cdot \text{K}) (8) = 320 \text{ J/(mol of A + inerts)} \cdot \text{K}$$

Thus the slope of the adiabatic is

$$\frac{C_p}{-\Delta H_r} = \frac{320}{80\,000} = 0.004 = \frac{1}{250}$$

Drawing various adiabatics in Fig. 19.11 it seems that the one shown on Fig. E19.1a looks best. So now tabulate  $X_A$  versus  $1/(-r'_A)$  from Fig. 19.11. This gives

$X_A$	$-r'_A$	$1/(-r'_A)$
0.8	0.05	20
0.78	0.1	10
0.70	0.2	5
0.60	0.225	4.4
0.50	0.2	5
0.26	0.1	10
0.10	0.05	20
0	0.03	33

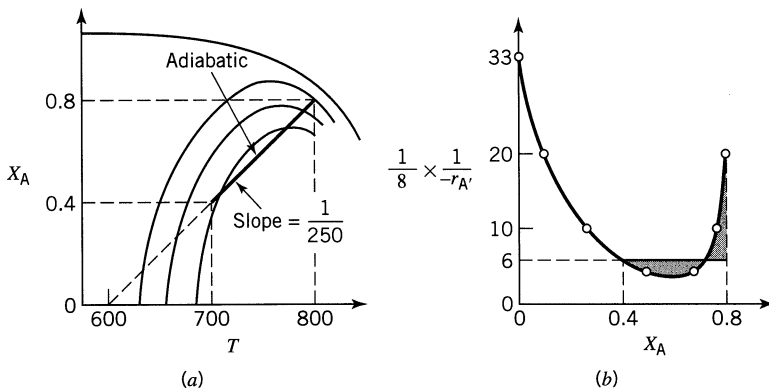
Plotting  $1/(-r'_A)$  versus  $X_A$  gives Fig. E19.1b. This tells right away that a recycle reactor should be used. Thus

$$\frac{W}{F_{A0}} = \frac{X_A}{-\bar{r}'_A} = 0.8(6 \times 8) = 38.4 \text{ kg} \cdot \text{s/mol}$$

or

$$W = F_{A0}(38.4) = (100)(38.4) = \underline{\underline{3840 \text{ kg}}}$$

The recycle ratio, from Fig. E19.1b is  $R = 1$ .



**Figure E19.1a,b**

The feed is available at 300 K, but enters the reactor at 600 K (from Fig. E19.1a), so it must be heated. Thus

$$\begin{aligned} Q_1 &= n C_p \Delta T = (800 \text{ mol/s})(40 \text{ J/mol} \cdot \text{K})(600 - 300 \text{ K}) = 9.6 \times 10^6 \text{ J/s} \\ &= \underline{\underline{9.6 \text{ MW}}} \end{aligned}$$

The product stream leaves the reactor at 800 K and must be cooled to 300 K, thus

$$\begin{aligned} Q_2 &= n C_p \Delta T = (800 \text{ mol/s})(40 \text{ J/mol} \cdot \text{K})(300 - 800 \text{ K}) = -16 \times 10^6 \text{ J/s} \\ &= \underline{\underline{-16 \text{ MW}}} \end{aligned}$$

We show our recommended design in Fig. E19.1c.

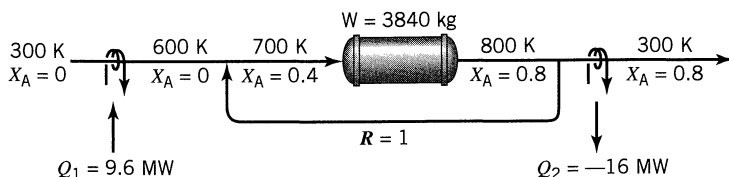


Figure E19.1c

### Preliminaries for a Set of Problems Dealing with Two Packed Bed Reactors in Series

Two catalyst filled packed bed reactors are to be designed to process 100 mol/s of reactant A so as to produce product R. Feed gas enters at 2.49 MPa and 300 K, the allowable  $T_{\max} = 900 \text{ K}$ , unless otherwise noted,  $T_{\min} = 300 \text{ K}$ , the product stream is wanted at 300 K, and the thermodynamics and kinetics of the exothermic reaction are given to us in Fig. 19.11. Prepare a sketch of your recommended design and on it show

- the flow arrangement selected: plug, recycle (give  $R$  value), or mixed (when ever  $R > 5$ ). Do not consider injection of cold fluid between stages unless the problem states that you are permitted to do so.
- weight of catalyst needed in each stage.
- location and duty of heat exchangers.
- temperature of the flowing streams.

### EXAMPLE 19.2 DESIGN OF A TWO ADIABATIC PACKED BED SYSTEM

Work out a good design for 85% conversion of a pure A feed to two packed beds.

#### SOLUTION

First determine the slope of the adiabatic line and draw it lightly on Fig. 18.11.

$$\text{slope} = \frac{C_p}{-\Delta H_r} = \frac{40}{80\,000} = \frac{1}{2000}$$



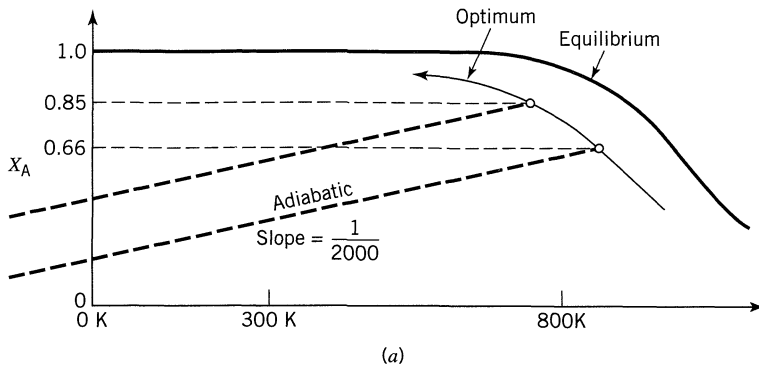


Figure E19.2a

This gives a very shallow adiabatic, as sketched in Fig. E19.2a. The rate continually increases as you move along this adiabatic, thus use a mixed flow reactor operating at the optimum.

To minimize the amount of catalyst needed Chapter 6 says use the method of maximization of rectangles, so tabulate  $X_A$  versus  $1/(-r'_A)_{\text{opt}}$

$X_A$	$(-r'_A)_{\text{opt}}$	$1/(-r'_A)_{\text{opt}}$
0.85	0.05	20
0.785	0.1	10
0.715	0.2	5
0.66	0.28	3.6
0.58	0.5	2
0.46	1.0	1

And use the method of maximization of rectangles as shown in Fig. E19.2b. Then from the performance equation

$$\frac{W}{F_0} = (X_A) \frac{1}{(-r'_A)_{\text{opt}}} = \left( \text{shaded area} \right) \text{ in Fig. E19.2b}$$

we have

$$W_1 = F_{A0} (\text{area})_1 = 100 (2.376) = \underline{\underline{237.6 \text{ kg}}}$$

and

$$W_2 = F_{A0} (\text{area})_2 = 100 (3.819) = \underline{\underline{381.9 \text{ kg}}}$$

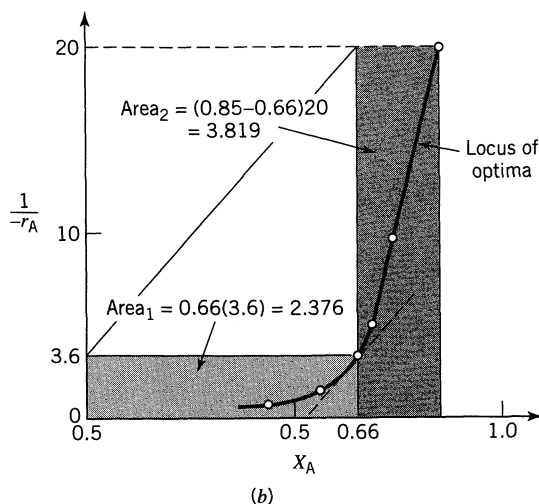


Figure E19.2b

Now to heat exchange:

**For the first reactor.** If we want to cool the feed before introducing it into the first reactor we'd have to cool it to

$$820 - 2000(0.6) = -380 \text{ K}$$

which is well below absolute zero. This is impossible. So we have to cool it somewhere inside the recycle reactor loop as shown in Fig. E19.2c. But wherever you put the exchanger the amount of heating or cooling needed is the same.

So to go to 66% conversion at 820°C the amount of heat needed per mole of A is

$$\underbrace{(820 - 300)40}_{\text{heat in}} + 0.66 \underbrace{(-80000)}_{\text{heat out}} = -32\,000 \text{ J/mol}$$

But for 100 mol/s of feed

$$Q_1 = (32\,000 \text{ J/mol})(100 \text{ mol/s}) = \underline{\underline{-3.2 \text{ MW}}} \text{ (cooling)}$$

**For the second reactor.** To go from  $X_A = 0.66$  at 820 K to  $X_A = 0.85$  at 750 K requires, per mole

$$(750 - 820)40 + (0.85 - 0.66)(-80\,000) = -18\,000 \text{ J/mol}$$

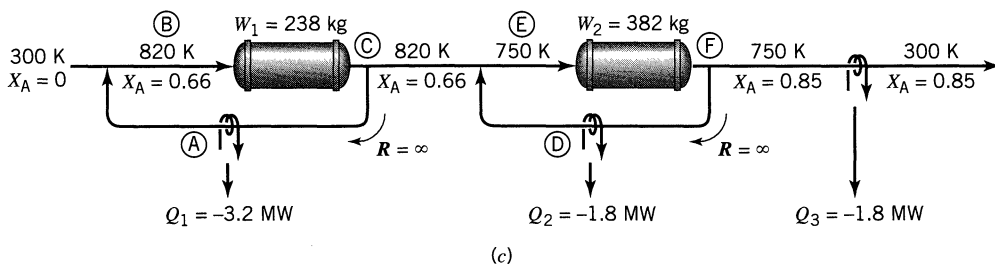
So for 100 mol/s

$$Q_2 = (-18\,000)(100) = \underline{\underline{-1.8 \text{ MW}}} \text{ (cooling)}$$

Similarly for the exchanger needed to cool the exit stream from 750 K to 300 K

$$Q_3 = 100(40)(300 - 750) = \underline{\underline{-1.8 \text{ MW}}}$$

So our recommended design is shown in Fig. E19.2c.



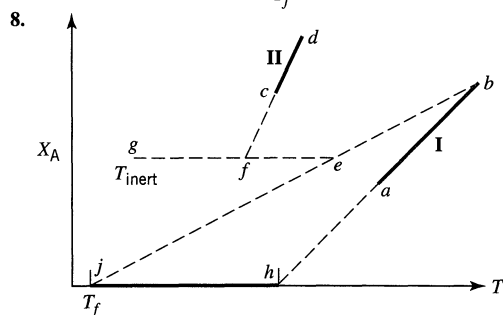
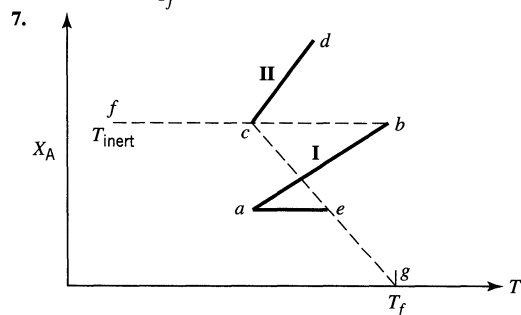
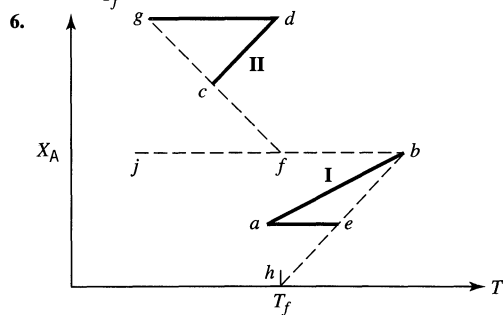
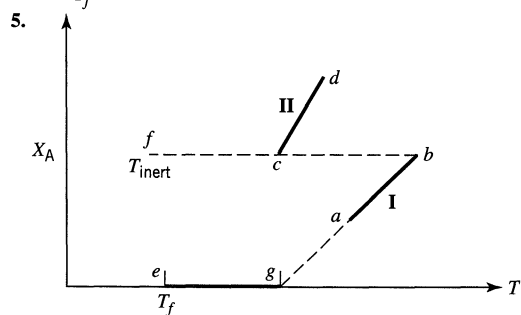
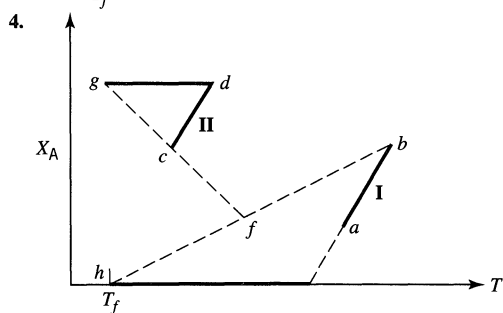
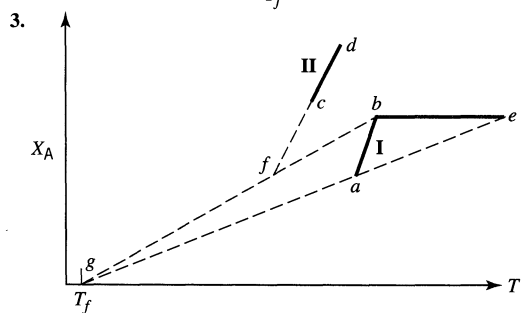
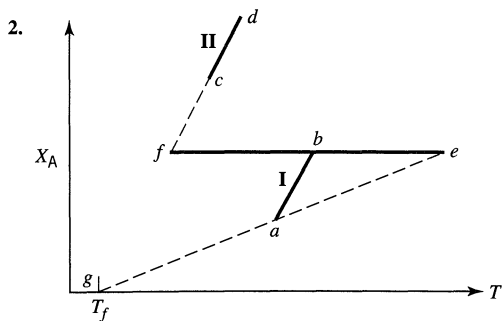
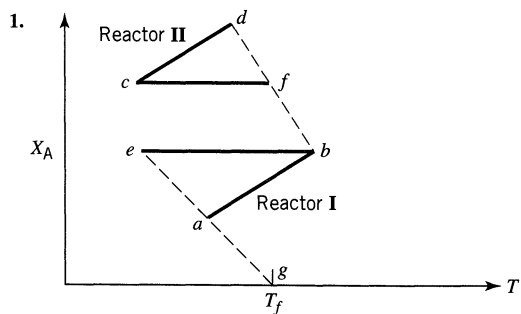
**Figure E19.2c** Note: exchanger  $Q_1$  can be placed at A, B, or C and exchanger  $Q_2$  can be placed at D, E, or F.

## REFERENCES

- Froment, G. F., First Symp. on C.R.E., Washington, D.C., June 1970, Advances in Chemistry Series No. 109, A.C.S., 1972.
- and Bischoff, K. B., *Chemical Reactor Analysis and Design*, 2nd ed., John Wiley and Sons, 1990.
- Horn, F., *Z. Electrochemie*, **65**, 295 (1961a).
- , *Chem. Eng. Sci.*, **14**, 20 (1961b).
- Konoki, K. K., *Chem. Eng. (Japan)*, **21**, 408 (1956a).
- , *Chem. Eng. (Japan)*, **21**, 780 (1956b).
- , *Chem. Eng. (Japan)*, **24**, 569 (1960).
- , *Chem. Eng. (Japan)*, **25**, 31 (1961).

## PROBLEMS

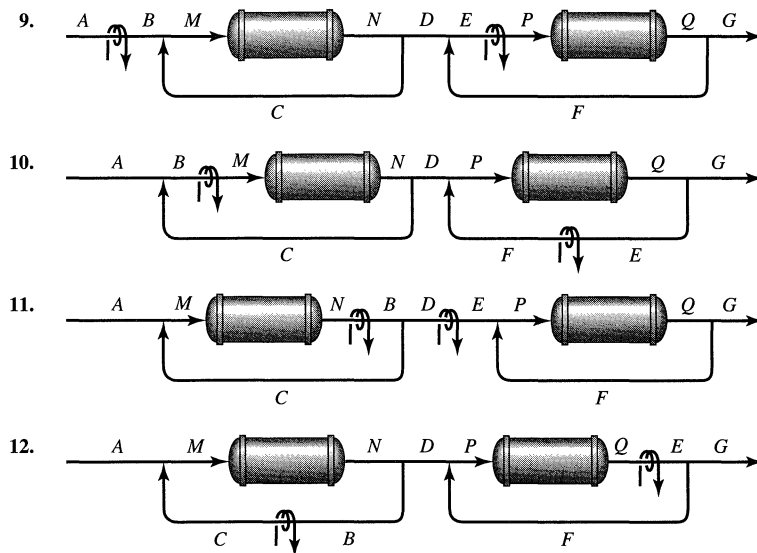
- 19.1–19.8.** Sketch the flow sheet for the two reactor system represented by the  $X_A$  versus  $T$  diagrams Figs. P.19.1 to Fig. P.19.8, and on the sketch show
- the flow rate of all streams for each 100 mol of entering fluid, and where pertinent give the recycle ratios.
  - the location of the heat exchangers and indicate whether they cool or heat.



Figures P19.1 to P19.8

**19.9–19.12.** Sketch the  $X_A$  versus  $T$  diagram for the two packed bed reactor system shown in Figs. P19.9 to P19.12 for an exothermic reaction where

- conversion:  $X_{A1} = 0.6$ ,  $X_{A2} = 0.9$ .
- recycle ratio:  $R_1 = 2$ ,  $R_2 = 1$ .
- heat exchangers all cool the reacting fluid.



**Figures P19.9 to p19.12**

---

For the single reactor situation outlined in the text and followed by Example 19.1 let us here consider four alternatives. We plan to use

- 19.13.** . . . pure A feed,  $X_A = 0.85$ , in a reactor which follows the optimal temperature progression.
  - 19.14.** . . . a 50% A–50% inert feed,  $X_A = 0.70$ , in an adiabatic reactor of your choice.
  - 19.15.** . . . a 20% A–80% inert feed to an adiabatic reactor of your choice whose outlet is at  $X_A = 0.75$  and  $T = 825$  K.
  - 19.16.** . . . a 5% A–95% inert feed,  $X_A = 0.5$ , in an adiabatic reactor of your choice.
-

For the two-reactor situation outlined in the text and followed by Example 19.2 let us consider five alternatives, thus

**19.17.** . . . a pure A feed,  $X_A = 0.85$ .

**19.18.** . . . a pure A feed,  $X_A = 0.85$  and  $T_{\max} = 550$  K. In this problem, do not worry about the possibility of an unstable operating point. But before you build such a unit, you'd better check for this—otherwise you'll be in trouble.

**19.19.** . . . a 20% A–80% inert feed,  $X_A = 0.85$

**19.20.** . . . a 40% A–60% inert feed,  $X_A = 0.95$

**19.21.** . . . a 5% A–95% inert feed,  $X_A = 0.95$  (try cold feed injection)

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# Chapter 20

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## Reactors with Suspended Solid Catalyst, Fluidized Reactors of Various Types

The formation of phthalic anhydride is highly exothermic, and even with the most careful design the heat removal from packed bed reactors can become uncheckable, leading to temperature runaways, meltdowns, and even explosions. If the chief engineer of those reactors had been required to sit on the reactor during start up, there would be fewer chief engineers about.<sup>1</sup>

The invention of the fluidized bed with its suspended and rapidly mixing solids completely overcame this dangerous situation. This is because the rapid mixing of solids, and the large heat sink (the solids) will only allow the bed temperature to change very slowly, and it can be easily controlled.

Another problem—catalyst formulators (those magicians) have been very successful in creating better and better catalysts, those that give higher and higher rates of reaction. But to use the whole of the catalyst volume effectively we must keep the Thiele modulus

$$M_T = L \sqrt{\frac{k'''}{\mathcal{D}_e}} < 0.4$$

This means using smaller and smaller particles as  $k'''$  is made larger and larger.

This leads us to use suspended solids. Also note that with these very effective catalysts the required residence time of reactant gas becomes very small, say a few seconds for a large 30-m high reactor.

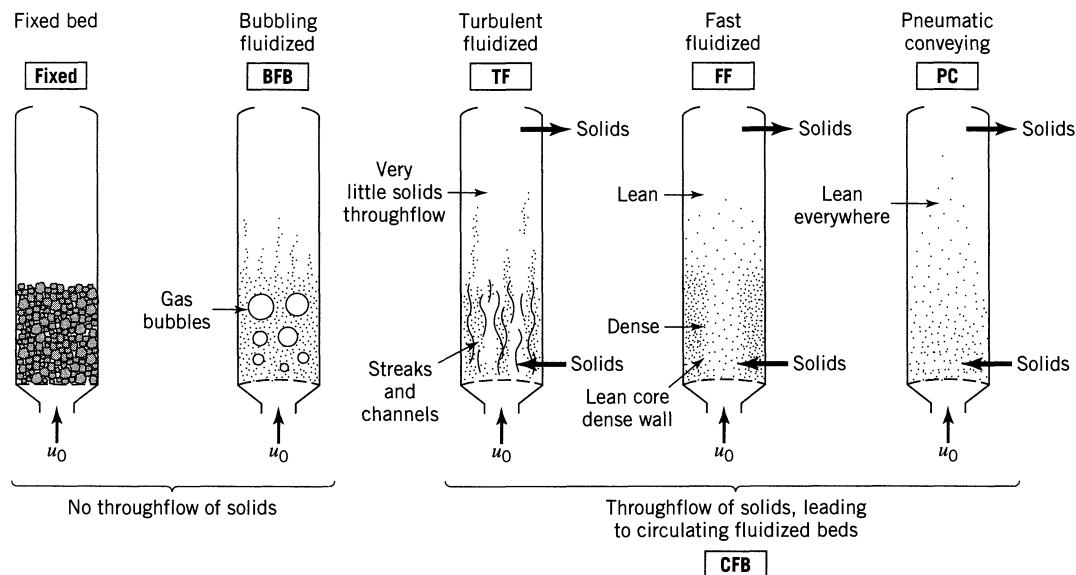
Figure 20.1 shows the transition from fixed to BFB to TF to FF to PC reactors.

### 20.1 BACKGROUND INFORMATION ABOUT SUSPENDED SOLIDS REACTORS

This is a vast subject, but we must be brief and can only touch on the highlights. See Kunii and Levenspiel (1991) for a much more complete presentation.

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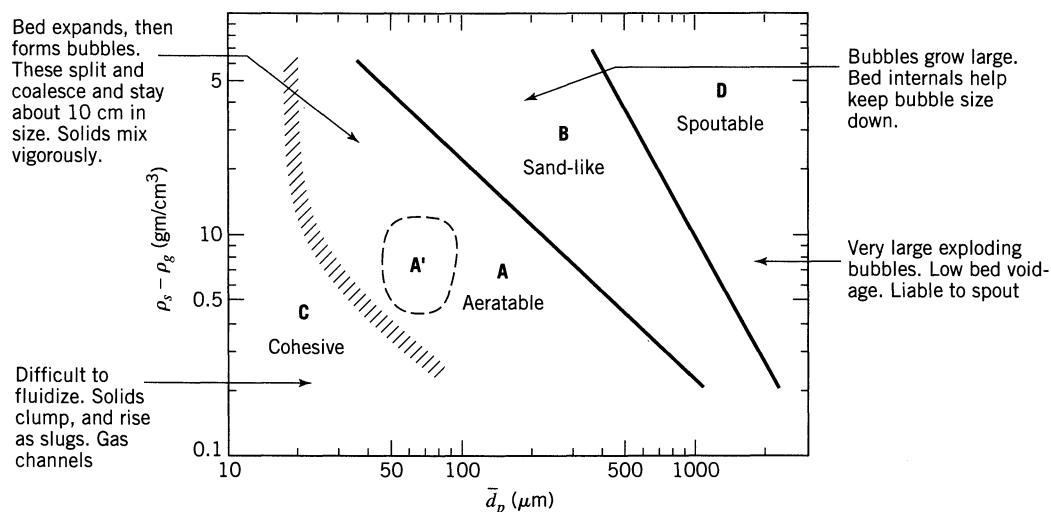
<sup>1</sup> “They ought to give medals for making phthalic,” *Chem. Week*, **70**, 40 (1952).



**Figure 20.1** *G/S* contacting regimes, from low to very high gas velocity.

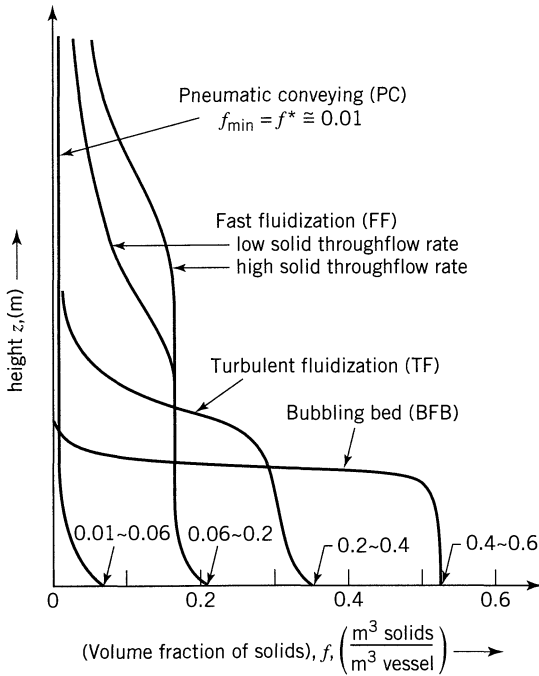
First, Geldart (1973) and Geldart and Abrahamson (1978) looked at how different kinds of solids behaved when fluidized, and came up with the following simple classification of solids which we now call the Geldart classification, thus Geldart A, B, C, D. These are shown and described in Fig. 20.2.

Next consider the distribution of solids in the vertical vessel. Let  $f$  be the volume fraction of solids at height  $z$  of the vessel. Then as shown in Fig. 20.3 when we go to higher and higher gas velocities the solids spread throughout the vessel.



**Figure 20.2** Geldart classification of solids in BFB.





**Figure 20.3** Distribution of solids in the various contacting regimes.

**G/S Contacting Regimes.** To develop the language that tells what contacting regime we have at hand consider solids of size  $d_p$  in a bed of cross-sectional area  $A$  which is fed gas at a superficial gas velocity  $u_0$ , as shown in Fig. 20.4.

To simplify the equations let us start by defining two dimensionless quantities

$$d_p^* = d_p \left[ \frac{\rho_g(\rho_s - \rho_g)g}{\mu^2} \right]^{1/3} \quad (1)$$

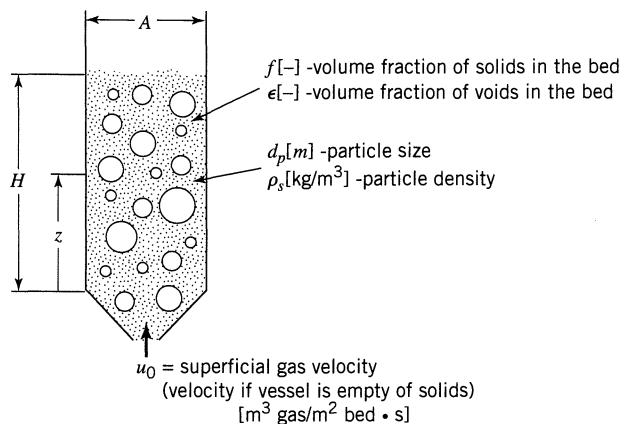
$$u^* = u \left[ \frac{\rho_g^2}{\mu(\rho_s - \rho_g)g} \right]^{1/3} = \frac{(\text{Re}_p)}{d_p^*} \quad (2)$$

$$\left. \begin{array}{l} (1) \\ (2) \end{array} \right\} \text{Re}_p = u^* d_p^*$$

**Minimum Fluidizing Velocity.** The solids will be suspended when the pressure drop exceeds the weight of solids. This happens when the gas velocity exceeds the minimum fluidizing velocity  $u_{mf}$ . This velocity is given by Ergun (1952), and in dimensionless form is

$$150(1 - \epsilon_{mf})u_{mf}^* + 1.75(u_{mf}^*)^2 d_p^* = \epsilon_{mf}^3 (d_p^*)^2 \quad (3)$$

**Terminal Velocity,  $u_t$ .** Individual particles are blown out of the bed when the gas velocity exceeds what is called the terminal velocity,  $u_t$ . Haider and Levens-



**Figure 20.4** Notation for a bed of suspended solids.

piel (1989) give this velocity for *spherical particles* as

$$u_t^* = \left[ \frac{18}{(d_p^*)^2} + \frac{0.591}{(d_p^*)^{1/2}} \right]^{-1} \quad (4)$$

and for *irregularly shaped particles* of sphericity  $\phi_s$

$$u_t^* = \left[ \frac{18}{(d_p^*)^2} + \frac{2.335 - 1.744 \phi_s}{(d_p^*)^{1/2}} \right]^{-1} \quad (5)$$

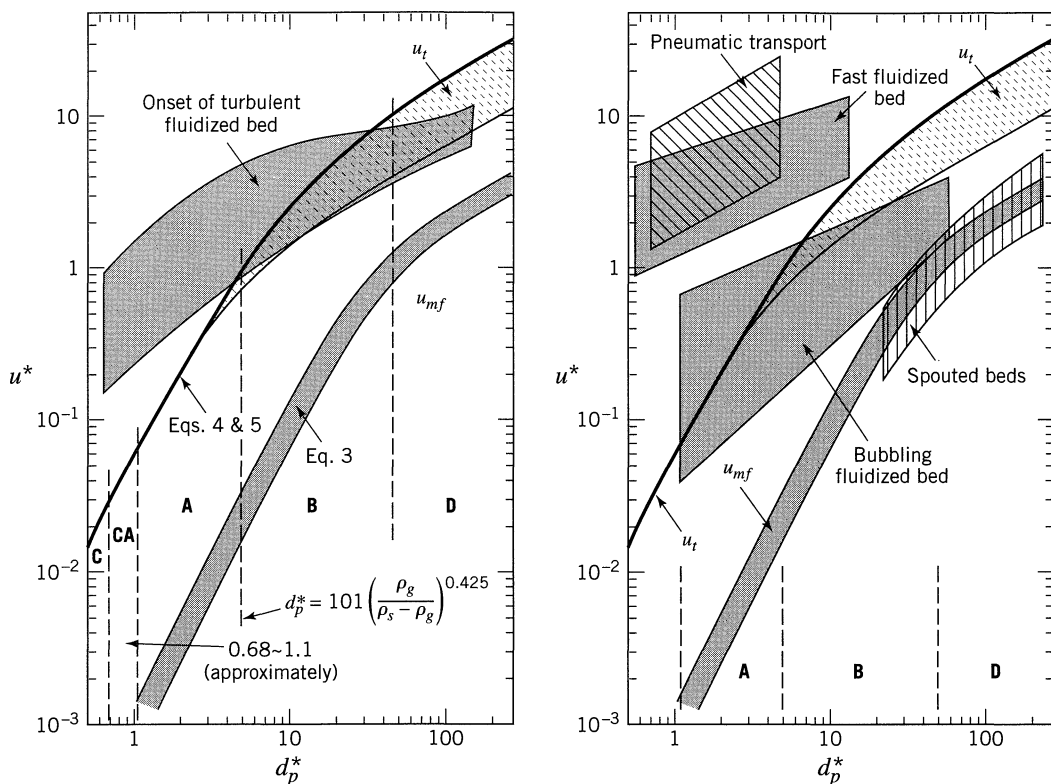
where the particle sphericity  $\phi_s$  is defined as

$$\phi_s = \left( \frac{\text{surface of a sphere}}{\text{surface of a particle}} \right)_{\text{same volume}} \quad (6)$$

For fine particles we evaluate the size by screen analysis, which gives  $d_{\text{scr}}$ . Unfortunately, there is no general relationship between  $d_{\text{scr}}$  and  $d_p$ . The best we can say for pressure drop considerations is

- $d_p = \phi_s d_{\text{scr}}$  for irregular particles with no seeming longer or shorter dimension
- $d_p \cong d_{\text{scr}}$  for irregular particles with one somewhat longer dimension but with length ratio not greater than 2:1 (eggs, for example)
- $d_p \cong \phi_s^2 d_{\text{scr}}$  for irregular particles with one shorter dimension but with length ratio not less than 1:2 (pillows, for example)

Although a single particle will be entrained by a stream of gas flowing faster than  $u_t$ , this finding does not extend to a fluidized bed of particles. In the BFB the gas velocity can be many times greater than  $u_t$  with very little carryover of solids. Thus the single particle terminal velocity is not very useful in estimating when entrainment of solids will become appreciable.



**Figure 20.5** General flow regime diagram for the whole range of  $G/S$  contacting.

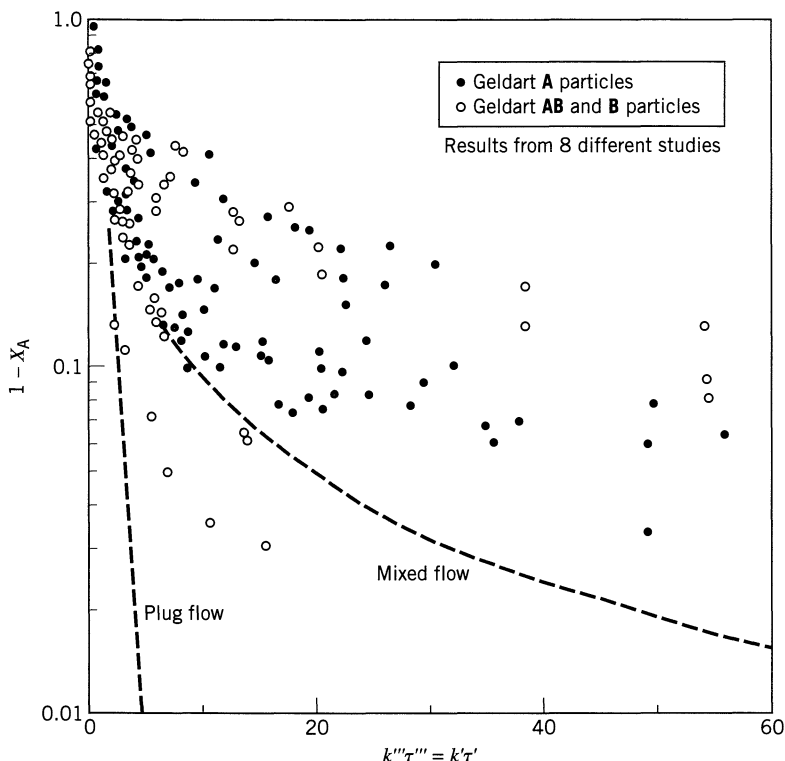
**General Chart Showing  $G/S$  Contacting Regimes.** Grace (1986) prepared a graph to show the expected behavior of  $G/S$  systems all the way from BFB to CFB. Figure 20.5 shows a somewhat modified version of this chart. In it you will see Eqs. 3, 4, and 5, which tell when the bed will fluidize and when solids will begin to entrain from the vessel.

We now look at the various contacting regimes in detail and see what predictions are available for each regarding reactor behavior.

## 20.2 THE BUBBLING FLUIDIZED BED—BFB

Pass gas upward through a bed of fine particles. For superficial (or inlet) gas velocities  $u_0$  much in excess of this minimum the bed takes on the appearance of a boiling liquid with large bubbles rising rapidly through the bed. In this state we have the *bubbling fluidized bed*, BFB. Industrial reactors particularly for solid catalyzed gas-phase reactions often operate as bubbling beds with gas velocities  $u_0 = 5 \sim 30 u_{mf}$ .

Calculations show that the conversion in bubbling beds may vary from plug flow to well below mixed flow, see Fig. 20.6, and for many years the perplexing and embarrassing thing about this was that often we could not reliably estimate



**Figure 20.6** Conversion of reactant in BFB is usually poorer than for both plug flow and mixed flow. Adapted from Kunii and Levenspiel (1991).

or guess what it would be for any new situation. Because of this, scale-up was cautious and uncertain, and preferably left to others.

It was soon recognized that this difficulty stemmed from lack of knowledge of the contacting and flow pattern in the bed: in effect, the bypassing of much of the solids by the rising bubble gas. This led to the realization that adequate prediction of bed behavior had to await a reasonable flow model for the bed.

Since the bubbling bed represents such severe deviations from ideal contacting, not just minor ones as with other single-fluid reactors (packed beds, tubes, etc.), it would be instructive to see how this problem of flow characterization has been attacked. A wide variety of approaches have been tried. We consider these in turn.

**Dispersion and Tanks in Series Model.** The first attempts at modeling naturally tried the simple one-parameter models; however, observed conversion well below mixed flow cannot be accounted for by these models so this approach has been dropped by most workers.

**RTD Models.** The next class of models relied on the RTD to calculate conversions. But since the rate of catalytic reaction of an element of gas depends on the amount of solid in its vicinity, the effective rate constant is low for bubble gas, high for emulsion gas. Thus any model that simply tries to calculate conver-

sion from the RTD and the fixed rate constant in effect assumes that all elements of gas, both slow and fast moving, spend the same fraction of time in each of the phases. As we will show when we treat the details of gas contacting in fluidized beds this assumption is a shaky one, hence the direct use of the RTD to predict conversions, as developed for linear systems in Chapter 11, is quite inadequate.

**Contact Time Distribution Models.** To overcome this difficulty and still use the information given by the RTD, models were proposed which assumed that faster gas stayed mainly in the bubble phase, the slower in the emulsion. Gilliland and Knudsen (1971) used this approach and proposed that the effective rate constant depends on the length of stay of the element of gas in the bed, thus

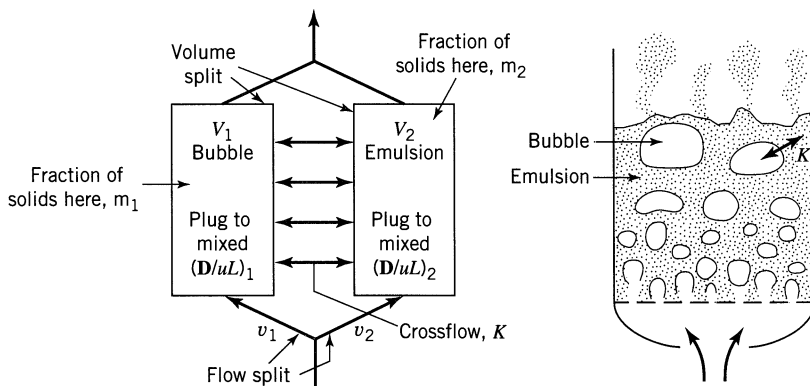
$$\left. \begin{array}{l} \text{short stay means small } k \\ \text{long stay means large } k \end{array} \right\} \quad \text{or } k = k_0 t^m$$

where  $m$  is a fitted parameter. Thus combining with Eq. 11.13 we find for the conversion

$$\frac{\bar{C}_A}{C_{A0}} = \int_0^\infty e^{-kt} \mathbf{E} dt = \int_0^\infty e^{-k_0 t^{m+1}} \mathbf{E} dt \quad (7)$$

The problem with this approach involves obtaining a meaningful  $\mathbf{E}$  function to use in Eq. 7 from a measured C-curve. This approach has also been discarded.

**Two-Region Models.** Recognizing that the bubbling bed consists of two rather distinct zones, the bubble phase and the emulsion phase, experimenters spent much effort in developing models based on this fact. Since such models contain six parameters, see Fig. 20.7, many simplifications and special cases have been explored (eight by 1962, 15 by 1972, and over two dozen to date), and even the complete six-parameter model of Fig. 20.7 has been used. The users of this model,



**Figure 20.7** Two-phase model to represent the bubbling fluidized bed, with its six adjustable parameters,  $v_1$ ,  $V_1$ ,  $(D/uL)_1$ ,  $(D/uL)_2$ ,  $m_1$ ,  $K$ .

those dealing with FCC reactors, claim that this model fits their data beautifully. However, they had to choose different sets of parameter values for each crude oil feed, in each of their FCC reactors. Also some of the values for their parameters made no physical sense, for example, a negative value for  $V_1$  or  $v_2$ .

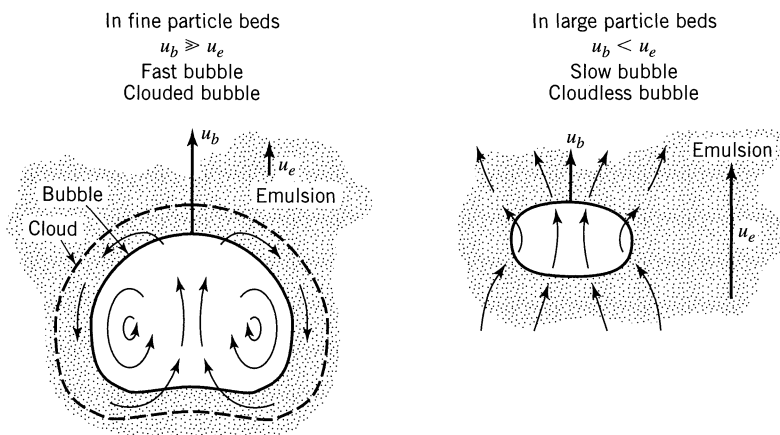
With this as the situation we should also discard this type of model which gives a perfect fit but predicts nothing, and brings no understanding with it. The reason is that we have no idea how to assign values to the parameters for new conditions. Thus this is just a curve-fitting model, and we should be able to do better.

**Hydrodynamic Flow Models.** The discouraging result with the previous approaches lead us reluctantly to the conclusion that we must know more about what goes on in the bed if we hope to develop a reasonable predictive flow model. In particular we must learn more about the behavior of rising gas bubbles, since they probably cause much of the difficulty.

Two developments are of particular importance in this regard. The first is Davidson's remarkable theoretical development and experimental verification [see Davidson and Harrison (1963) for details] of the flow in the vicinity of a single rising bubble in a fluidized bed which is otherwise at minimum fluidizing conditions. What he found was that the rise velocity of the bubble  $u_{br}$  depends only on the bubble size, and that the gas behavior in the vicinity of the bubble depends only on the relative velocity of rising bubble and of gas rising in the emulsion  $u_e$ . In the extremes he found completely different behavior, as shown in Fig. 20.8. For catalytic reactions we are only interested in fine particle beds, so let us ignore the large particle extreme from now on.

Now, for the fine particle bed gas circulates within the bubble plus a thin cloud surrounding the bubble. Thus the bubble gas forms a vortex ring and stays segregated from the rest of the gas in the bed. Theory says that

$$\left( \frac{\text{thickness of cloud}}{\text{diameter of bubble}} \right) \cong \frac{u_e}{u_{br}} \quad (8)$$



**Figure 20.8** Extremes of gas flow in the vicinity of rising gas bubbles in BFBs.

As an example if the bubble rises 25 times as fast as the emulsion gas (not all that uncommon because this ratio is 100 or more in some industrial operations), then the cloud thickness is just 2% of the bubble diameter. This is the regime which interests us.

The second finding on single bubbles is that every rising gas bubble drags behind it a wake of solids. We designate this wake by  $\alpha$ , where

$$\alpha = \left( \frac{\text{volume of wake}}{\text{volume of bubble}} \right) \cdot \cdot \cdot \begin{cases} \alpha \text{ varies between 0.2 and 2.0} \\ \text{depending on the research study} \end{cases} \quad (9)$$

See Rowe and Partridge (1962, 1965) for the original study which discovered this.

### 20.3 THE K-L MODEL FOR BFB

Hydrodynamic type flow models can be developed to represent the BFB, based on the above two seemingly simple findings. Let us consider and develop the simplest of these, the K-L BFB model.

Pass an excess of gas upward through a bed of fine particles. With a large enough bed diameter we get a freely bubbling bed of fast bubbles. As simplifications, assume the following:

- The bubbles are all spherical, all of the same size  $d_b$ , and all follow the Davidson model. Thus the bed contains bubbles surrounded by thin clouds rising through an emulsion. We ignore the upflow of gas through the cloud because the cloud volume is small compared to that of the bubble. This is the regime where  $u_b \gg u_e$  (see Fig. 20.8).
- The emulsion stays at minimum fluidization conditions, thus the relative G/S velocity stays constant in the emulsion.
- Each bubble drags up a wake of solids behind it. This generates a circulation of solids in the bed, upflow behind the bubbles, and downflow everywhere else in the bed. If this downflow of solids is rapid enough then gas upflow in the emulsion is impeded, can actually stop, and even reverse itself. Such downflow of gas has been observed and recorded, and occurs when

$$u_0 > (3 \text{ to } 11) u_{mf}$$

We ignore any upflow or downflow of gas in the emulsion. We show this model in Fig. 20.9.

Let

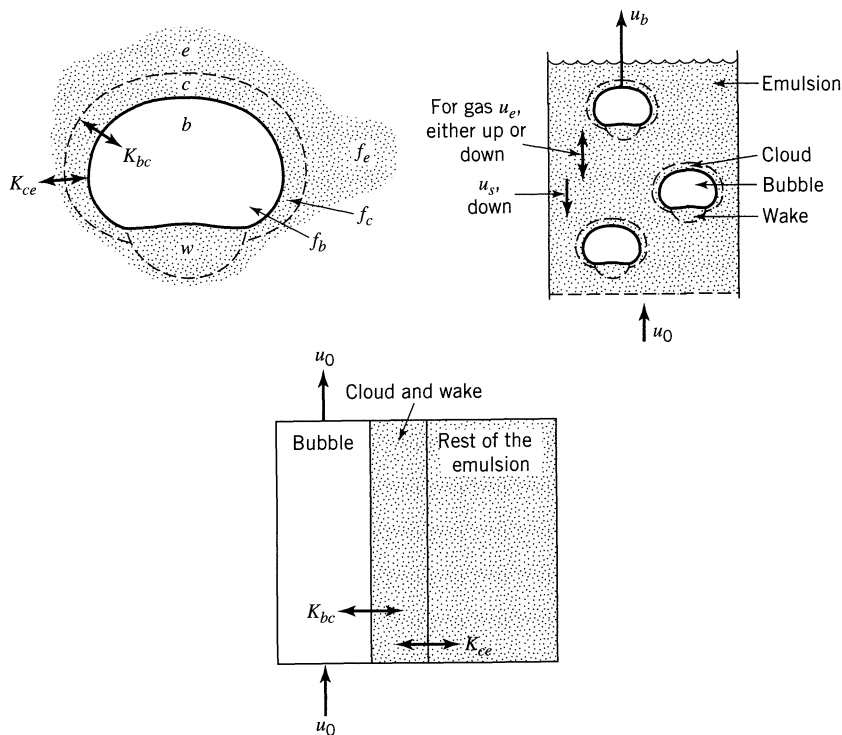
$u_0$  = superficial gas velocity in the bed,  $\text{m}^3 \text{ gas}/\text{m}^2 \text{ bed} \cdot \text{s}$

$d$  = diameter, m

$\epsilon$  = fraction of voids in the bed

subscripts  $b, c, e, w$  refer to bubble, cloud, emulsion, and wake, respectively.

subscripts  $m, mf, f$  refer to packed bed, minimum fluidization, and bubbling fluidized bed conditions, respectively.



**Figure 20.9** Model and symbols used to describe the K-L bubbling gas fluidized bed.

In essence, given  $u_{mf}$ ,  $\epsilon_{mf}$ ,  $u_0$ ,  $\alpha$ , and the effective bubble size in the bed  $d_b$ , this model tells you all the other properties of the bed—flows, region volumes, interchange rates, and consequently reactor behavior.

## Material Balance for Gas and for Solids

From Kunii and Levenspiel (1991) a material balance for the bed material gives

$$u_{br} = 0.711(gd_b)^{1/2} \quad \text{m/s ... rise velocity of a single bubble in a bed otherwise at } u_{mf} \quad (10)$$

↑  
acceleration of gravity =  $9.8 \text{ m/s}^2$

$$u_b = u_0 - u_{mf} + u_{br}, \text{ m/s} \quad \text{rise velocity of bubbles in a bubbling bed} \quad (11)$$

$$\delta = \text{bed fraction in bubbles, } \frac{\text{m}^3 \text{ bubbles}}{\text{m}^3 \text{ bed}} \quad (12)$$

$$\delta = \frac{u_0 - u_{mf}}{u_b} = 1 - \frac{u_{br}}{u_b}, \quad \text{and for } u_b \gg u_{mf} \text{ we can use } \delta \cong \frac{u_0}{u_b}$$



Useful relationships:

$$H_m(1 - \epsilon_m) = H_{mf}(1 - \epsilon_{mf}) = H_f(1 - \epsilon_f)$$

$$1 - \delta = \frac{1 - \epsilon_f}{1 - \epsilon_{mf}} = \frac{H_{mf}}{H_f} \dots H = \text{height}$$

$$u_s = \frac{\alpha \delta u_b}{1 - \delta - \alpha \delta}, \text{ m/s} \quad \dots \text{downflow of emulsion solids}$$

$$u_e = \frac{u_{mf}}{\epsilon_{mf}} - u_s, \text{ m/s} \quad \dots \text{rise velocity of emulsion gas (can be + or -)}$$

Using Davidson's theoretical expression for bubble-cloud circulation and the Higbie theory for cloud-emulsion diffusion the interchange of gas between bubble and cloud is then found to be

$$K_{bc} = 4.50 \left( \frac{u_{mf}}{d_b} \right) + 5.85 \left( \frac{\mathcal{D}^{1/2} g^{1/4}}{d_b^{5/4}} \right) = \frac{\text{(interchange volume between } b \text{ and } c, \text{ or } c \text{ and } b)/s}{\text{volume of bubble}}, \text{ s}^{-1} \quad (13)$$

and between cloud-wake and emulsion

$$K_{ce} = 6.77 \left( \frac{\epsilon_{mf} \mathcal{D} u_{br}}{d_b^3} \right)^{1/2} = \frac{\text{interchange volume/s}}{\text{volume of bubble}}, \text{ s}^{-1} \quad (14)$$

$$f_b = 0.001 \sim 0.01 = \frac{\text{volume of solids in bubble}}{\text{volume of bed}} \dots \text{rough estimate from experiment} \quad (15)$$

$$f_c = \delta(1 - \epsilon_{mf}) \left[ \frac{3u_{mf}/\epsilon_{mf}}{u_{br} - u_{mf}/\epsilon_{mf}} + \alpha \right] = \frac{\text{volume of solids in cloud and wake}}{\text{volume of bed}} \quad (16)$$

$$f_e = \overbrace{(1 - \epsilon_{mf})(1 - \delta)}^{(1 - \epsilon_f)} - f_c - f_b = \frac{\text{volume of solids in the rest of the emulsion}}{\text{volume of bed}} \quad (17)$$

$$f_b + f_c + f_e = f_{\text{total}} = 1 - \epsilon_f \quad (18)$$

$$H_{\text{BFB}} = H_f = W/\rho_s A(1 - \epsilon_f) \quad (19)$$

## Application to Catalytic Reactions

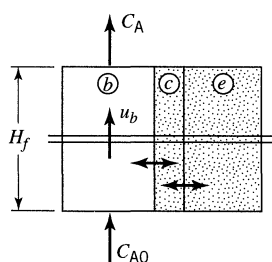
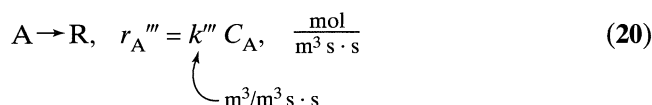
In our development we make two questionable assumptions:

- We ignore the flow of gas through the cloud since the cloud volume is very small for fast bubbles.
- We ignore the flow of gas, either up or down, through the emulsion since this flow is much smaller than the flow through the bubbles.

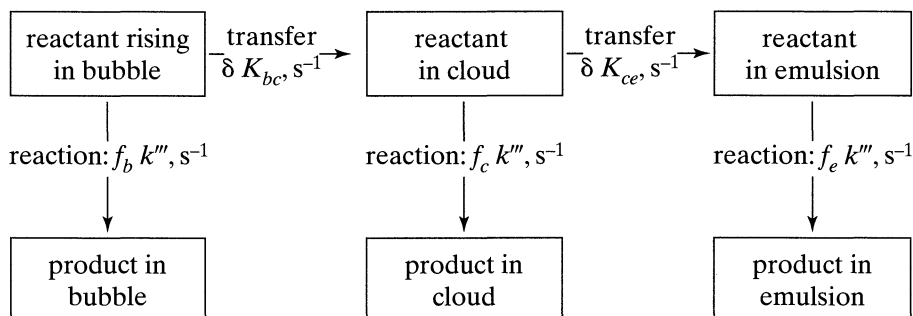
In effect, we consider the emulsion gas as stagnant. Of course more general expressions can be developed for beds where bubbles have thick clouds (not too large and fast bubbles), or where flow through the emulsion is significant ( $u_0$  close to  $u_{mf}$ , thus where  $u_0 \cong 1-2 u_{mf}$ ). However, for fast bubble, vigorously bubbling fine particle beds the above assumptions are reasonable.

We next see how to calculate performance in such a bed.

**First-Order Reaction.** Let the reaction be



Then for any slice of bed we have



Accounting for these five resistances in series—parallel, eliminating cloud and emulsion concentrations, and integrating from the bottom to the top of the

bed gives

$$\ln \frac{C_{A0}}{C_A} = K''' \tau''' = \underbrace{\left[ f_b k''' + \frac{1}{\delta \cdot K_{bc}} + \frac{1}{f_c k''' + \frac{1}{\delta \cdot K_{ce}} + \frac{1}{f_e k'''}} \right]}_{\substack{\text{five resistances} \\ K''', \text{ effective rate constant for the fluidized bed, } \text{m}^3/\text{m}^3 \cdot \text{s} \cdot \text{s}}} \cdot \underbrace{\frac{f_{\text{total}} H_{\text{BFB}}}{u_0}}_{\substack{\tau''', \text{ m}^3 \cdot \text{s} / \text{m}^3}} \quad (21)$$

We also find that the average gas composition seen by the solids is approximately (from S. Kimura, personal communication)

$$\bar{C}_A, \text{ bathing the solids} = \frac{C_{A0} - C_A}{K''' \tau'''} = \frac{C_{A0} X_A v_0}{K''' V_s} = \frac{C_{A0} X_A v_0}{K' W} \quad (22)$$

↑  
of solids alone,  $W/\rho_s$

This quantity is important for noncatalytic  $G/S$  reactions because it is this  $C_A$  that the solids see and react with.

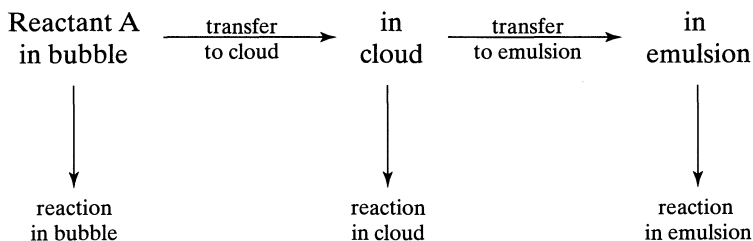
Let us now look at packed bed reactors. Assuming plug flow  $K_{bc} \rightarrow \infty$ ,  $K_{ce} \rightarrow \infty$ , so Eq. 21 reduces to

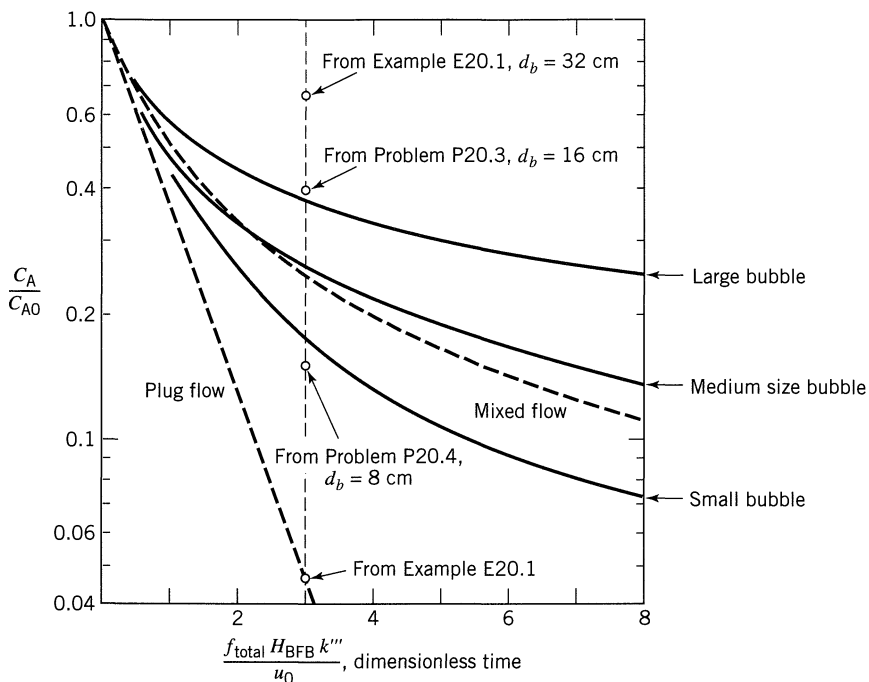
$$\text{for plug flow} \begin{cases} \ln \frac{C_{A0}}{C_{Ap}} = k''' \tau''' = \frac{k''' H_p (1 - \epsilon_p)}{u_0} = k' \tau' = \frac{k' W}{u_0 A_t} & (23) \\ \bar{C}_{Ap} = \frac{C_{A0} - C_{Ap}}{k''' \tau'''} & (24) \end{cases}$$

Comparing Eq. 21 with 23, and Eq. 22 with 24 shows that a fluidized bed can be treated as a plug flow reactor if

$K'''$  is replaced by  $k'''$

**Comments.** The five terms in brackets of the performance equation, Eq. 21, represent the complex series-parallel resistances to mass transfer and reaction or





**Figure 20.10** Performance of a fluidized bed as a function of bubble size, as determined by Eq. 21. Compare with the plug flow and mixed flow predictions.

For very fast reaction (large  $k'''$  value) very little A gets as far as the emulsion and the first two terms dominate. For slow reaction the latter terms become increasingly important.

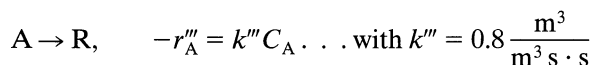
Since the bubble size is the one quantity which governs all the rate quantities with the exception of  $k'''$ , we can plot the performance of a fluidized bed as a function of  $d_b$ , as shown in Fig. 20.10. Note that large  $d_b$  gives poor performance because of extensive bypassing of bubble gas, and that the performance of the bed can drop considerably below mixed flow.

For multiple reactions the effect of this flow is much more serious still. Thus for reactions in series the lowering in amount of intermediate formed can be and usually is quite drastic.

Finally we have kept this presentation very brief. To help understand how to use it please look at the following illustrative example.

### EXAMPLE 20.1 First-Order Catalytic Reaction in a BFB

Reactant gas ( $u_0 = 0.3$  m/s,  $v_0 = 0.3 \pi$  m<sup>3</sup>/s) passes upward through a 2-m diameter fluidized bed ( $u_{mf} = 0.03$  m/s,  $\epsilon_{mf} = 0.5$ ) containing 7 tons of catalyst ( $W = 7000$  kg,  $\rho_s = 2000$  kg/m<sup>3</sup>). Reaction proceeds as follows:



- Calculate the conversion of reactant.
- Find the proper mean concentration of A seen by the solids.
- If gas were made to flow downward through the solids we would have a packed bed. Assuming plug flow of gas find the conversion of reactant for this situation.

### Additional Data

$$C_{A0} = 100 \text{ mol/m}^3, \mathcal{D} = 20 \times 10^{-6} \text{ m}^2/\text{s}, \alpha = 0.33$$

Estimated bubble size in the bed:  $d_b = 0.32 \text{ m}$

See Fig. E20.1 which represents this system.

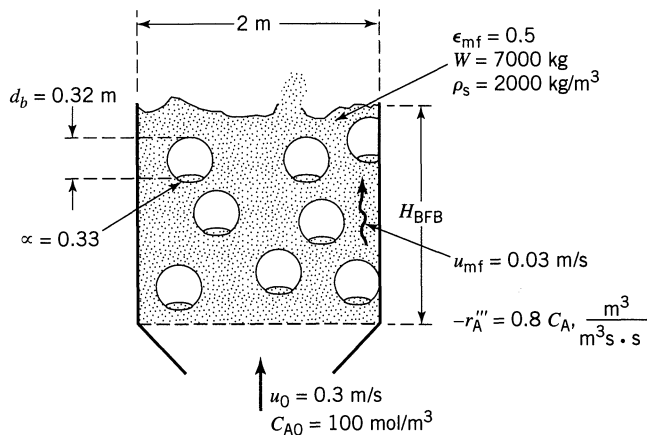


Figure E20.1

### SOLUTION

**Preliminary** Determine the rise velocity of bubbles

$$u_{br} = 0.711 (9.8 \times 0.32)^{1/2} = 1.26 \text{ m/s}$$

$$u_b = 0.30 - 0.03 + 1.26 = 1.53 \text{ m/s}$$

Now see whether the fast bubble model of this chapter applies.

- Check for slugging: The bubble size (32 cm) is small compared to the bed size (200 cm), hence no slugging.
- Check the fast bubble assumption: Take the velocity ratio

$$\frac{u_b}{u_f} = \frac{u_b}{u_{mf}/\epsilon_{mf}} = \frac{1.53}{0.03/0.5} = 25.5$$

Since the bubble rises  $\sim 25$  times as fast as the emulsion gas we have a fast bubble with thin cloud—less than 1 cm thick.

Thus we can safely use the **bubbling bed model** of this chapter.

(a) **Calculate  $X_A$ .** Replacing numbers into the expressions for this model gives, in turn,

$$\delta = \frac{0.30}{1.53} = 0.196$$

$$\epsilon_f = 1 - (1 - \epsilon_{mf})(1 - \delta) = 1 - 0.5(1 - 0.196) = 0.60$$

$$K_{bc} = 4.50 \left( \frac{0.03}{0.32} \right) + 5.85 \left( \frac{(20 \times 10^{-6})^{1/2} (9.8)^{1/4}}{(0.32)^{5/4}} \right) = 0.614 \text{ s}^{-1}$$

$$K_{ce} = 6.77 \left( \frac{0.5(20 \times 10^{-6}) 1.26}{(0.32)^3} \right)^{1/2} = 0.133 \text{ s}^{-1}$$

$$\left. \begin{aligned} f_b &= 0.001 \sim 0.01, \text{ choose it to be } 0.001 \\ f_c &= 0.196(1 - 0.5) \left( \frac{3 \times 0.03/0.5}{1.26 - 0.03/0.5} + 0.33 \right) = 0.047 \\ f_e &= (1 - 0.6) - 0.047 - 0.001 = 0.352 \end{aligned} \right\} f_b + f_c + f_e = (1 - \epsilon_f) = 0.4$$

$$H_{\text{BFB}} = \frac{7000}{2000(\pi)(1 - 0.6)} = 2.785 \text{ m}$$

$$\ln \frac{C_{A0}}{C_A} = \frac{\left[ \frac{0.001(0.8) + \frac{1}{\frac{1}{0.196(0.614)} + \frac{1}{0.047(0.8) + \frac{1}{\frac{1}{0.196(0.133)} + \frac{1}{0.354(0.8)}}}}}{(0.001 + 0.047 + 0.352)} \right] \cdot \frac{2.785(0.4)}{0.3}}{[0.0415] \cdot (9.284)} = 0.385$$

Therefore

$$\frac{C_A}{C_{A0}} = 0.68 \dots \text{ or } \underline{\underline{X_A = 32\%}} \text{ (see Fig. 20.10)}$$

(b) **Find  $\bar{C}_A$  seen by the solids.** Since every particle samples all the gas in the bed,  $\tau''' = (C_{A0} - C_A)/-r_A''$ , or

$$\bar{C}_A = \frac{(C_{A0} - C_A) v_0}{k''' V_s} = \frac{(100 - 68) 0.3 \pi}{(0.8)(3.5)} = \underline{\underline{11 \text{ mol/m}^3}}$$

(c) **Calculate  $X_A$  for a fixed bed.** From Eq. 11.44 or 11.51, for plug flow,

$$\ln \frac{C_{A0}}{C_{Ap}} = k''' \tau''' = k''' \frac{f_{\text{total}} H_{\text{BFB}}}{u_0} = k''' \frac{V_s}{v_0} = (0.8) \left( \frac{3.5}{0.3 \pi} \right) = 2.97$$

Therefore

$$\frac{C_{Ap}}{C_{A0}} = 0.05 \quad \dots \text{or} \quad \underline{\underline{X_A = 95\%}}$$

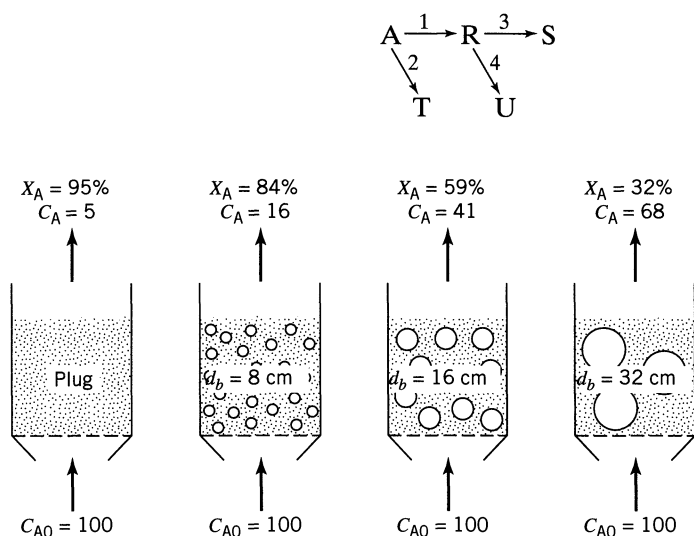
This point is shown in Fig. 20.10.

### Comments

- The conversion in the fluidized bed is drastically lower than in the packed bed (32% vs. 95%), and is even much below mixed flow (75%). This comes from the severe bypassing of reactant gas in the large gas bubbles. Reduce the size of bubbles in the bed and the conversion will rise spectacularly.
- Gas enters at  $C_{A0} = 100$ , leaves at  $C_A = 68$ ; however, the solids see a much lower concentration of A, or  $C_A = 11$ . Thus the solids, mostly in the emulsion, are starved for gaseous reactant. This sort of finding, quite general for fast bubble beds, is of great importance in  $G/S$  reactions. Thus in combustion and roasting of fine solids these solids may be starved for  $O_2$  even though the off gas from the bed may contain a significant amount of oxygen.
- Example 20.1 and the solutions to Problems 20.1 and 20.2 at the end of this chapter tell how conversion is affected by bubble size according to the K-L model. This is shown in Fig. 20.11. In all four cases the rate constant is the same and the catalyst is fixed at 7 tons, so  $k''' \tau''' = f_{\text{total}} H_{\text{BFB}} k'''/u_0 = 2.97$ .

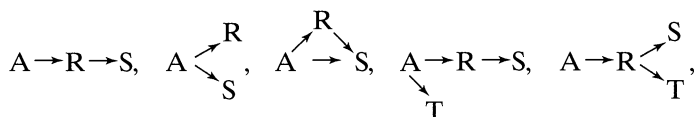
## Multiple Reactions and Product Distribution in Fluidized Beds

A derivation similar to that for single first-order reactions can be developed for the Denbigh reaction system

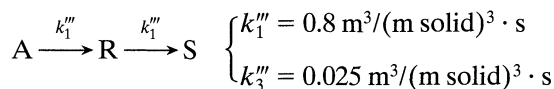


**Figure 20.11** Different bubble size gives different reactor performance. Data from Example 20.1 and Problems 20.3 and 20.4.

and its special cases

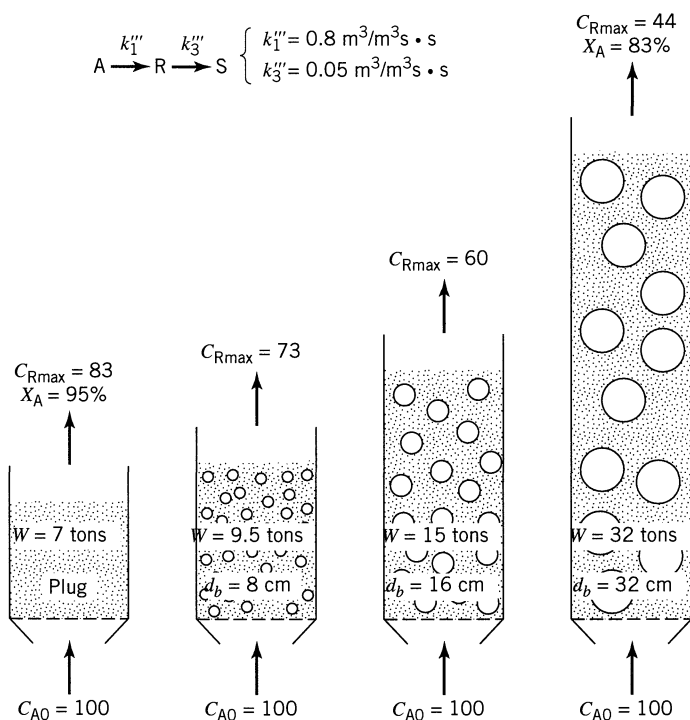


These derivations are rather tedious, we will not give them here, but we refer the reader to Levenspiel (1996) Chapter 25 for them. However, to illustrate the general findings let us take one example:



Let us suppose that these reactions take place in a BFB reactor having a gas flow rate similar to that of Example 20.1.

Let us see how much catalyst is needed to achieve  $C_{R, \max}$  for different sizes of bubbles in the BFB. The results are shown in Fig. 20.12.



**Figure 20.12** Different bubble sizes give different bed sizes for maximum production of intermediate.



The results of the calculations verify the general findings on bubbling fluidized beds.

- The BFB always needs more catalyst than a fixed bed to achieve a given conversion of reactant, or to reach  $C_{R, \max}$ .
- For reactions in series the BFB always gives a lower yield of intermediate compared to a fixed bed.
- For reactions in parallel of the same reaction order the product distribution is the same in fixed and BFBs.

## Final Remarks About BFB

The expressions developed in this chapter show that if we know  $\epsilon_{mf}$ , estimate  $\alpha$ , and measure  $u_{mf}$  and  $u_0$ , then all flow quantities and regional volumes can be determined in terms of one parameter, the bubble size. Figure 20.9 then represents the model as visualized. The use of this model to calculate chemical reactor behavior is straightforward and direct. The special feature of this model is that its one parameter can be tested against what is measured and what is observed.

Various other hydrodynamic models have been proposed recently, using other combinations of assumptions such as

Changing bubble size with height in the bed  
Negligible bubble-cloud resistance  
Negligible cloud-emulsion resistance  
Nonspherical bubbles

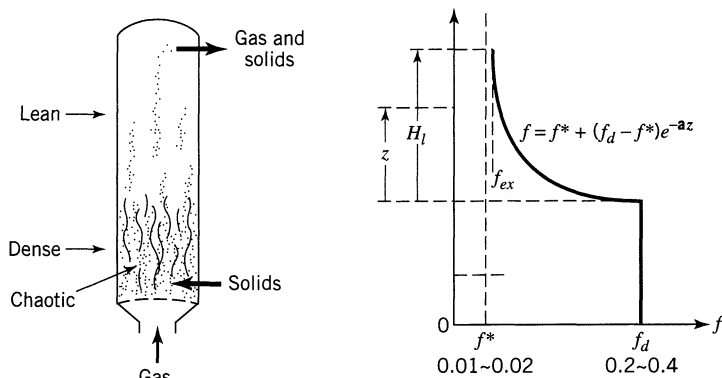
In all cases the underlying rationale for these hydrodynamic models rests on the observation that beds with identical solids and gas flow rates may develop either large bubbles or small bubbles depending on bed diameter, distributor design, baffle arrangement, etc.; thus, bubble size must enter as the primary parameter in the model. A consequence of this argument is that *models which do not allow for different bubble sizes* at given imposed bed conditions *certainly cannot be adequate*.

The power of this class of model should be apparent. For example, even the simplest of these models, the one considered here, gives unexpected predictions (e.g., that most of the gas in the bed may be flowing downward) which are subsequently verified. More important still, this type of model can be tested, it can be shown to be wrong, and it can be rejected, because its one parameter, the bubble size, can be compared with observation.

## 20.4 THE CIRCULATING FLUIDIZED BED—CFB

At gas velocities higher than those used for BFBs we successively enter the turbulent (TB), fast fluidized (FF), and the pneumatic conveying (PC) regimes. In these contacting regimes solids are entrained out of the bed and must be replaced. Thus in continuous operations we have the CFB, shown in Fig. 20.1.

Flow models are very sketchy for these flow regimes. Let us see what is known.



**Figure 20.13** The TB and its solid distribution.

### The Turbulent Bed (TB)

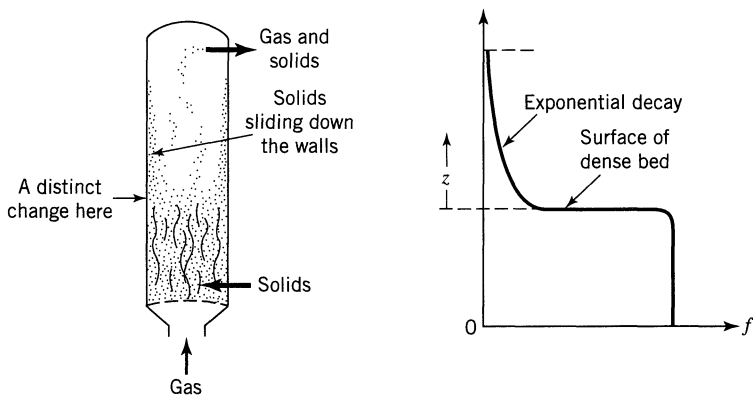
At higher gas velocities the BFB transforms into a TB—no distinct bubbles, much churning, and violent solid movement. The surface of the dense bed fades and solids are found increasingly in the lean region above the dense bed.

The concentration of solids in the upper lean region can be reasonably represented by an exponential decay function which starts from the value in the lower region  $f_d$  and falls to  $f^*$  the limiting value in an infinitely high vessel. This is the value for pneumatic conveying.

The flow of gas in the dense region is somewhere between the BFB and plug flow. The TB is shown in Fig. 20.13.

Unfortunately no reasonable flow model has been developed for the dense region of a TB. Research is needed here.

In beds of both coarse and fine solids one may observe a somewhat different solid distribution with height—a distinct difference between dense and lean regions and a sharp dense phase surface, as shown in Fig. 20.14. This behavior is more typical of fluidized combustors, not catalytic reaction systems.



**Figure 20.14** Behavior of a TB of large and small particles.

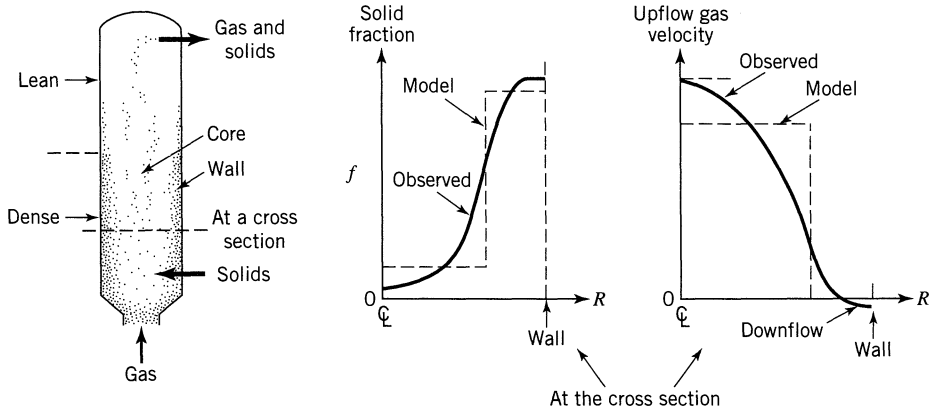


Figure 20.15 Behavior of a FF bed.

### The Fast Fluidized Bed (FF)

At even higher gas velocity (see Fig. 20.5) the bed enters the FF regime. One characteristic of this transition is that the entrainment of solids rises dramatically at this point. Bi et al. (1995) found this transition to occur at

$$u_{\text{TB-FF}} = 1.53 \sqrt{\frac{(\rho_s - \rho_g)g d_p}{\rho_g}}$$

In the FF regime the solid movement in the lower region of the vessel becomes less chaotic and seems to settle to a lean core surrounded by a denser annulus or wall zone.

The upper region retains its exponential decay behavior.

Figure 20.15 shows the distribution of solids in the whole FF bed and at a cross section. The model which represents the FF bed is shown in Fig. 20.16.

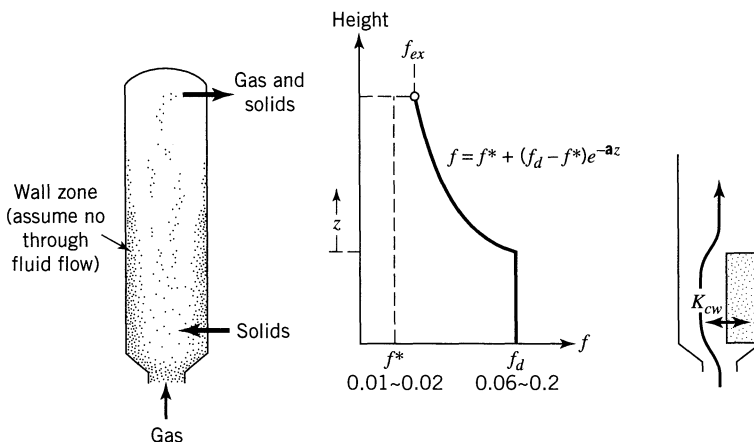


Figure 20.16 Model for a FF reactor.

The quantities that need to be known to predict the behavior of the FF reactor are “ $a$ ,”  $K_{cw}$ ,  $f^*$ , and  $f_d$ . Measurements show that

$$\begin{aligned} u_0 a &= 2 - 4 \text{ s}^{-1} && \text{for Geldart A solids} \\ &= 5 \text{ s}^{-1} && \text{for Geldart AB solids} \\ &= 7 \text{ s}^{-1} && \text{for Geldart B solids} \end{aligned}$$

Measured values for  $f^*$  and  $f_d$  have been summarized by Kunii and Levenspiel (1995). Values for  $K_{cw}$  have yet to be measured. The best we can do today is estimate their order of magnitude from  $K_{bc}$  and  $K_{ce}$  of the BFB. So at this time we cannot predict reactor behavior. However, to see how to make the material balance and conversion calculation see the numerical example given in Kunii and Levenspiel (1997).

## Pneumatic Conveying (PC)

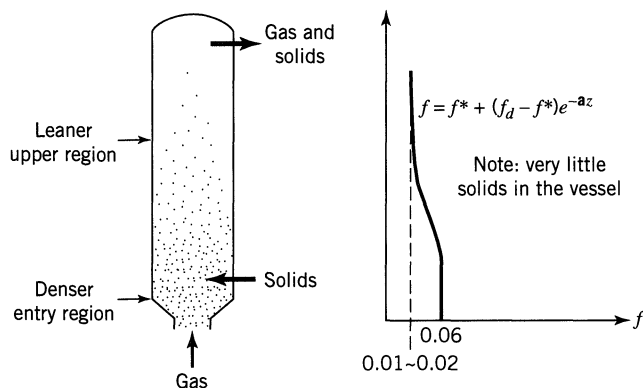
Finally at the highest gas velocities we exceed what is called the *choking velocity*. Above this the bed is in pneumatic transport. This transition velocity depends on the solid flow rate, and according to Bi and Fan (1991) occurs at

$$\frac{u_{\text{FF-PC}}}{\sqrt{g d_p}} = 21.6 \left( \frac{G_s}{\rho_g u_{\text{FF-PC}}} \right)^{0.542} (d_p^*)^{0.315}$$

In the PC regime particles are well distributed in the reactor, with no wall or downflow zone, but with a slight decrease in solid fraction with height. So we can assume plug flow of solids and of gas up the vessel.

## The Downflow CFB

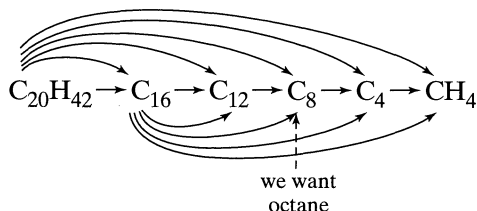
Fluidized catalytic cracking reactors, called “cat crackers” or FCC reactors, are one of society’s most important large-scale reactors. On an average, each such



**Figure 20.17** Model for a PC reactor.

unit processes about 6000 m<sup>3</sup>/day (40 000 barrels/day) of crude oil to produce gasoline, diesel fuel, and jet aircraft fuel to power the engines of today. There are about 420 FCC reactors in the world today, running day and night to satisfy the needs of our insatiable societies.

These reactors take long chain hydrocarbons and crack them to produce a whole host of shorter chain hydrocarbons. To illustrate



The original cat cracker was invented in the early 1940s and was one of chemical engineering's most important contributions to World War II. However, those early units did not use very selective catalysts and, with their large deviations from plug flow, gave very little of whatever intermediate was desired.

In the 1960s better (more selective) and more active catalysts were created, and the needed reaction time for the oil vapor was consequently reduced to seconds, so the upflow FF reactors were invented. Approaching closer to plug flow gave the designer better control of product distribution, and allowed production of a larger fraction of desired product: for example, octane for automobile fuel.

With this development, most of the BFBs in the world were cut up for scrap to be replaced by upflow FF reactors.

Today, approaching year 2000, engineers want to do better still. Why? Because increasing the production of desired product by 1% would increase the profit per reactor by \$1 million to \$2 million/year. As Fig. 20.16 shows, the upflow FF reactor has a practically stagnant or a downsliding wall zone of catalyst and gas, and this results in deviation from plug flow.

How to avoid this? The obvious answer is to use a downflow FF reactor. These can operate at very high gas velocities, and remain close to plug flow.

Today much exciting research is going on in this area, and we may some day, not too far in the future, see many of the upflow short contact time FCC units be replaced by downflow units. The payoff for this would be enormous.

## Remarks About CFB

Here we have sketched the three regimes of CFB and their general behavior; however, we have not presented their performance equations. The reason is that the parameters for their reasonable models are uncertain today; hence, the predictions based on these models will likewise be uncertain. Still the general material balances and the form of the performance equations are available, see Kunii and Levenspiel (1991, 1997).

## 20.5 THE JET IMPACT REACTOR

The idea here is to force two streams, one of reactant, the other of a very hot heat carrier or catalyst, to collide at very high velocity and thereby mix intensely and react at high temperature.

For an all-gas product, the product stream is rapidly quenched, while for a gas-solid product, a cyclone separates the two phases, after which the gas is rapidly cooled. By using the word “rapidly” we mean that the whole operation—mixing, reacting, separating and quenching—is done in 0.1 to 0.3 seconds.

This type of reactor aims to challenge fast fluidization with its 1 to 10 second gas residence time as the prime reactor for the catalytic cracking of petroleum. The claim is that the higher cracking temperature and shorter residence time will give a very different—and better—distribution of reaction products.

Another application is to ultrapyrolyze cellulose and other biomass wastes. Commercial tests show that one can transform about 75% of wood into oil, and about 70% of sawdust into oil—useful liquids having the consistency of light engine oil. Much research is proceeding on this application (from Bergougnou, 1998).

### REFERENCES

- Bergougnou, M. A. private communication, 1998.  
 Bi, H. T., and Fan, L. S., Paper 101e, A.I.Ch.E. Annual Meeting, Los Angeles, 1991.  
 Bi, H. T., Grace, J. R., and Zhu, J. X., *Trans. I. Chem. E.*, **73**, 154 (1995).  
 Davidson, J. F., and Harrison, D., *Fluidized Particles*, Cambridge Univ. Press, New York, 1963.  
 Ergun, S., *Chem. Eng. Prog.*, **48**, 89 (1952).  
 Geldart, D., *Powder Technol.*, **7**, 285 (1973).  
 —, and Abrahamson, A. A., *Powder Technol.*, **19**, 133 (1978).  
 Gilliland, E. R., and Knudsen, C. W., *Chem. Eng. Prog. Symp. Ser.* **67 (116)**, 168 (1971).  
 Grace, J. R., *Can. J. Chem. Eng.*, **64**, 353 (1986).  
 Haider, A., and Levenspiel, O., *Powder Technol.*, **58**, 63 (1989).  
 Kimura, S., private communication.  
 Kunii, D., and Levenspiel, O., *Fluidization Engineering*, 2nd ed., Butterworth-Heinemann, Boston, MA, 1991.  
 —, in *Fluidization VIII*, Tours, p. 17 (1995).  
 —, *Chem. Eng. Sci.*, **52**, 2471 (1997).  
 Levenspiel, O., *Chemical Reactor Omnibook*, OSU Bookstores, Corvallis, OR, 1996.  
 Rowe, P. N., and Partridge, B. A., *Proc. Symp. on Interaction between Fluids and Particles*, p. 135, *I. Chem. E.* (1962); *Trans. I. Chem. E.*, **43**, 157 (1965).

### PROBLEMS

A suggestion for raising the conversion in Example 20.1 is to use more solids. So for the same bed diameter (2 m) and same mean bubble size (0.32 m) find  $X_A$  and the mean concentration of gas seen by the solids  $C_A$  if we use

**20.1.** . . . 14 tons of catalyst

**20.2.** . . . 21 tons of catalyst

In Example 20.1 the conversion is very low and unsatisfactory. One suggestion for improvement is to insert baffles into the bed and thereby cut down the effective bubble size. Find  $X_A$  if

20.3. . . .  $d_b = 16$  cm

20.4. . . .  $d_b = 8$  cm

In Example 20.1 another suggestion for improving performance is to use a shallower bed, keeping  $W$  unchanged, thereby decreasing the superficial gas velocity. Find  $X_A$  if we double the bed cross-sectional area (thus make  $u_0 = 15$  cm/s) and

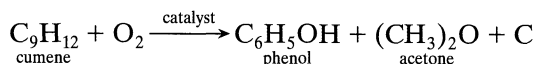
20.5. . . . keep  $d_b$  unchanged at  $d_b = 32$  cm

20.6. . . . make  $d_b = 8$  cm by suitable baffles

20.7. In Example 20.1 still another suggestion is to use a narrower and taller bed, keeping  $W$  unchanged. Following this suggestion find  $X_A$  if we halve the bed cross-sectional area (thus make  $u_0 = 60$  cm/s) and keep  $d_b = 32$  cm.

20.8. Example 20.1 showed that a 7-ton bed with 32-cm bubbles gave 32% conversion. Suppose we diluted the catalyst 1:1 with inert solids ending up with a 14-ton bed. How would this affect the conversion of reactant? Would it be higher or lower than 32%?

20.9. Mathis and Watson in *AIChE J.*, **2**, 518 (1956) reported on the catalytic conversion of cumene in both fluidized and packed beds of catalyst



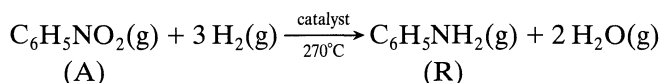
In very dilute cumene-air mixtures the kinetics are essentially first-order reversible with respect to cumene with an equilibrium conversion of 94%.

In packed bed experiments ( $H_m = 76.2$  mm) using downflow of gas ( $u_0 = 64$  mm/s) the conversion of cumene was found to be 60%. However, with upflow of gas at the same flow rate in the same bed, the solids fluidize ( $u_{mf} = 6.1$  mm/s) and bubbles of gas were observed roughly 13.5 mm in diameter. What conversion do you expect to find under these conditions?

Estimated values:

$$\begin{aligned} \epsilon_m &= 0.4, & D_{\text{cumene-air}} &= 2 \times 10^{-5} \text{ m}^2/\text{s} \\ \epsilon_{mf} &= 0.5, & \alpha &= 0.33 \end{aligned}$$

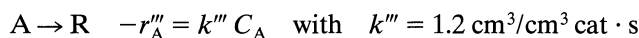
- 20.10.** Calculate the conversion in a fluidized bed reactor for the catalytic hydrogenation of nitrobenzene to aniline.



Data:

$H_m = 1.4 \text{ m}$	$\rho_c = 2.2 \text{ g/cm}^3$	$d_b = 10 \text{ cm}$
$d_t = 3.55 \text{ m}$	$\mathcal{D}_{\text{eff}} = 0.9 \text{ cm}^2/\text{s}$	$\alpha = 0.33$
$T = 270^\circ\text{C}$	$u_{mf} = 2 \text{ cm/s}$	$\epsilon_m = 0.4071$
	$u_0 = 30 \text{ cm/s}$	$\epsilon_{mf} = 0.60$

We plan to use an excess of hydrogen in which case we can ignore expansion, and can assume simple first-order kinetics:



- 20.11.** In a laboratory packed bed reactor ( $H_m = 10 \text{ cm}$  and  $u_0 = 2 \text{ cm/s}$ ) conversion is 97% for the first-order reaction  $\text{A} \rightarrow \text{R}$ .

- (a) Determine the rate constant  $k'''$  for this reaction.
- (b) What would be the conversion in a larger fluidized bed pilot plant ( $H_m = 100 \text{ cm}$  and  $u_0 = 20 \text{ cm/s}$ ) in which the estimated bubble size is 8 cm?
- (c) What would be the conversion in a packed bed under the conditions of part (b)?

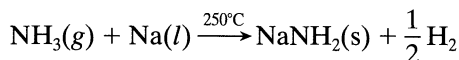
Data: From experiment,  $u_{mf} = 3.2 \text{ cm/s}$ ,  $\epsilon_{mf} \cong \epsilon_m = 0.5$

From the literature,  $\mathcal{D} \cong \mathcal{D}_e = 3 \times 10^{-5} \text{ cm}^2/\text{s}$ ,  $\alpha = 0.34$



## Fluid–Fluid Reactions: Kinetics

Heterogeneous fluid-fluid reactions are made to take place for one of three reasons. First, the product of reaction may be a desired material. Such reactions are numerous and can be found in practically all areas of the chemical industry where organic syntheses are employed. An example of liquid-liquid reactions is the nitration of organics with a mixture of nitric and sulfuric acids to form materials such as nitroglycerin. The chlorination of liquid benzene and other hydrocarbons with gaseous chlorine is an example of gas-liquid reactions. In the inorganic field we have the manufacture of sodium amide, a solid, from gaseous ammonia and liquid sodium:



Fluid-fluid reactions may also be made to take place to facilitate the removal of an unwanted component from a fluid. Thus, the absorption of a solute gas by water may be accelerated by adding a suitable material to the water which will react with the solute being absorbed. Table 23.1 shows the reagents used for various solute gases.

The third reason for using fluid-fluid systems is to obtain a vastly improved product distribution for homogeneous multiple reactions than is possible by using the single phase alone. Let us turn to the first two reasons, both of which concern the reaction of materials originally present in different phases.

The following factors will determine how we approach this process.

**The Overall Rate Expression.** Since materials in the two separate phases must contact each other before reaction can occur, both the mass transfer and the chemical rates will enter the overall rate expression.

**Equilibrium Solubility.** The solubility of the reacting components will limit their movement from phase to phase. This factor will certainly influence the form of the rate equation since it will determine whether the reaction takes place in one or both phases.

**The Contacting Scheme.** In gas-liquid systems semibatch and countercurrent contacting schemes predominate. In liquid-liquid systems mixed flow (mixer-

**Table 23.1** Absorption Systems with Chemical Reaction<sup>a</sup>

Solute Gas	Reagent
CO <sub>2</sub>	Carbonates
CO <sub>2</sub>	Hydroxides
CO <sub>2</sub>	Ethanolamines
CO	Cuprous amine complexes
CO	Cuprous ammonium chloride
SO <sub>2</sub>	Ca(OH) <sub>2</sub>
SO <sub>2</sub>	Ozone-H <sub>2</sub> O
SO <sub>2</sub>	HCrO <sub>4</sub>
SO <sub>2</sub>	KOH
Cl <sub>2</sub>	H <sub>2</sub> O
Cl <sub>2</sub>	FeCl <sub>2</sub>
H <sub>2</sub> S	Ethanolamines
H <sub>2</sub> S	Fe(OH) <sub>3</sub>
SO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>
C <sub>2</sub> H <sub>4</sub>	KOH
C <sub>2</sub> H <sub>4</sub>	Trialkyl phosphates
Olefins	Cuprous ammonium complexes
NO	FeSO <sub>4</sub>
NO	Ca(OH) <sub>2</sub>
NO	H <sub>2</sub> SO <sub>4</sub>
NO <sub>2</sub>	H <sub>2</sub> O

<sup>a</sup> Adapted from Teller (1960).

settlers) and batch contacting are used in addition to counter and concurrent contacting.

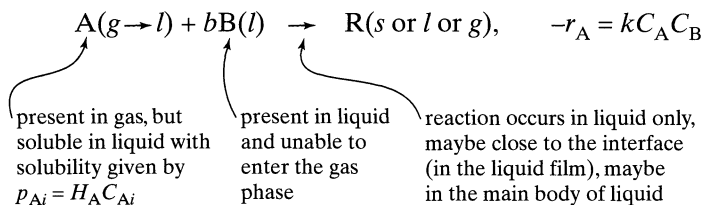
Many possible permutations of rate, equilibrium, and contacting pattern can be imagined; however, only some of these are important in the sense that they are widely used on the technical scale.

## 23.1 THE RATE EQUATION

For convenience in notation let us talk of *G/L* reactions, even though what we say holds equally for *L/L* reactions. Further, let us assume that gaseous A is soluble in the liquid but that B does not enter the gas. Thus A must enter and move into the liquid phase before it can react, and reaction occurs in this phase alone.

Now the overall rate expression for the reaction will have to account for the mass transfer resistance (to bring reactants together) and the resistance of the chemical reactions step. Since the relative magnitude of these resistances can vary greatly we have a whole spectrum of possibilities to consider.

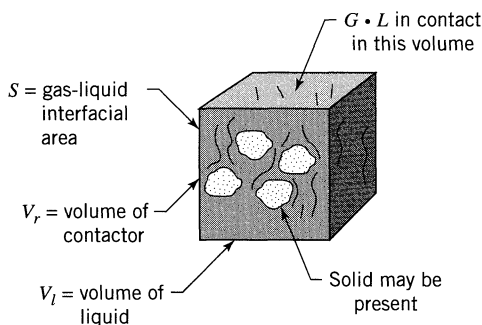
Our analysis considers the following second-order reaction



For notation consider a unit volume of contactor  $V_r$  with its gas, liquid, and solid

$$f_l = \frac{V_l}{V_r}, \quad f_g = \frac{V_g}{V_r}, \quad \epsilon = f_l + f_g,$$

$$a_l = \frac{S}{V_l}, \quad a = \frac{S}{V_r}$$



The rate of reaction is usefully written in a number of ways, as follows:

$$\left. \begin{aligned} -r_A''' &= -\frac{1}{V_r} \frac{dN_A}{dt} \\ -r_{Al} &= -\frac{1}{V_l} \frac{dN_A}{dt} \\ -r_A'' &= -\frac{1}{S} \frac{dN_A}{dt} \end{aligned} \right\} \quad (1)$$

These rates are related by

$$r_A''' V_r = r_{Al} V_l = r_A'' S$$

or

$$r_A''' = f_l r_{Al} = a r_A''$$

Since reactant A must move from gas to liquid for reaction to occur, diffusional resistances enter the rate. Here we will develop everything in terms of the two-film theory. Other theories can and have been used; however, they give essentially the same result, but with more impressive mathematics.

### The Rate Equation for Straight Mass Transfer (Absorption) of A

Here we have two resistances in series, of the gas film and of the liquid film. Thus, as shown in Fig. 23.1, the rate of transfer of A from gas to liquid is given by the rate expressions, for the gas film

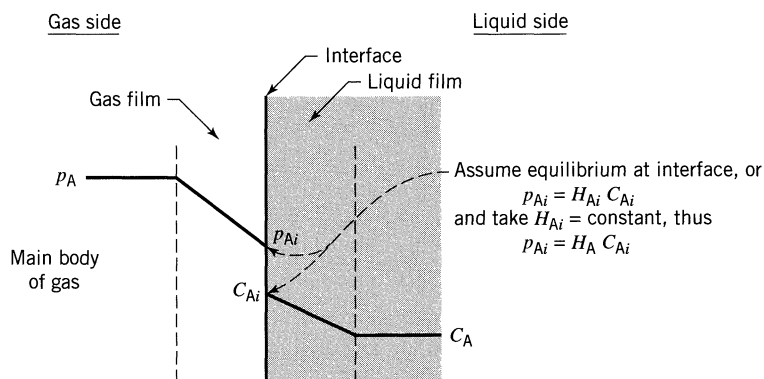
$$r_A'' = k_{Ag} (p_A - p_{Ai}) \quad \dots \text{or} \quad -r_A''' = \bar{k}_{Ag} a (p_A - p_{Ai}) \quad (2)$$

$\frac{\text{mol}}{\text{m}^2 \cdot \text{Pa} \cdot \text{s}}$                        $\frac{\text{mol}}{\text{m}^3 \text{ contactor} \cdot \text{Pa} \cdot \text{s}}$

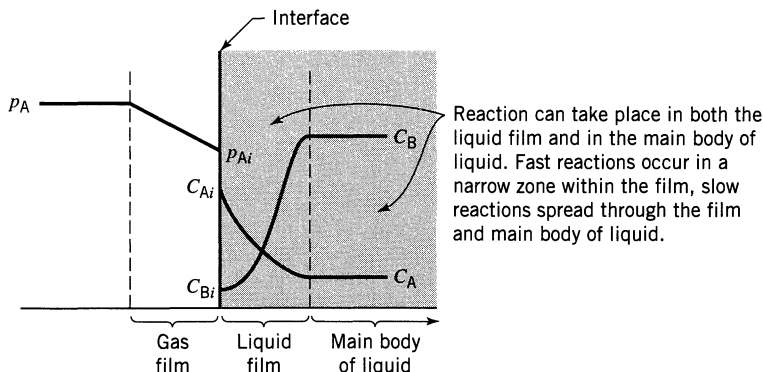
and for the liquid film

$$r_A'' = k_{Al} (C_{Ai} - C_A) \quad \dots \text{or} \quad -r_A''' = k_{Al} a (C_{Ai} - C_A) \quad (3)$$

$\frac{\text{m}^3 \text{ liquid}}{\text{m}^2 \text{ surface} \cdot \text{s}}$                        $\frac{\text{m}^3 \text{ liquid}}{\text{m}^3 \text{ contactor} \cdot \text{s}}$



**Figure 23.1** Setting up the rate equation for straight mass transfer based on the two film theory.



**Figure 23.2** Setting up the rate equation for absorption of A in the liquid, and reaction in the liquid, based on the two-film theory.

Combining Eqs. 2 and 3 with Henry's law  $p_{Ai} = H_A C_{Ai}$  to eliminate the unknown interface conditions  $p_{Ai}$  and  $C_{Ai}$  we obtain the final rate expression for straight mass transfer at any point in the absorber.

$$-r_A''' = \frac{1}{\frac{1}{k_{Ag}a} + \frac{H_A}{k_{Al}a}} (p_A - \underbrace{H_A C_A}_{\substack{\text{Pa} \cdot \text{m}^3 \text{ liquid} \\ \text{mol}}}) \quad (4)$$

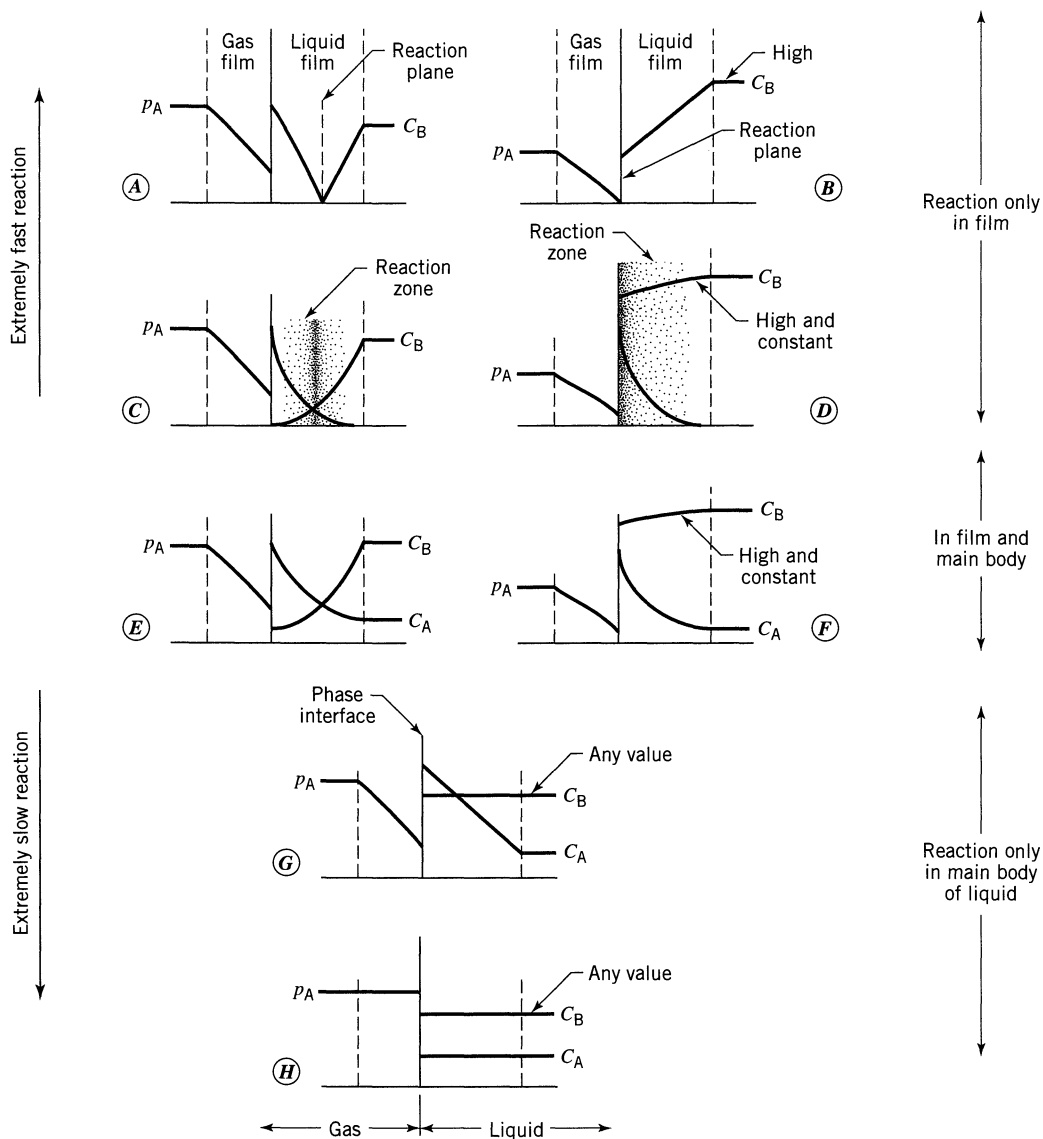
## The Rate Equation for Mass Transfer and Reaction

Here we have three factors to consider: what happens in the gas film; in the liquid film; and in the main body of the liquid, as shown in Fig. 23.2.

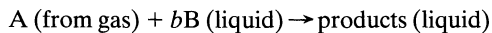
All sorts of special forms of the rate equation can result depending on the relative values of the rate constants  $k$ ,  $k_g$ , and  $k_l$ , the concentration ratio of reactants  $p_A/C_B$ , and Henry's law constant  $H_A$ . It turns out that there are eight cases to consider, going from the extreme of infinitely fast reaction rate (mass transfer control) to the other extreme of very slow reaction rate (no mass transfer resistance need be considered).

The eight special cases, each with its particular rate equation, are, from infinitely fast to very slow reaction, as follows:

- Case A: Instantaneous reaction with low  $C_B$
- Case B: Instantaneous reaction with high  $C_B$
- Case C: Fast reaction in liquid film, with low  $C_B$
- Case D: Fast reaction in liquid film, with high  $C_B$



**Figure 23.3** Interface behavior for the liquid-phase reaction



for the complete range of rates of the reaction and of the mass transfer.

**Case E and F:** Intermediate rate with reaction in the film and in the main body of the liquid

**Case G:** Slow reaction in main body but with film resistance

**Case H:** Slow reaction, no mass transfer resistance

We show these eight cases in Fig. 23.3.

We discuss these special cases and present their particular rate equations later, after we present the general rate equation.

$$-r_A''' = \frac{1}{\underbrace{\frac{1}{k_{Ag}a}}_{\text{gas film resistance}} + \underbrace{\frac{H_A}{k_{Al}aE}}_{\text{liquid film resistance}} + \underbrace{\frac{H_A}{kC_{Bf}f_l}}_{\text{liquid bulk resistance}}} p_A \quad (5)$$

The absorption of A from gas is larger when reaction occurs within the liquid film than for straight mass transfer. Thus for the same concentrations at the two boundaries of the liquid film we have

$$\left( \begin{array}{c} \text{Liquid film} \\ \text{enhancement} \\ \text{factor} \end{array} \right), E = \left( \frac{\text{rate of take up of A} \\ \text{when reaction occurs}}{\text{rate of take up of A for} \\ \text{straight mass transfer}} \right)_{\text{same } C_{Ai}, C_A, C_{Bi}, C_B \text{ in the two cases}} \quad (6)$$

The value of  $E$  is always greater or equal to one. The only problem now is to evaluate  $E$ , the enhancement factor. Figure 23.4 shows that  $E$  is dependent on two quantities:

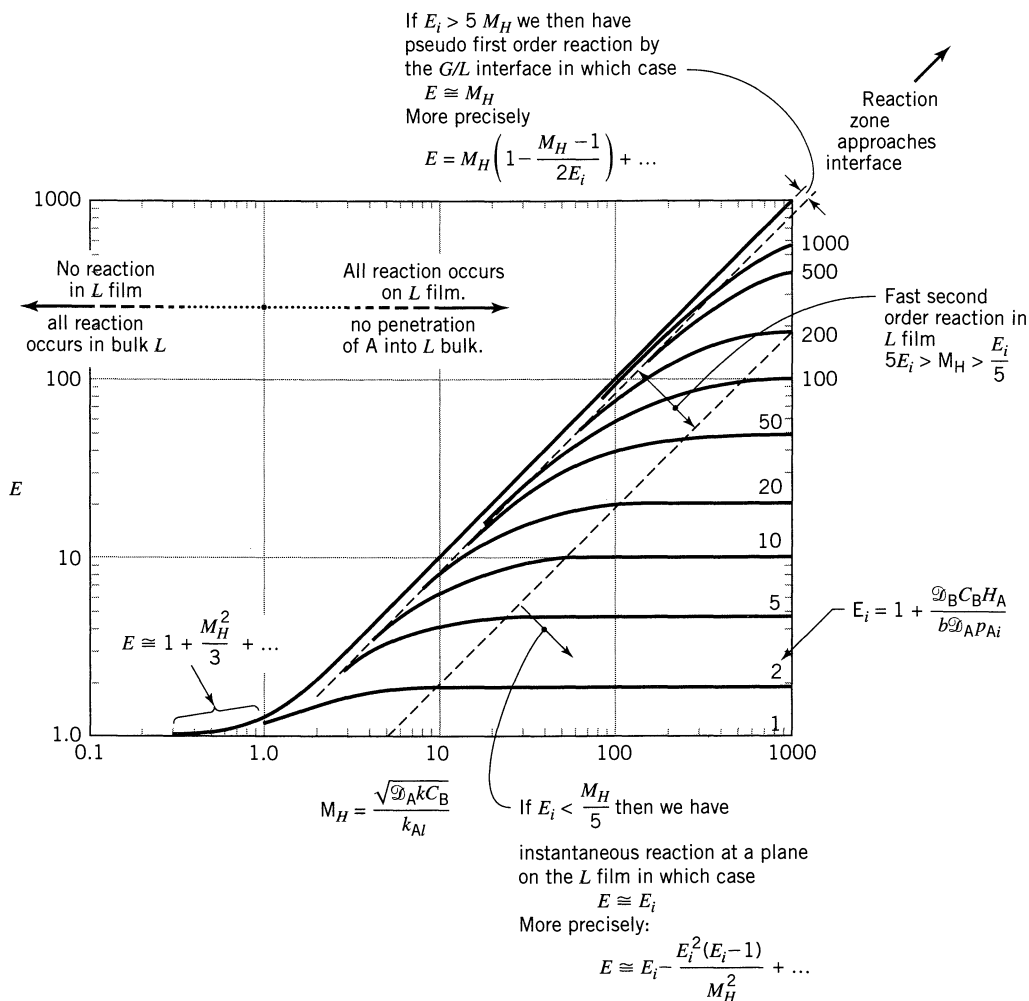
$$E_i = \left( \begin{array}{c} \text{the enhancement factor for} \\ \text{an infinitely fast reaction} \end{array} \right) \quad (7)$$

$$M_H^2 = \left( \begin{array}{c} \text{maximum possible conversion in the} \\ \text{film compared with maximum transport} \\ \text{through the film} \end{array} \right) \quad (8)$$

$M_H$  stands for the Hatta modulus, in recognition of the scientist who first dealt with this problem, Hatta (1932).

Let us now examine the eight special cases.

**Case A: Instantaneous Reaction with Respect to Mass Transfer.** Since an element of liquid can contain either A or B, but not both, reaction will occur at a plane between A-containing and B-containing liquid. Also, since reactants must diffuse to this reaction plane the rate of diffusion of A and B will determine the rate, so that a change in  $p_A$  or  $C_B$  will move the plane one way or the other (see Fig. 23.5). At steady state the flow rate of B toward the reaction zone will be  $b$



**Figure 23.4** The enhancement factor for fluid-fluid reactions as a function of  $M_H$  and  $E_i$ , modified from the numerical solution of van Krevelens and Hoftijzer (1954).

times the flow rate of  $A$  toward the reaction zone. Thus,

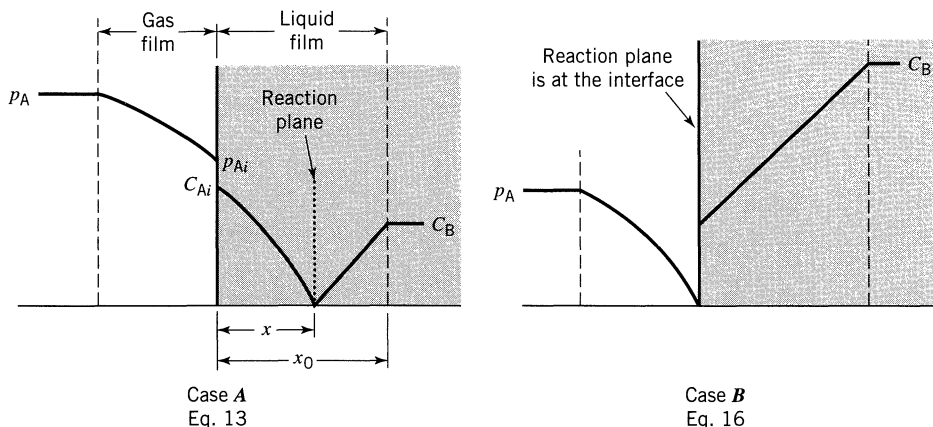
$$-r_A'' = -\frac{r_B''}{b} = \underbrace{k_{Ag}(p_A - p_{Ai})}_{\text{A in gas film}} = \underbrace{k_{Ai}(C_{Ai} - 0)}_{\text{A in liquid film}} \frac{x_0}{x} = \underbrace{\frac{k_{Bi}}{b}(C_B - 0)}_{\text{B in liquid film}} \frac{x_0}{x_0 - x} \quad (9)$$

where  $k_{Ag}$  and  $k_{Ai}$ ,  $k_{Bi}$  are the mass transfer coefficients in gas and liquid phases. The liquid side coefficients are for straight mass transfer without chemical reaction and are therefore based on flow through the whole film of thickness  $x_0$ .

At the interface the relationship between  $p_A$  and  $C_A$  is given by the distribution coefficient, called Henry's law constant for gas-liquid systems. Thus,

$$p_{Ai} = H_A C_{Ai} \quad (10)$$





**Figure 23.5** Concentration of reactants as visualized by the two-film theory for an infinitely fast irreversible reactions of any order,  $A + bB \rightarrow \text{products}$ . Case **A**—low  $C_B$ , Case **B**—high  $C_B$  (see Eq. 17).

In addition, since the movement of material within the film is visualized to occur by diffusion alone, the transfer coefficients for A and B are related by<sup>1</sup>

$$\frac{k_{Al}}{k_{Bl}} = \frac{\mathcal{D}_{Al}/x_0}{\mathcal{D}_{Bl}/x_0} = \frac{\mathcal{D}_{Al}}{\mathcal{D}_{Bl}} \quad (12)$$

Eliminating the unmeasured intermediates  $x$ ,  $x_0$ ,  $p_{Ai}$ ,  $C_{Ai}$  by Eqs. 9, 10, and 12, we obtain

for Case A:  $\left( k_{Ag} p_A > \frac{k_{Bl} C_B}{b} \right)$

$$-r_A'' = -\frac{1}{S} \frac{dN_A}{dt} = \frac{\frac{\mathcal{D}_{Bl} C_B}{\mathcal{D}_{Al} b} + \frac{p_A}{H_A}}{\frac{1}{H_A k_{Ag}} + \frac{1}{k_{Al}}} \quad (13)$$

For the special case of negligible gas-phase resistance, for example, if you used pure reactant A in the gas phase, then  $p_A = p_{Ai}$  or  $k_g \Rightarrow \infty$ , in which case Eq.

<sup>1</sup> Alternatives to the film theory are also in use. These models [Higbie (1935); Danckwerts (1950, 1955)] view that the liquid at the interface is continually washed away and replaced by fresh fluid from the main body of the liquid, and that this is the means of mass transport. These unsteady-state surface renewal theories all predict

$$\frac{k_{Al}}{k_{Bl}} = \sqrt{\frac{\mathcal{D}_{Al}}{\mathcal{D}_{Bl}}} \quad (11)$$

as opposed to Eq. 12, for the film theory.

With the exception of this one difference, these models, so completely different from a physical standpoint, give essentially identical predictions of steady-state behavior. Because of this, and because the film theory is so much easier to develop and use than the other theories, we deal with it exclusively.

13 reduces to

$$-r_A'' = k_{Ai} C_{Ai} \left( 1 + \frac{\mathcal{D}_{Bl} C_B}{b \mathcal{D}_{Al} C_{Ai}} \right) \quad (14)$$

**Case B: Instantaneous Reaction; High  $C_B$ .** Returning to the general situation shown in Fig. 23.5, if the concentration of B is raised, or more precisely, if

$$k_{Ag} p_A \leq \frac{k_{Bl}}{b} C_B \quad (15)$$

then this condition, combined with Eq. 5, requires that the reaction zone move to and stay at the interface rather than remain in the liquid film. This is shown in Fig. 23.5. When this happens, the resistance of the gas-phase controls, and the rate is not affected by any further increase in concentration of B. In addition, Eq. 9 simplifies to

$$\text{for Case B:} \quad \left( k_{Ag} p_A \leq \frac{k_{Bl} C_B}{b} \right) \quad \boxed{-r_A'' = -\frac{1}{S} \frac{dN_A}{dt} = k_{Ag} p_A} \quad (16)$$

Equation 17 tells whether Case A or Case B applies in any situation. Thus,

$$\boxed{\begin{array}{l} \text{if } k_{Ag} p_A \geq \frac{k_{Bl}}{b} C_B, \text{ then use Eq. 13: Case A} \\ \text{if } k_{Ag} p_A \leq \frac{k_{Bl}}{b} C_B, \text{ then use Eq. 16: Case B} \end{array}} \quad (17)$$

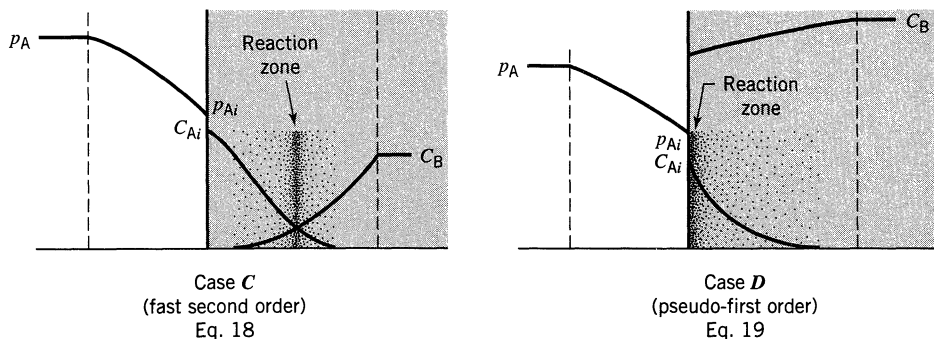
Let us now look at the other cases.

**Case C: Fast Reaction; Low  $C_B$ .** The plane of reaction for case A now spreads into a zone of reaction in which A and B are both present. However, reaction is fast enough so that this reaction zone remains totally within the liquid film. Thus, no A enters the main body of liquid to react there.

Since the last resistance term in the general rate equation, Eq. 5, is negligible (large  $k$ ), the rate form for this case is

$$-r_A''' = \frac{1}{\frac{1}{k_{Ag} a} + \frac{H_A}{k_{Al} a E}} p_A \quad (18)$$

**Case D: Fast Reaction; High  $C_B$ , Hence Pseudo First-Order Rate with Respect to A.** For the special case where  $C_B$  does not drop appreciably within the film, it can be taken to be constant throughout, and the second-order reaction rate (Case C) simplifies to the more easily solved first-order rate expression. Thus,



**Figure 23.6** Location of reaction in the liquid film for a fast (but not infinitely fast) second-order reaction. Case *C*—low  $C_B$ , Case *D*—high  $C_B$ .

the general rate expression, Eq. 5, reduces to

$$-r_A''' = \frac{1}{\frac{1}{k_{Ag}a} + \frac{H_A}{a\sqrt{\mathcal{D}_A k C_B}}} p_A \quad (19)$$

Figure 23.6 sketches Cases *C* and *D*.

**Cases E and F: Intermediate Rate with Respect to Mass Transfer.** Here reaction is slow enough for some A to diffuse through the film into the main body of the fluid. Consequently, A reacts both within the film and in the main body of the fluid. Here we have to use the general rate expression with its three resistances, Eq. 5.

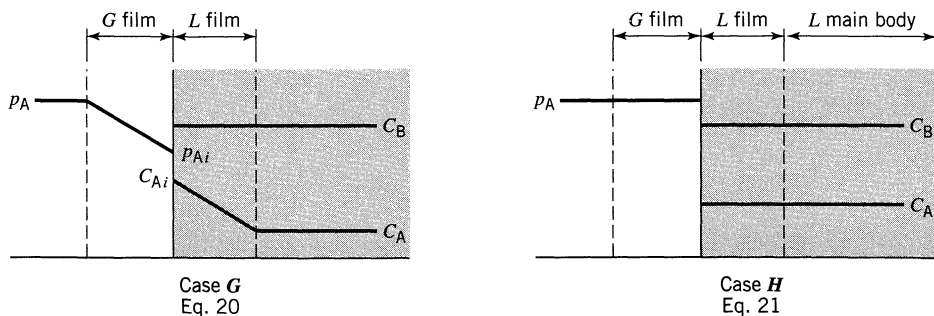
**Case G: Slow Reaction with Respect to Mass Transfer.** This represents the somewhat curious case where all reaction occurs in the main body of the liquid; however, the film still provides a resistance to the transfer of A into the main body of liquid. Thus, three resistances enter into the rate expression, and Eq. 5 reduces to

$$-r_A''' = \frac{1}{\frac{1}{k_{Ag}a} + \frac{H_A}{k_{Al}a} + \frac{H_A}{k C_B f_l}} p_A \quad (20)$$

**Case H: Infinitely Slow Reaction.** Here the mass transfer resistance is negligible, the compositions of A and B are uniform in the liquid, and the rate is determined by chemical kinetics alone.

$$-r_A''' = \frac{k f_l}{H_A} p_A C_B = k f_l C_A C_B \quad (21)$$

Figure 23.7 shows cases *G* and *H*.



**Figure 23.7** Slow reactions Case **G** still shows film resistance. Case **H** shows no film resistance.

## Review of the Role of the Hatta Number, $M_H$

To tell whether reaction is fast or slow, we focus on unit surface of gas-liquid interface, we assume that gas-phase resistance is negligible, and we define a film conversion parameter

$$\begin{aligned}
 M_H^2 &= \frac{\text{maximum possible conversion in the film}}{\text{maximum diffusional transport through the film}} \\
 &= \frac{k C_{Ai} C_{B0} x_0}{\frac{\mathcal{D}_{Ai}}{x_0} \cdot C_{Ai}} = \frac{k C_{B0} \mathcal{D}_{Ai}}{k_{Ai}^2}
 \end{aligned}
 \quad (22)$$

If  $M_H \gg 1$ , all reaction occurs in the film, and surface area is the controlling rate factor. On the other hand, if  $M_H \ll 1$  no reaction occurs in the film, and bulk volume becomes the controlling rate factor. More precisely, it has been found that:

1. If  $M_H > 2$ , reaction occurs in the film and we have Cases **A**, **B**, **C**, **D**.
2. If  $0.02 < M_H < 2$ , we then have the intermediate Cases **E**, **F**, **G**.
3. If  $M_H < 0.02$ , we have the infinitely slow reaction of Case **H**.

When  $M_H$  is large, we should pick a contacting device which develops or creates large interfacial areas; energy for agitation is usually an important consideration in these contacting schemes. On the other hand, if  $M_H$  is very small, all we need is a large volume of liquid. Agitation to create large interfacial areas is of no benefit here.

Table 24.1 of the next chapter presents typical data for various contacting devices, and from this we see that spray or plate columns should be efficient devices for systems with fast reaction (or large  $M_H$ ), while bubble contactors should be more efficient for slow reactions (or small  $M_H$ ).

## Clues to the Kinetic Regime from Solubility Data

For reactions which occur in the film, the phase distribution coefficient  $H$  can suggest whether the gas-phase resistance is likely to be important or not. To

show this we write the expression for straight mass transfer of A across the gas and liquid films

$$-\frac{1}{S} \frac{dN_A}{dt} = \frac{1}{\frac{1}{k_{Ag}} + \frac{H_A}{k_{Al}}} \Delta p_A \quad (23)$$

Now for slightly soluble gases  $H_A$  is large; hence, with all other factors unchanged the above rate equation shows that the liquid film resistance term is large. The reverse holds for highly soluble gases. Thus, we see that:

Gas film resistance controls for highly soluble gases.

Liquid film resistance controls for slightly soluble gases.

**Table 23.2** Typical Values of  $H_A = p_{Ai}/C_{Ai}$ , Pa · m<sup>3</sup>/mol, for Common Gases in Water

	N <sub>2</sub>	H <sub>2</sub>	O <sub>2</sub>	CO	CO <sub>2</sub>	NH <sub>3</sub>
20°C	1.45 × 10 <sup>5</sup>	1.23 × 10 <sup>5</sup>	0.74 × 10 <sup>5</sup>	0.96 × 10 <sup>5</sup>	2600	0.020
60°C	2.16 × 10 <sup>5</sup>	1.34 × 10 <sup>5</sup>	1.13 × 10 <sup>5</sup>	1.48 × 10 <sup>5</sup>	6300	0.096

slightly soluble gas ←————→ highly soluble gas

Note that gases are more soluble at lower temperatures. Additional values for many different gases can be extracted, with difficulty, from Perry and Green (1984) and from references given by Danckwerts (1970).

Since a highly soluble gas is easy to absorb and has its main resistance in the gas phase, we would not need to add a liquid-phase reactant B to promote the absorption. On the other hand, a sparingly soluble gas is both difficult to absorb and has its main resistance in the liquid phase; hence it is this system which would benefit greatly by a reaction in the liquid phase.

## Final Comments

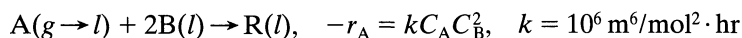
To find the size of process unit needed for a given job (this is discussed in the next chapter), we need to know the overall rate of reaction. This chapter explains how to evaluate the overall rate of reaction.

Many sources report on the physical and chemical constants used in this chapter. I recommend the following ones:

- Doraiswamy and Sharma (1984): an extensive treatment of this whole subject
- Shah (1979): evaluation of the mass transfer coefficients in various types of equipment. Also experimental devices for finding these coefficients.
- Danckwerts (1970): easy to follow discussion, sources for Henry's law constants, equations to use for finding mass transfer coefficients.

**EXAMPLE 23.1 FINDING THE RATE OF A G/L REACTION**

Air with gaseous A bubbles through a tank containing aqueous B. Reaction occurs as follows:



For this system

$$\begin{aligned} k_{Ag}a &= 0.01 \text{ mol/hr} \cdot \text{m}^3 \cdot \text{Pa} & f_l &= 0.98 \\ k_{Al}a &= 20 \text{ hr}^{-1} & H_A &= 10^5 \text{ Pa} \cdot \text{m}^3/\text{mol}, \text{ very low solubility} \\ \mathcal{D}_{Al} &= \mathcal{D}_{Bl} = 10^{-6} \text{ m}^2/\text{hr} & a &= 20 \text{ m}^2/\text{m}^3 \end{aligned}$$

For a point in the absorber-reactor where

$$p_A = 5 \times 10^3 \text{ Pa} \quad \text{and} \quad C_B = 100 \text{ mol/m}^3$$

- locate the resistance to reaction (what % is in the gas film, in the liquid film, in the main body of liquid)
- locate the reaction zone
- determine the behavior in the liquid film (whether pseudo first-order reaction, instantaneous, physical transport, etc.)
- calculate the rate of reaction ( $\text{mol/m}^3 \cdot \text{hr}$ )

**SOLUTION**

This chapter has only analyzed second-order reactions, however, this problem deals with a third-order reaction. Since no analysis is available for other than second-order reactions, let us replace our third-order reaction with a second-order approximation. Thus,

$$kC_A C_B^2 \Rightarrow (kC_B)C_A C_B$$

To find the rate from the general expression (Eq. 5), we need to first evaluate  $E_i$  and  $M_H$ . Let us do this:

$$\left. \begin{aligned} M_H &= \frac{\sqrt{\mathcal{D}_A k C_B^2}}{k_{Al}} = \frac{\sqrt{10^{-6} 10^6 100^2}}{1} = 100 \\ (E_i)_{\text{first guess}} &= 1 + \frac{\mathcal{D}_B C_B H_A}{b \mathcal{D}_{AP_{Ai}}} = 1 + \frac{100 \times 10^5}{2(5 \times 10^5)} = 10^3 \end{aligned} \right\}$$

guess  $p_{Ai} = p_A$   $\nearrow$

Since  $(E_i)_{\text{first guess}} > 5 M_H$ , then for any other smaller guess for  $p_{Ai}$  we will still have  $E_i > 5 M_H$ . Therefore, from Fig. 23.4 we have pseudo first-order reaction

in the film with

$$E = M_H = 100$$

Now to the rate expression, Eq. 5,

$$\begin{aligned} -r_A''' &= \frac{p_A}{\frac{1}{k_{Ag}a} + \frac{H_A}{k_{Al}aE} + \frac{H_A}{kC_B^2 f_l}} \\ &= \frac{5 \times 10^3}{\underbrace{\frac{1}{0.01}}_{\frac{2}{3}} + \underbrace{\frac{10^5}{20(100)}}_{\frac{1}{3}} + \underbrace{\frac{10^5}{(10^6)(100^2)(.098)}}_{\sim 0}} = 33 \text{ mol/hr} \cdot \text{m}^3 \text{ reactor} \end{aligned}$$

Thus,

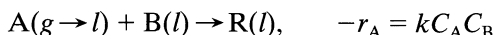
- (a) 2/3 of the resistance is in the gas film, 1/3 is in the liquid film ←
- (b) the reaction zone is in the liquid film ←
- (c) reaction proceeds by a pseudo first-order reaction of A, at the interface ←
- (d) the rate is  $-r_A''' = 33 \text{ mol/hr} \cdot \text{m}^3$  ←

## REFERENCES

- Danckwerts, P. V., *Trans. Faraday Soc.*, **46**, 300 (1950).  
 ———, *AIChE J.*, **1**, 456 (1955).  
 ———, *Gas-Liquid Reactions*, McGraw-Hill, New York, 1970.  
 Doraiswamy, L. K., and Sharma, M. M., *Heterogeneous Reactions*, Vol. 2, John Wiley and Sons, New York, 1984.  
 Hatta, S., Technological Reports, Tôhoku University, **10**, 119 (1932); from Sherwood, T. K., and Pigford, R. L., *Absorption and Extraction*, McGraw-Hill, New York, 1952.  
 Higbie, R., *Trans. A.I.Ch.E.*, **31**, 365 (1935).  
 Perry, R. H., and Green, D. W., *Chemical Engineers' Handbook*, 6th ed., Section 3, McGraw-Hill, New York, 1984.  
 Shah, Y. T., *Gas-Liquid-Solid Reactor Design*, McGraw-Hill, New York, 1979.  
 Teller, A. J., *Chem. Eng.*, **67**, 111 (July 11, 1960).  
 van Krevelen, D. W., and Hoftijzer, P. J., *Rec. Trav. Chim.*, **67**, 563 (1948); *Trans. I. Chem. E.*, **32**, 5360 (1954).

## PROBLEMS

Gaseous A absorbs and reacts with B in liquid according to



in a packed bed under conditions where

$$\begin{aligned} k_{Ag}a &= 0.1 \text{ mol/hr} \cdot \text{m}^2 \text{ of reactor} \cdot \text{Pa} & f_l &= 0.01 \text{ m}^3 \text{ liquid/m}^3 \text{ reactor} \\ k_{Al}a &= 100 \text{ m}^3 \text{ liquid/m}^3 \text{ reactor} \cdot \text{hr} & \mathcal{D}_{Al} &= \mathcal{D}_{Bl} = 10^{-6} \text{ m}^2/\text{hr} \\ a &= 100 \text{ m}^2/\text{m}^3 \text{ reactor} \end{aligned}$$

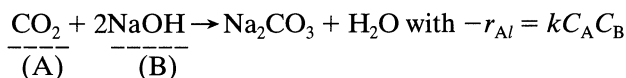
At a point in the reactor where  $p_A = 100 \text{ Pa}$  and  $C_B = 100 \text{ mol/m}^3 \text{ liquid}$

- (a) calculate the rate of reaction in  $\text{mol/hr} \cdot \text{m}^3$  of reactor.  
 (b) describe the following characteristics of the kinetics:
- location of the major resistance (gas film, liquid film, main body of liquid)
  - behavior in the liquid film (pseudo first-order reaction, instantaneous, second-order reaction, physical transport)
- for the following values of reaction rate and Henry's law constant.

	$k, \text{ m}^3 \text{ liquid/mol} \cdot \text{hr}$	$H_A, \text{ Pa} \cdot \text{m}^3 \text{ liquid/mol}$
23.1.	10	$10^5$
23.2.	$10^6$	$10^4$
23.3.	10	$10^3$
23.4.	$10^{-4}$	1
23.5.	$10^{-2}$	1
23.6.	$10^8$	1

23.7. Redo Example 23.1 with just one change. Let us suppose that  $C_B$  is very low, or  $C_B = 1$ .

23.8. At high pressure  $\text{CO}_2$  is absorbed into a solution of  $\text{NaOH}$  in a packed column. The reaction is as follows:



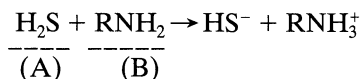
Find the rate of absorption, the controlling resistance, and what is happening in the liquid film, at a point in the column where  $p_A = 10^5 \text{ Pa}$  and  $C_B = 500 \text{ mol/m}^3$ .

$$\begin{aligned} \text{Data: } k_{Ag}a &= 10^{-4} \text{ mol/m}^2 \cdot \text{s} \cdot \text{Pa} & H_A &= 25\,000 \text{ Pa} \cdot \text{m}^3/\text{mol} \\ k_{Al} &= 1 \times 10^{-4} \text{ m/s} & \mathcal{D}_A &= 1.8 \times 10^{-9} \text{ m}^2/\text{s} \\ a &= 100 \text{ m}^{-1} & \mathcal{D}_B &= 3.06 \times 10^{-9} \text{ m}^2/\text{s} \\ k &= 10 \text{ m}^3/\text{mol} \cdot \text{s} & f_l &= 0.1 \end{aligned}$$

This problem was adapted from Danckwerts (1970).



- 23.9.** Hydrogen sulfide is absorbed by a solution of methanolamine (MEA) in a packed column. At the top of the column, gas is at 20 atm and it contains 0.1% of  $\text{H}_2\text{S}$ , while the absorbent contains  $250 \text{ mol/m}^3$  of free MEA. The diffusivity of MEA in solution is 0.64 times that of  $\text{H}_2\text{S}$ . The reaction is normally regarded as irreversible and instantaneous.



For the flow rates and packing used

$$k_{\text{A}}a = 0.03 \text{ s}^{-1}$$

$$k_{\text{Ag}}a = 60 \text{ mol/m}^3 \cdot \text{s} \cdot \text{atm}$$

$$H_{\text{A}} = 1 \times 10^{-4} \text{ m}^3 \cdot \text{atm/mol}, \text{ Henry's law constant for } \text{H}_2\text{S} \text{ in water.}$$

- (a) Find the rate of absorption of  $\text{H}_2\text{S}$  in MEA solution.
- (b) To find out whether it is worthwhile using MEA absorbent, determine how much faster is absorption with MEA compared to absorption in pure water.

This problem was adapted from Danckwerts (1970).

# Chapter 24

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## Fluid–Fluid Reactors: Design

We must first choose the right kind of contactor, then find the size needed. There are two kinds of contactor—towers and tanks, and Fig. 24.1 shows some examples. As may be expected, these contactors have widely different  $G/L$  volume ratios, interfacial areas,  $k_g$  and  $k_l$ , and concentration driving forces. The particular properties of the system you are dealing with, the solubility of gaseous reactant, the concentration of reactants, etc.—in effect the location of the main resistance in the rate equation—will suggest that you use one class of contactor and not the other.

Table 24.1 shows some of the characteristics of these contactors.

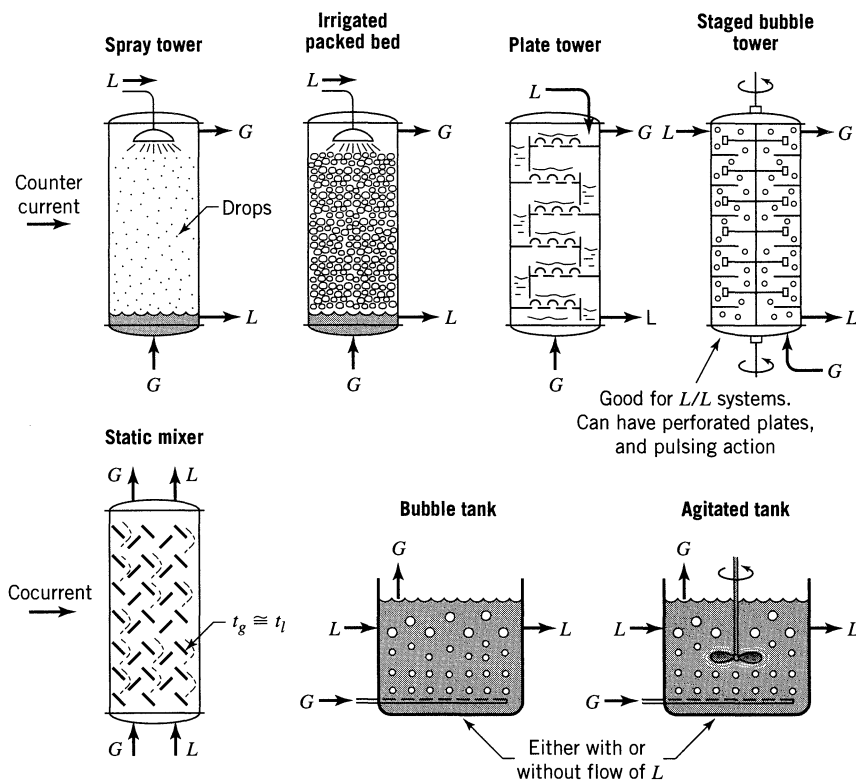
### Factors to Consider in Selecting a Contactor

(a) **Contacting pattern.** We idealize these as shown in Fig. 24.2.

- Towers approximate plug  $G$ /plug  $L$ .
- Bubble tanks approximate plug  $G$ /mixed  $L$ .
- Agitated tanks approximate mixed  $G$ /mixed  $L$ .

As we shall see, towers have the largest mass transfer driving force and in this respect have an advantage over tanks. Agitated tanks have the smallest driving force.

- (b)  **$k_g$  and  $k_l$ .** For liquid droplets in gas  $k_g$  is high,  $k_l$  is low. For gas bubbles rising in liquid  $k_g$  is low,  $k_l$  is high.
- (c) **Flow rates.** Packed beds work best with relative flow rates of about  $F_l/F_g \cong 10$  at 1 bar. Other contactors are more flexible in that they work well in a wider range of  $F_l/F_g$  values.
- (d) **If the resistance is in the gas and/or liquid films** you want a large interfacial area “a,” thus most agitated contactors and most columns. If the  $L$  film dominates, stay away from spray contactors. If the  $G$  film dominates stay away from bubble contactors.
- (e) **If the resistance is in the main body** of the  $L$  you want large  $f_l = V_l/V_r$ . Stay away from towers. Use tank contactors.
- (f) **Solubility.** For very soluble gases, those with a small value of Henry’s law constant  $H$  (ammonia, for example), gas film controls, thus you should



**Figure 24.1** Tower and tank contactors for  $G/L$  reactions.

avoid bubble contactors. For gases of low solubility in the liquid, thus high  $H$  value ( $O_2$ ,  $N_2$ , as examples) liquid film controls, so avoid spray towers.

**(g) Reaction lowers the resistance of the liquid film, so**

- For absorption of highly soluble gases, chemical reaction is not helpful.
- For absorption of slightly soluble gases, chemical reaction is helpful and does speed up the rate.

**Nomenclature.** We use the following symbols in our development.

$A_{cs}$  = cross-sectional area of column.

$a$  = interfacial contact area per unit volume of reactor ( $m^2/m^3$ ).

$f_l$  = volume fraction of liquid (-).

$i$  = any participant, reactant or product, in the reaction.

A, B, R, S = participants in the reaction.

U = carrier or inert component in a phase, hence neither reactant nor product.

$T$  = total moles in the reacting (or liquid) phase.

$Y_A = p_A/p_U$ , moles A/mole inert in the gas (-).

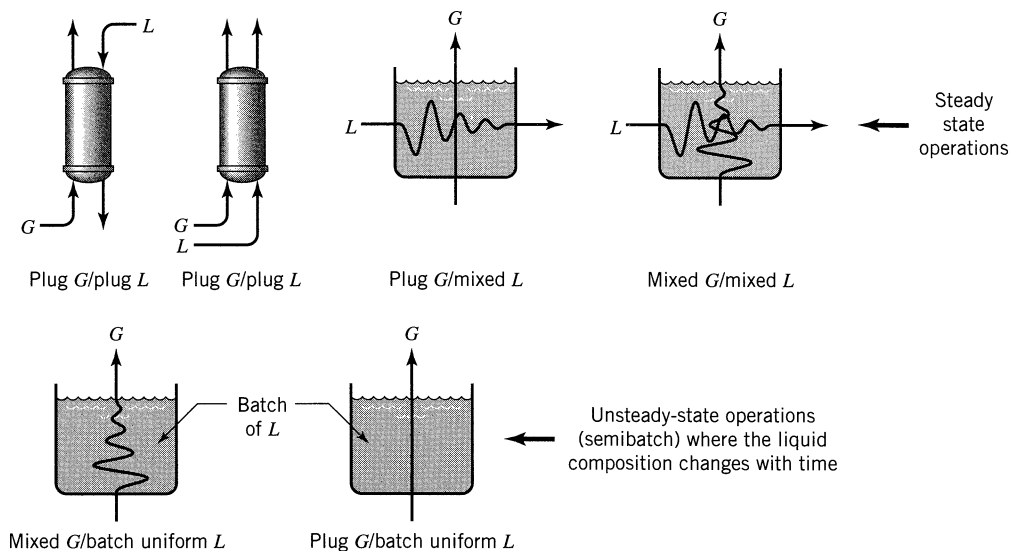
$X_A = C_A/C_U$ , moles A/mole inert in the liquid (-).

$F'_g, F'_l$  = molar flow rate of all the gas and the liquid (mol/s).

$F_g = F'_g p_U/\pi$ , upward molar flow rate of inerts in the gas (mol/s).

**Table 24.1** Characteristics of *G/L* Contactors (from Kramers and Westerterp, 1961).

Flow Pattern	Contactor	$a$ ( $\text{m}^2/\text{m}^3$ )	$f_t = \frac{V_l}{V}$ (-)	Capacity	Comments
Counter Current Flow	Spray tower	60	0.05	Low	Good for very soluble gases high $k_g/k_l$
	Packed bed	100	0.08	High	Good all rounder, but must have $F_l/F_g \approx 10$
	Plate tower	150	0.15	Medium-high	
Cocurrent flow	Staged bubble column	200	0.9	Low	Needs mechanical mixer or pulsing device. Good for slightly soluble gases and $L_1/L_2$ . Has low $k_g/k_l$ .
	Static mixer	200	0.2–0.8	Very high	Very flexible, little reported data $t_g \approx t_l$ .
Mixed flow of <i>L</i>	Bubble tank	20	0.98	Medium	Cheap to build
	Agitated tank	200	0.9	Medium	Cheap to build but needs a mechanical agitator



**Figure 24.2** Contacting patterns for  $G/L$  contactors.

$F_l = F'_l C_U / C_T$ , downward molar flow rate of inerts in the liquid phase (mol/s).

With this nomenclature, we have the following relationships among the various concentration measures.

$$\pi = p_A + p_B + \cdots + p_U$$

$$C_T = C_A + C_B + \cdots + C_U$$

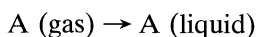
$$dY_A = d\left(\frac{p_A}{p_U}\right) = \frac{p_U dp_A - p_A dp_U}{p_U^2} \stackrel{\text{dilute}}{\approx} \frac{dp_A}{p_U}$$

$$dX_A = d\left(\frac{C_A}{C_U}\right) = \frac{C_U dC_A - C_A dC_U}{C_U^2} \stackrel{\text{dilute}}{\approx} \frac{dC_A}{C_U}$$

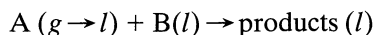
The performance equations which are written in terms of  $F_g$  and  $F_l$  are useful when the flowing streams have inert carrier material. The equation written in terms of  $F'_g$  and  $F'_l$  are useful when the flowing streams only contain reactive materials and no inerts.

## 24.1 STRAIGHT MASS TRANSFER

Since the approach for reacting systems is a straightforward extension of straight mass transfer, let us first develop equations for absorption alone of A by liquid



then go to reacting systems.



Note the similarity in the performance equations.

### Plug Flow *G*/Plug Flow *L*—Countercurrent Flow in a Tower

To develop the performance equation, we combine the rate equation with the material balance. Thus for steady-state countercurrent operations we have for a differential element of volume

$$(A \text{ lost by gas}) = (A \text{ gained by liquid}) = (-r_A''')dV_r$$

or

$$\begin{aligned} F_g dY_A &= F_l dX_A = (-r_A''')dV_r \quad (1) \\ \frac{F_g \pi dp_A}{(\pi - p_A)^2} &= d \left( \frac{F'_g p_A}{\pi} \right) = \frac{F_g dp_A}{\pi - p_A} = \frac{F_l C_T dC_A}{(C_T - C_A)^2} \quad (-r_A''')a = k_{Ag} a(p_A - p_{Ai}) = k_{Al} a(C_{Ai} - p_A) \end{aligned}$$

Integrating for the whole tower gives

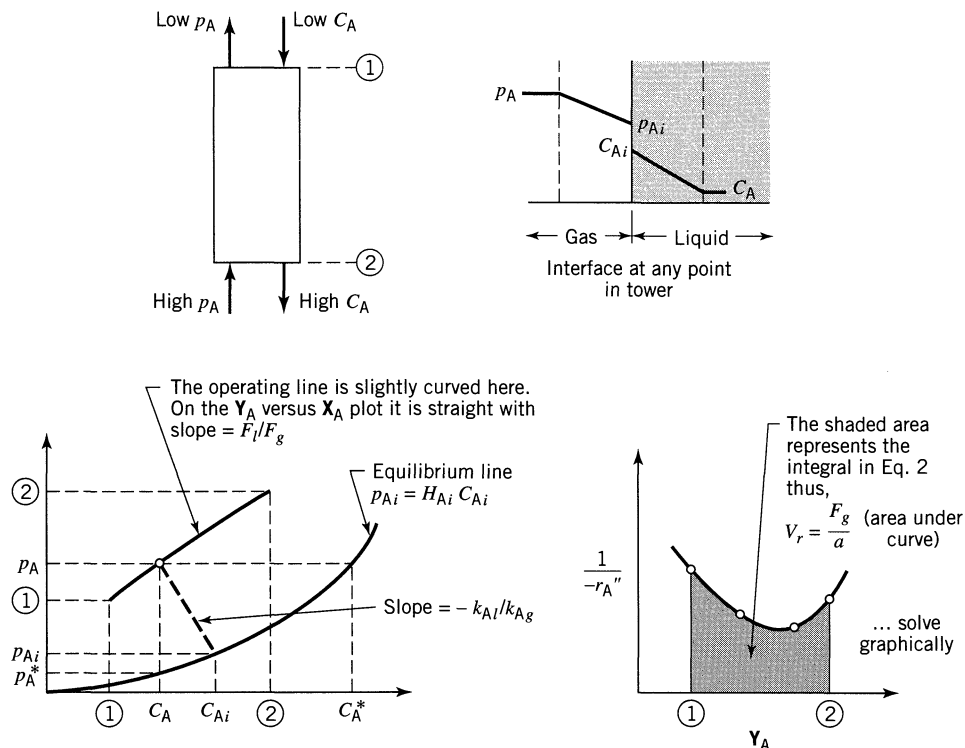
$$\begin{aligned} V_r &= \frac{F_g}{a} \int_{Y_{A1}}^{Y_{A2}} \frac{dY_A}{\pi - p_A} = \frac{F_l}{a} \int_{X_{A1}}^{X_{A2}} \frac{dX_A}{C_T - C_A} \\ &= F_g \pi \int_{p_{A1}}^{p_{A2}} \frac{dp_A}{k_{Ag} a(\pi - p_A)^2(p_A - p_{Ai})} = \int_{p_{A1}}^{p_{A2}} \frac{F'_g dp_A}{k_{Ag} a(\pi - p_A)(p_A - p_{Ai})} \quad (2) \\ &= F_l C_T \int_{C_{A1}}^{C_{A2}} \frac{dC_A}{k_{Al} a(C_T - C_A)^2(C_{Ai} - C_A)} = \int_{C_{A1}}^{C_{A2}} \frac{F'_g dC_A}{k_{Al} a(C_T - C_A)(C_{Ai} - C_A)} \end{aligned}$$

In brief, the design procedure is summarized in Fig. 24.3. For dilute systems  $C_A \ll C_T$  and  $p_A \ll \pi$ , so  $F'_g \cong F_g$  and  $F'_l \cong F_l$ . In this situation the differential material balance becomes

$$\frac{F_g}{\pi} dp_A = \frac{F_l}{C_T} dC_A = -r_A'''' dV_r \quad (3)$$

and for any two points in the absorber

$$p_{A2} - p_{A1} = \frac{F_l \pi}{F_g C_T} (C_{A2} - C_{A1}) \quad (4)$$



**Figure 24.3** Illustration of the design procedure for straight mass transfer in countercurrent towers.

The rate expression reduces to

$$\begin{aligned}
 -r_A''' &= (-r_A'')a = \left( \frac{1}{\frac{1}{k_{Ag}a} + \frac{H_A}{k_{Al}a}} \right) (p_A - p_A^*) \\
 &= K_{Ag}a(p_A - p_A^*) = K_{Al}a(C_A^* - C_A)
 \end{aligned} \quad (5)$$

Thus the general integrated rate expression of Eq. 2 becomes, with Eq. 3,

$$\begin{aligned}
 V_r &= hA_{cs} = \frac{F_g}{\pi} \int_{p_{A1}}^{p_{A2}} \frac{dp_A}{-r_A'''} = \frac{F_l}{C_T} \int_{C_{A1}}^{C_{A2}} \frac{dC_A}{-r_A'''} \\
 &= \frac{F_g}{\pi K_{Ag}a} \int_{p_{A1}}^{p_{A2}} \frac{dp_A}{p_A - p_A^*} = \frac{F_l}{C_T K_{Al}a} \int_{C_{A1}}^{C_{A2}} \frac{dC_A}{C_A^* - C_A}
 \end{aligned} \quad (6)$$

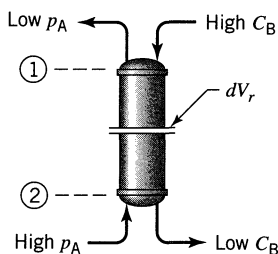
coefficient on gas basis  $\frac{1}{K_{Ag}} = \frac{1}{k_{Ag}} + \frac{H_A}{k_{Al}}$       gas in equilibrium with liquid  $C_A$ , or  $p_A^* = H_A C_A$       coefficient on liquid basis  $\frac{1}{K_{Al}} = \frac{1}{H_A k_{Ag}} + \frac{1}{k_{Al}}$       liquid in equilibrium with gas  $p_A$ , or  $C_A^* = p_A/H_A$

For the other contacting patterns of Fig. 24.2 plug  $G$ /plug  $L$  cocurrent, mixed  $G$ /mixed  $L$ , plug  $G$ /mixed  $L$ , mixed  $G$ /plug  $L$ , mixed  $G$ /batch  $L$  see Levenspiel (1996) Chapter 42, or recall the equations and methods from your lessons in mass transfer and unit operations.

## 24.2 MASS TRANSFER PLUS NOT VERY SLOW REACTION

Here we only treat the reaction  $A(g \rightarrow l) + bB(l) \rightarrow \text{products}(l)$ . We assume that the rate is fast enough so that no unreacted  $A$  enters the main body of the liquid. This assumes that the Hatta modulus is not very much smaller than unity.

### Plug Flow $G$ /Plug Flow $L$ —Mass Transfer + Reaction in a Countercurrent Tower



For a differential slice of absorber-reactor we write

$$\underbrace{\left( \begin{array}{c} \text{A lost} \\ \text{by gas} \end{array} \right)}_{\text{I}} = \frac{1}{b} \underbrace{\left( \begin{array}{c} \text{B lost} \\ \text{by liquid} \end{array} \right)}_{\text{II}} = \underbrace{\left( \begin{array}{c} \text{disappearance} \\ \text{of A by reaction} \end{array} \right)}_{\text{III}}$$

or

$$F_g dY_A = -\frac{F_l dX_B}{b} = (-r_A''') dV_r \quad (7)$$

**For Dilute Systems.**  $p_U \cong \pi$  and  $C_U \cong C_T$  in which case the above expressions simplify to

$$\frac{F_g}{\pi} dp_A = -\frac{F_l}{b C_T} dC_B = (-r_A'') a dV_r \quad (8)$$



Rearranging and integrating I and II, II and III, I and III gives the following:

In general

$$V_r = F_g \int_{Y_{A1}}^{Y_{A2}} \frac{dY_A}{(-r_A'')a}$$

$$= \frac{F_l}{b} \int_{X_{B2}}^{X_{B1}} \frac{dX_B}{(-r_B'')a} \quad \dots \text{with} \quad F_g(Y_{A2} - Y_{A1}) = \frac{F_l}{b}(X_{B1} - X_{B2}) \quad (9)$$

For dilute systems

$$V_r = \frac{F_g}{\pi} \int_{p_{A1}}^{p_{A2}} \frac{dp_A}{(-r_A'')a}$$

$$= \frac{F_l}{bC_T} \int_{C_{B2}}^{C_{B1}} \frac{dC_B}{(-r_A'')a} \quad \dots \text{with} \quad \frac{F_g}{\pi}(p_{A2} - p_{A1}) = \frac{F_l}{bC_T}(C_{B1} - C_{B2}) \quad (10)$$

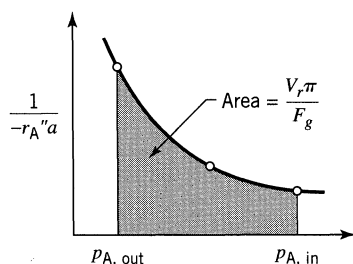
also good from point 1 to and point  $i$  in the tower

**To Solve for  $V_r$**

- pick a few  $p_A$  values, usually  $p_{A1}$ ,  $p_{A2}$  and one intermediate value are enough, and for each  $p_A$  find the corresponding  $C_B$ .
- evaluate the rate for each point from

$$(-r_A'')a = \left[ \frac{1}{\frac{1}{k_{Ag}a} + \frac{H_A}{k_{Al}aE} + \frac{H_A}{kC_B f_i}} \right] p_A$$

- integrate the performance equation graphically



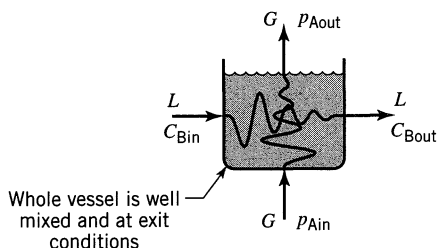
### Plug Flow $G$ /Plug Flow $L$ —Mass Transfer + Reaction in a Cocurrent Tower

Here simply change  $F_l$  to  $-F_l$  (for upflow of both streams) or  $F_g$  to  $-F_g$  (for downflow of both streams) in the equations for countercurrent flow. Be sure to find the proper  $C_B$  value for each  $p_A$ . The rest of the procedure remains the same.

### Mixed Flow *G*/Mixed Flow *L*—Mass Transfer + Reaction in an Agitated Tank Contactor

Since the composition is the same everywhere in the vessel make an accounting about the vessel as a whole. Thus,

$$\left( \begin{array}{c} \text{A lost} \\ \text{by gas} \end{array} \right) = \frac{1}{b} \left( \begin{array}{c} \text{B lost} \\ \text{by liquid} \end{array} \right) = \left( \begin{array}{c} \text{disappearance of} \\ \text{A by reaction} \end{array} \right)$$



In symbols these equalities become

$$F_g(\mathbf{Y}_{Ain} - \mathbf{Y}_{Aout}) = \frac{F_l}{b}(\mathbf{X}_{Bin} - \mathbf{X}_{Bout}) = (-r_A''')|_{\text{at exit conditions for both } G \text{ and } L} V_r \quad (11)$$

and for dilute systems

$$\frac{F_g}{\pi}(p_{Ain} - p_{Aout}) = \frac{F_l}{bC_T}(C_{Bin} - C_{Bout}) = (-r_A''')|_{\text{at exit}} V_r \quad (12)$$

**To find  $V_r$** , the solution is direct; evaluate  $-r_A'''$  from known stream compositions and solve Eq. 11 or 12.

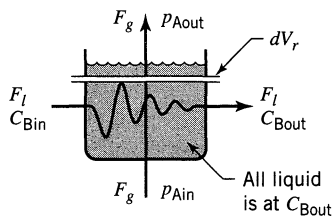
**To find  $C_{Bout}$  and  $p_{Aout}$  given  $V_r$** , guess  $p_{Aout}$ , evaluate  $C_{Bout}$ , then  $-r_A'''$ , then  $V_r$ . Compare the calculated  $V_r$  value with the true value. If different, guess another  $p_{Aout}$ .

### Plug Flow *G*/Mixed Flow *L*—Mass Transfer + Reaction in Bubble Tank Contactors

Here we must make two accountings, a differential balance for the loss of A from the gas because *G* is in plug flow, and an overall balance for B because *L* is in mixed flow.

Focusing on a bit of rising gas, we have

$$\left( \begin{array}{c} \text{A lost} \\ \text{by gas} \end{array} \right) = \left( \begin{array}{c} \text{disappearance of} \\ \text{A by reaction} \end{array} \right) \quad \dots \text{ or } \dots \quad F_g d\mathbf{Y}_A = (-r_A''')|_{L \text{ at exit conditions}} dV_r \quad (13)$$



For the liquid as a whole and for the gas as a whole, a balance about the whole reactor gives

$$\left( \begin{array}{c} \text{all A lost} \\ \text{by gas} \end{array} \right) = \frac{1}{b} \left( \begin{array}{c} \text{all B lost} \\ \text{by liquid} \end{array} \right) \quad \dots \text{ or } \dots \quad F_g \Delta Y_A = \frac{F_l}{b} \Delta X_B \quad (14)$$

Integrating Eq. 13 along the path of the bubble and also using Eq. 14 gives

In general

$$V_r = F_g \int_{Y_{Aout}}^{Y_{Ain}} \frac{dY_A}{(-r_A'')a} \quad \dots \text{with} \dots \quad F_g(Y_{Ain} - Y_{Aout}') = \frac{F_l}{b}(X_{Bin} - X_{Bout}) \quad (15)$$

for liquid at  $C_{Bout}$

For dilute systems

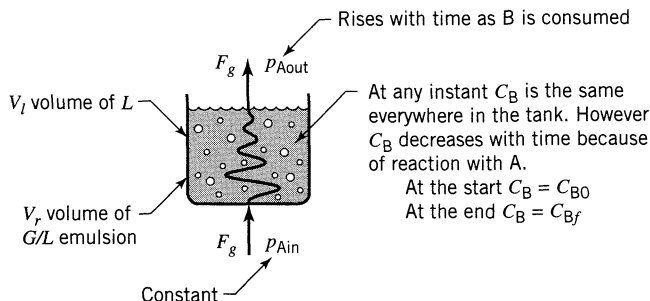
$$V_r = \frac{F_g}{\pi} \int_{p_{Aout}}^{p_{Ain}} \frac{dp_A}{(-r_A'')a} \quad \dots \text{with} \dots \quad \frac{F_g}{\pi}(p_{Ain} - p_{Aout}) = \frac{F_l}{bC_T}(C_{Bin} - C_{Bout}) \quad (16)$$

If  $V_r$  is to be found and the exit conditions are known, then the procedure is direct. Pick a number of  $p_A$  values and integrate graphically.

If  $p_{Aout}$  and  $C_{Bout}$  are to be found in a reactor of known volume  $V_r$ , then we require a trial and error solution. Simply guess  $C_{Bout}$  and then see if  $V_{calculated} = V_{given}$ .

### Mixed Flow $G$ /Batch Uniform $L$ —Absorption + Reaction in a Batch Agitated Tank Contactor

Since this is not a steady-state operation, composition and rates all change with time, as shown in Fig. 24.4. At any instant the material balance equates the three



**Figure 24.4** History of a batch of reacting liquid.

quantities shown below and thus in general

$$\underbrace{F_g(Y_{Ain} - Y_{Aout})}_{\text{I: loss of A from gas}} = - \underbrace{\frac{V_l}{b} \frac{dC_B}{dt}}_{\text{II: decrease of B with time in L}} = \underbrace{(-r_A''')V_r}_{\text{III: disappearance of A or B by reaction. In the rate expression use } p_{Aout} \text{ since G is in mixed flow.}} \quad (17)$$

For dilute systems

$$\frac{F_g}{\pi}(p_{Ain} - p_{Aout}) = - \frac{V_l}{b} \frac{dC_B}{dt} = (-r_A''')V_r \quad (18)$$

### To Find the Time Needed for a Given Operation

- Choose a number of  $C_B$  values, say  $C_{B0}$ ,  $C_{Bf}$  and an intermediate  $C_B$  value. For each  $C_B$  value guess  $p_{Aout}$ .
- Next calculate  $M_H$ ,  $E_i$ , and then  $E$  and  $-r_A'''$ . This may require trial and error, but not often.
- See if terms I and III are equal to each other

$$(-r_A''')V_r \stackrel{?}{=} F_g \left( \frac{p_{Ain}}{\pi - p_{Ain}} - \frac{p_{Aout}}{\pi - p_{Aout}} \right)$$

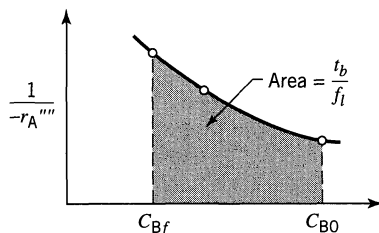
and keep adjusting  $p_{Aout}$  until they do.

As a shortcut: if  $p_A \ll \pi$  and if  $E = M_H$  then  $E$  is independent of  $p_A$  in which case I and III combine to give

$$-r_A''' = p_{Ain} / \left( \frac{\pi V_r}{F_g} + \frac{1}{k_{Ag}a} + \frac{H_A}{k_{Al}aE} + \frac{H_A}{k_{Bf}f_l} \right)$$

- Next combine terms II and III to find the processing time

$$t = \frac{f_I}{b} \int_{C_{Bf}}^{C_{B0}} \frac{dC_B}{-r_A'''} \quad \dots \text{solve graphically} \quad (19)$$



- This time can be compared with the minimum needed if all A reacts and none escapes the vessel. This situation is represented by  $p_{Aout} = 0$  at all times. Thus

$$t_{\min} = \frac{\frac{1}{b} V_l (C_{B0} - C_{Bf})}{F_g \left( \frac{p_{Ain}}{\pi - p_{Ain}} \right)} = \frac{\frac{1}{b} \left( \text{amount of B reacted away in the vessel} \right)}{\left( \text{amount of A entering the vessel in unit time} \right)} \quad (20)$$

- Combining  $t$  and  $t_{\min}$  gives the efficiency of utilization of A. Thus

$$\left( \frac{\text{percent of entering A which reacts with B}}{\right) = \frac{t_{\min}}{t} \quad (21)$$

Example 24.6 illustrates this procedure for batch absorber-reactors.

### EXAMPLE 24.1 TOWERS FOR STRAIGHT ABSORPTION

The concentration of undesirable impurity in air (at 1 bar =  $10^5$  Pa) is to be reduced from 0.1% (or 100 Pa) to 0.02% (or 20 Pa) by absorption in pure water. Find the height of tower required for countercurrent operations.

#### Data

For consistency let us use SI units throughout.

For the packing

$$k_{Ag}a = 0.32 \text{ mol/hr} \cdot \text{m}^3 \cdot \text{Pa}$$

$$k_{Al}a = 0.1/\text{hr}$$

The solubility of A in water is given by Henry's law constant

$$H_A = p_{Ai}/C_{Ai} = 12.5 \text{ Pa} \cdot \text{m}^3/\text{mol}$$

The flow rates per meter squared cross section of tower are

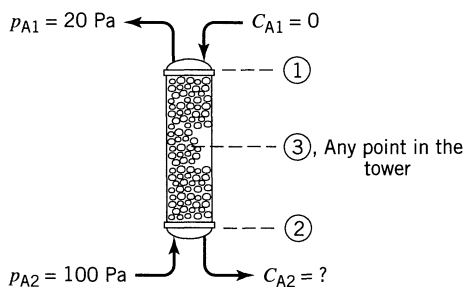
$$F_g/A_{cs} = 1 \times 10^5 \text{ mol/hr} \cdot \text{m}^2$$

$$F_l/A_{cs} = 7 \times 10^5 \text{ mol/hr} \cdot \text{m}^2$$

The molar density of liquid under all conditions is

$$C_T = 56\,000 \text{ mol/m}^3$$

Figure E24.1 shows the quantities known at this point.



**Figure E24.1**

## SOLUTION

Our strategy is to first solve the material balance, then determine the tower height. Since we are dealing with dilute solutions we may use the simplified form of the material balance. So for any point in the tower  $p_A$  and  $C_A$  are related by Eq. 4.

$$p_{A3} - p_{A1} = \frac{(F_l/A_{cs})}{(F_g/A_{cs})} \frac{\pi}{C_T} (C_{A3} - C_{A1})$$

or

$$p_{A3} - 20 = \frac{(7 \times 10^5)(1 \times 10^5)}{(1 \times 10^5)(56\,000)} (C_{A3} - 0)$$

or

$$C_{A3} = 0.08p_{A3} - 1.6$$

(i)

from which the concentration of A in the liquid leaving the tower is

$$C_{A2} = 0.08(100) - 1.6 = 6.4 \text{ mol/m}^3 \quad (\text{ii})$$

The expression for tower height is, from Eq. 6,

$$h = \frac{V_r}{A_{cs}} = \frac{(F_g/A_{cs})}{\pi(K_{Ag}a)} \int_{20}^{100} \frac{dp_A}{p_A - p_A^*} \quad (\text{iii})$$

Now evaluate terms

$$\frac{1}{(K_{Ag}a)} = \frac{1}{(k_{Ag}a)} + \frac{H_A}{(k_{Al}a)} = \frac{1}{0.32} + \frac{12.5}{0.1} = 3.125 + 125 = 128.125$$

This expression shows that

$$G \text{ film resistance} = 3.125/128.125 = 0.024, \text{ or } 2.4\%$$

$$L \text{ film resistance} = 125/128.125 = 0.976, \text{ or } 97.6\%$$

and

$$(K_{Ag}a) = 1/128.125 = 0.0078 \text{ mol/hr} \cdot \text{m}^3 \cdot \text{Pa} \quad (\text{iv})$$

Next evaluate  $p_A - p_A^*$ . Thus with Eq. (i) we get

$$\begin{aligned} p_A - p_A^* &= p_A - H_A C_A = p_A - 1.25(0.08p_A - 1.6) \\ p_A &= 20 \text{ Pa} \end{aligned} \quad (\text{v})$$

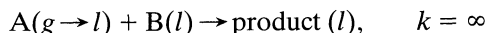
Inserting Eqs. (iv) and (v) in (iii) gives

$$\begin{aligned} h &= \frac{(1 \times 10^5 \text{ mol/hr} \cdot \text{m}^2)}{(10^5 \text{ Pa})(0.0078 \text{ mol/hr} \cdot \text{m}^3 \cdot \text{Pa})} \int_{20}^{100} \frac{dp_A}{20} \\ &= (128.125) \left( \frac{100 - 20}{20} \right) = \underline{\underline{512.5 \text{ m}}} \end{aligned}$$

**Comment.** Here the tower is very high, unacceptably high. Also note that most of the resistance (over 97%) lies in the liquid film, making this a liquid-film-controlling process. However, if we added component B to the liquid which reacts with A, we should be able to speed things up. Let's see if this is so.

**EXAMPLE 24.2 TOWERS FOR HIGH CONCENTRATION OF LIQUID REACTANT**

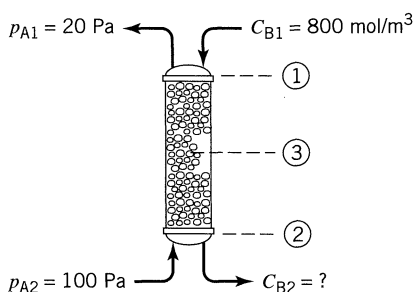
To the water of Example 24.1 add a high concentration of reactant B,  $C_{B1} = 800 \text{ mol/m}^3$  or approximately 0.8 N. Material B reacts with A extremely rapidly



Assume that the diffusivities of A and B in water are the same, thus

$$k_{Al} = k_{Bl} = k_l$$

Figure E24.2 shows what is known at this point.



**Figure E24.2**

**SOLUTION**

The strategy in solving the problem is as follows

- Step 1.** Express the material balance and find  $C_{B2}$  in the exit stream.
- Step 2.** Find which of the many forms of rate equation should be used.
- Step 3.** Determine the tower height.

**Step 1. Material balance.** For dilute solutions with rapid reaction Eq. 6 gives for any point in the tower,  $p_{A3}$ ,  $C_{B3}$

$$(p_{A3} - p_{A1}) = \frac{(F_l/A_{cs})\pi}{(F_g/A_{cs})bC_T} (C_{B1} - C_{B3})$$

or

$$(p_{A3} - 20) = \frac{(7 \times 10^5)(1 \times 10^5)}{(1 \times 10^5)(1)(56\,000)} (800 - C_{A3})$$

or

$$p_{A3} = 10\,020 - 12.5C_{B3}$$



At the bottom of the tower  $p_{A3} = p_{A2}$ , so

$$C_{B2} = \frac{1}{12.5} (10\,020 - 100) = 793.6 \text{ mol/m}^3$$

**Step 2.** *Form of rate equation to use.* Check both ends of the tower:

$$\text{at top} \begin{cases} k_{Ag}ap_A = (0.32)(20) = 6.4 \text{ mol/hr} \cdot \text{m}^3 \\ k_l a C_B = (0.1)(800) = 80 \text{ mol/hr} \cdot \text{m}^3 \end{cases}$$

$$\text{at bottom} \begin{cases} k_{Ag}ap_A = (0.32)(100) = 32 \\ k_l a C_B = (0.1)(793.6) = 79.36 \end{cases}$$

At both ends of the tower  $k_{Ag}p_A < k_l C_B$ ; therefore, gas-phase resistance controls and we have a pseudo first-order reaction as given by Eq. 16 of Chapter 23

$$-r_A''' = k_{Ag}ap_A = 0.32 p_A$$

**Step 3.** *Height of tower.* From Eq. 10

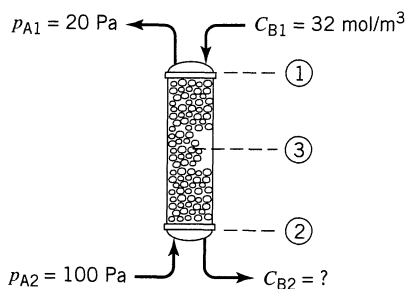
$$\begin{aligned} h &= \frac{(F_g/A_{cs})}{\pi} \int_{p_{A1}}^{p_{A2}} \frac{dp_A}{(-r_A''')} = \frac{10^5}{10^5} \int_{20}^{100} \frac{dp_A}{0.32 p_A} \\ &= \frac{1}{0.32} \ln \frac{100}{20} = \underline{\underline{5.03 \text{ m}}} \end{aligned}$$

**Comment.** Even though the liquid phase controls in physical absorption (see Example 24.1), it does not necessarily follow that it should still control when reaction occurs. In fact, we see here in Example 24.2 that it is the gas phase alone which influences the rate of the overall process. Reaction serves merely to eliminate the resistance of the liquid film. Also note the remarkable improvement in performance; 5 versus 500 m.

### EXAMPLE 24.3

### TOWERS FOR LOW CONCENTRATION OF LIQUID REACTANT; CASE A

Repeat Example 24.2 using a feed with  $C_{B1} = 32 \text{ mol/m}^3$ , instead of  $800 \text{ mol/m}^3$ , see Fig. E24.3.



**Figure E24.3**

### SOLUTION

As in the previous examples, solve by making a material balance, check the form of rate equation to use, then apply the performance equation to find the tower height.

**Step 1. Material Balance.** As in Example 24.2, for any point in the tower,

$$p_{A3} = 420 - 12.5C_{B3} \quad \text{or} \quad C_{B3} = \frac{420 - p_{A3}}{12.5}$$

and for the bottom of the tower where  $p_A = 100$  Pa,

$$C_{B2} = \frac{320}{12.5} = 25.6 \text{ mol/m}^3$$

**Step 2. Which Rate Form to Use.** Again check both ends of the tower to see which rate form applies

$$\text{at top} \begin{cases} k_{Ag}ap_A = 0.32(20) = 6.4 \\ k_laC_B = 0.1(32) = 3.2 \end{cases}$$

$$\text{at bottom} \begin{cases} k_{Ag}ap_A = 0.32(100) = 32 \\ k_laC_B = 0.1(35.6) = 2.56 \end{cases}$$

At both ends of the tower  $k_{Ag}ap_A > k_laC_B$ , therefore, the reaction takes place within the liquid film and Eq. 13 in Chapter 23 should be used,

$$-r_A''' = \frac{H_A C_B + p_A}{\frac{1}{k_{Ag}a} + \frac{H_A}{k_la}} = \frac{12.5 \left[ \frac{420 - p_{A3}}{12.5} \right] + p_A}{\frac{1}{0.32} + \frac{12.5}{0.1}} = 3.278 \text{ mol/m}^3 \text{ reactor} \cdot \text{hr}$$

**Step 3. Height of Tower.** From Eq. 6,

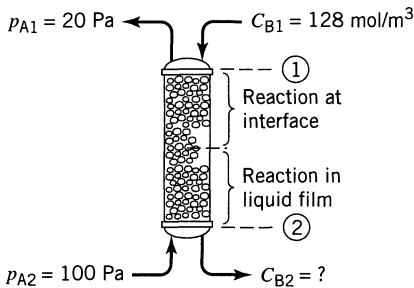
$$h = \frac{V_r}{A_{cs}} = \frac{10^5}{10^5} \int_{20}^{100} \frac{dp_A}{3.278} = \frac{100 - 20}{3.278} = \underline{\underline{24.4 \text{ m}}}$$

### EXAMPLE 24.4 TOWERS FOR INTERMEDIATE CONCENTRATIONS OF LIQUID REACTANT

Repeat Example 24.2 using a feed in which  $C_B = 128 \text{ mol/m}^3$ .

#### SOLUTION

Refer to Fig. E24.4, and solve as with the previous examples.



**Figure E24.4**

**Step 1. Material balance.** As with Examples 24.2 and 24.3 we have at any point in the tower,

$$p_{A3} = 1620 - 12.5C_{B3}$$

and at the bottom of the tower,

$$C_{B2} = \frac{1520}{12.5} = 121.6 \text{ mol/m}^3$$

**Step 2. Form of rate equation to use.** Check both ends of the tower:

$$\text{at top} \begin{cases} k_{Ag}ap_A = 6.4 \text{ mol/hr} \cdot \text{m}^3 \\ k_laC_B = 12.8 \text{ mol} \cdot \text{hr} \cdot \text{m}^3 \end{cases}$$

$$\text{at bottom} \begin{cases} k_{Ag}ap_A = 32 \\ k_laC_B = 12.16 \end{cases}$$

At the top  $k_{Ag}p_A < k_l C_B$ ; hence, Eq. 16 in Chapter 23 must be used. At the bottom  $k_{Ag}p_A > k_l C_B$ ; hence, Eq. 13 in Chapter 23 must be used.

Let us now find the condition at which the reaction zone just reaches the interface and where the form of rate equation changes. This occurs where

$$k_{Ag}p_A = k_l C_B \quad \text{or} \quad 0.32p_A = 0.1C_B$$

Solving with the material balance we find that the change occurs at  $p_A = 39.5$  Pa.

**Step 3. Height of Tower.** Writing the performance equation we have, from Eq. 6,

$$h = \frac{(F_g/A_{cs})}{\pi} \int_{p_{A1}}^{p_{A2}} \frac{dp_A}{-r_A'''} \quad (\text{iii})$$

Noting that two different rate forms must be used, we have

$$\begin{aligned} h &= \frac{(F_g/A_{cs})}{\pi} \int_{20}^{39.5} \frac{dp_A}{(k_{Ag}a)p_A} + \frac{F_g/A_{cs}}{\pi} \int_{39.5}^{100} \frac{(1/k_{Ag}a + H_A/k_l a)}{C_B H_A + p_A} dp_A \\ &= \frac{10^5}{10^5(0.32)} \ln \frac{39.5}{20} + \frac{10^5}{10^5} \int_{39.5}^{100} \frac{(1/0.32 + 12.5/0.1)}{(1620 - p_A + p_A)} dp_A \\ &= 2.1268 + \frac{128.125}{1620} (100 - 39.5) = \underline{\underline{6.91 \text{ m}}} \end{aligned}$$

**Comment.** In this example we see that two distinct zones are present. Situations may be encountered where even another zone may be present. For example, if the entering liquid contains insufficient reactant, a point is reached in the tower where all this reactant is consumed. Below this point physical absorption alone takes place in reactant-free liquid. The methods of these examples, when used together, deal in a straightforward manner with this three-zone situation and van Krevelens and Hoftijzer (1948) discuss actual situations where these three distinct zones are present.

Comparing solutions for the four examples shows how reaction increases the effectiveness of the absorption process.

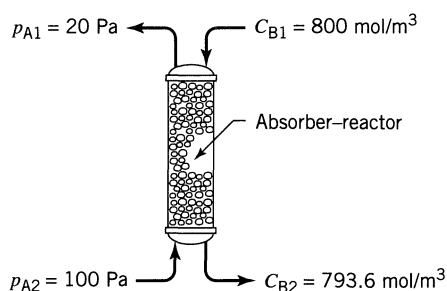
### EXAMPLE 24.5 REDO EXAMPLE 24.2 BY THE GENERAL METHOD

In Example 24.2 we found which of the eight special cases (see Fig. 23.3) applied and then used its corresponding rate equation (it was Eq. 23.16). Alternatively we could have used the general rate expression (Eq. 23.5). This is what we will show here.

**SOLUTION**

From Example 24.2 a material balance gives the tower end conditions, as shown in Fig. E24.5. Now the rate of reaction at any point in the tower is, from Eq. 23.5,

$$-r_A''' = \left( \frac{1}{\frac{1}{0.32} + \frac{12.5}{0.1E} + \frac{12.5}{\infty(C_B)}} \right) p_A = \left( \frac{1}{3.125 + \frac{125}{E}} \right) p_A \quad (\text{i})$$



**Figure E24.5**

Evaluate  $E$  at various points in the tower. For this we need to first evaluate  $M_H$  and  $E_i$ .

**At the Top of the Tower.** From Fig. 23.4

$$M_H = \frac{\sqrt{\mathcal{D}_B C_B k}}{k_{Al}} = \infty, \quad \text{because } k = \infty$$

$$E_i = 1 + \frac{\mathcal{D}_B C_B H_A}{\mathcal{D}_A p_{Ai}} = 1 + \frac{800(12.5)}{p_{Ai}} = \frac{10^4}{p_{Ai}} \quad (\text{ii})$$

We have to guess the value of  $p_{Ai}$ . It can be anywhere between 0 Pa (gas film controls) up to 20 Pa (liquid film controls). Let us guess no gas-phase resistance. Then  $p_{Ai} = p_A$ , in which case

$$E_i = \frac{10^4}{20} = 500$$

and from Fig. 23.4, for  $M_H = \infty$ ,  $E_i = 500$ , we see that

$$E = 500$$

Replacing in Eq. (i) we find

$$-r_A''' = \frac{1}{3.125 + \frac{125}{500}} p_A = \frac{1}{3.125 + 0.25} p_A = 0.296 p_A$$

93%
7%...resistance

Our guess was wrong, so let's try again. Let us guess the other extreme,  $p_{Ai} = 0$ , meaning that the total resistance is in the gas film. Then from Eq. (ii) we see that  $E_i = \infty$ ,  $E = \infty$  and the rate equation becomes

$$-r_A''' = \frac{1}{\underbrace{3.125 + 0}_{\text{gas film control}}} p_A = 0.32 p_A \quad (\text{iii})$$

Thus our guess was correct.

**At the Bottom of the Tower.** We follow the same procedure and find the same result. Thus the rate at all points in the tower is given by Eq. (iii). The height of the tower, from Eq. 10, is then (see step 3 of Example 24.2)

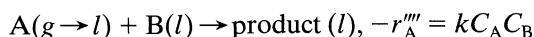
$$\underline{\underline{h = 5.03 \text{ m}}}$$

**Suggestion.** Whenever  $M_H > E_i$  we end up having to guess  $p_{Ai}$ , and that is tedious. In those cases try to use the special case expressions.

In other cases (and this is what we usually find) the general rate equation is easier to use.

### EXAMPLE 24.6 REACTION OF A BATCH OF LIQUID

We wish to lower the concentration of B in the liquid ( $V_l = 1.62 \text{ m}^3$ ,  $C_U = 5555.6 \text{ mol/m}^3$ ) of an agitated tank reactor by bubbling gas ( $F_g = 9000 \text{ mol/hr}$ ,  $\pi = 10^5 \text{ Pa}$ ) containing A ( $p_{Ain} = 1000 \text{ Pa}$ ) through it. A and B react as follows:



- (a) How long must we bubble gas through the vessel to lower the concentration from  $C_{B0} = 555.6$  to  $C_{Bf} = 55.6 \text{ mol/m}^3$ ?
- (b) What percent of entering A passes through the vessel unreacted?

#### Additional Data

$$k_{Ag}a = 0.72 \text{ mol/hr} \cdot \text{m}^3 \cdot \text{Pa}$$

$$f_l = 0.9 \text{ m}^3 \text{ liquid/m}^3 \text{ total}$$

$$k_{Al}a = 144 \text{ hr}^{-1}$$

$$\mathcal{D}_A = \mathcal{D}_B = 3.6 \times 10^{-6} \text{ m}^2/\text{hr},$$

$$a = 100 \text{ m}^2/\text{m}^3$$

$$H_A = 10^3 \text{ Pa} \cdot \text{m}^3/\text{mol}$$

$$k = 2.6 \times 10^5 \text{ m}^3/\text{mol} \cdot \text{hr}$$

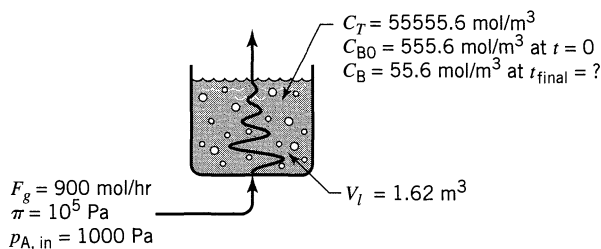


Figure E24.6

**SOLUTION**

Let us sketch what is known in Fig. E24.6.

*At the start*

$$M_H = \frac{\sqrt{\mathcal{D}_B k C_B}}{k_{Al}} = \frac{\sqrt{3.6 \times 10^{-6} (2.6 \times 10^5) (555.6)}}{144/100} = 15.84$$

$$E_i = 1 + \frac{C_B H_A}{p_{Ai}} = \frac{555.6(10^3)}{1000} \quad 555.6, \text{ or higher}$$

$\uparrow$   
 or lower

$$\therefore E = M_H = 15.84$$

Since  $p_A \ll \pi$  and  $E = M_H$  the text says we can use the shortcut outlined above Eq. 19. Let us do it.

$$\begin{aligned}
 -r_A''' &= p_{A\text{in}} \left/ \left( \frac{\pi V_r}{F_g} + \frac{1}{k_{Ag} a} + \frac{H_A}{k_{Al} a E} + \frac{H_A}{k C_B f_l} \right) \right. \\
 &= 1000 \left/ \left( \frac{10^5 (1.62)}{9000} + \frac{1}{0.72} + \frac{10^3}{144(15.84)} + \frac{10^3}{2.6 \times 10^5 (555.6) 0.9} \right) \right. \\
 &= 50.44 \text{ mol/m}^3 \cdot \text{hr}
 \end{aligned}$$

*At the end*, following a similar treatment, we find

$$\left. \begin{aligned} M_H &= 5 \\ E_i &= 55.6, \text{ or higher} \end{aligned} \right\} E = M_H = 5.0$$

$$-r_A''' = 1000 \left/ \left( \frac{10^5 (1.62)}{9000} + \frac{1}{0.72} + \frac{10^3}{144(5)} + \sim 0 \right) \right. = 48.13 \text{ mol/m}^3 \cdot \text{hr}$$

The rate of reaction at the beginning and at the end of the run is just about the same, so

$$-r'''_{A, \text{ave}} = \frac{50.44 + 48.13}{2} = 49.28$$

Thus the run time needed is

$$t = \frac{f_l}{b} \int_{C_{Bf}}^{C_{B0}} \frac{dC_B}{-r'''_A} = \frac{0.9(555.6 - 55.6)}{49.28} = \underline{\underline{9.13 \text{ hr}}}$$

The minimum time required is

$$t_{\min} = \frac{V_l(C_{B0} - C_{Bf})}{F_g(p_{Ain}/(\pi - p_{Ain}))} = \frac{1.62(555.6 - 55.6)}{9000(1000/(10^5 - 100))} = \underline{\underline{8.91 \text{ hr}}}$$

Thus the fraction of reactant which passes through the tank untreated is

$$\text{Fraction} = \frac{9.13 - 8.91}{8.19} = 0.025 = \underline{\underline{2.5\%}}$$

## REFERENCES

- van Krevelens, D. W., and Hoftijzer, P., *Rec. Trav. Chim.*, **67**, 563 (1948).  
Kramers, H., and Westerterp, K. R., *Elements of Chemical Reactor Design and Operation*,

## PROBLEMS

- 24.1.** The four  $p_A$  versus  $C_A$  sketches of Fig. 24.2 represent various possible ideal contacting schemes of gas with liquid. Sketch the contacting scheme for straight physical absorption corresponding to the  $p_A$  versus  $C_A$  operating lines  $XY$  shown in Fig. P24.1.

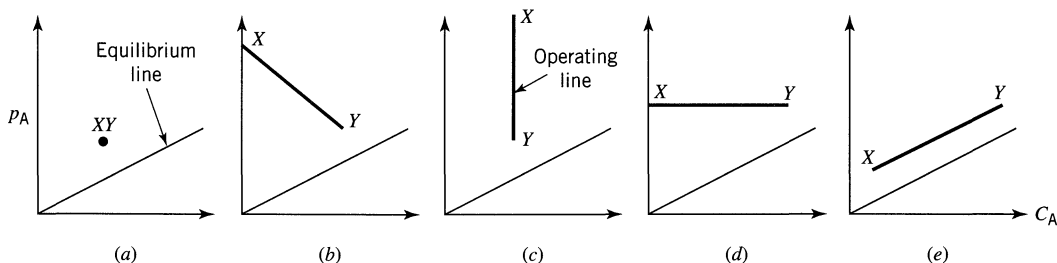
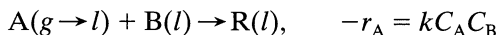


Figure P24.1



We plan to remove about 90% of the A present in a gas stream by absorption in water which contains reactant B. Chemicals A and B react in the liquid as follows:



B has a negligible vapor pressure, hence does not go into the gas phase. We plan to do this absorption in either a packed bed column, or an agitated tank contactor.

- (a) What volume of contactor is needed?  
 (b) Where does the resistance of absorption reaction lie?

### Data

For the gas stream:

$$\begin{aligned} F_g &= 90\,000 \text{ mol/hr at } \pi = 10^5 \text{ Pa} \\ p_{Ain} &= 1000 \text{ Pa} \\ p_{Aout} &= 100 \text{ Pa} \end{aligned}$$

Physical data

$$\begin{aligned} \mathcal{D} &= 3.6 \times 10^{-6} \text{ m}^2/\text{hr} \\ C_U &= 55\,556 \text{ mol H}_2\text{O}/\text{m}^3 \text{ liquid, at all } C_B \end{aligned}$$

For the packed bed

$$\begin{aligned} F_l &= 900\,000 \text{ mol/hr} & k_{Al}a &= 72 \text{ hr}^{-1} \\ C_{Bin} &= 55.56 \text{ mol/m}^3 & a &= 100 \text{ m}^2/\text{m}^3 \\ k_{Ag}a &= 0.36 \text{ mol/hr} \cdot \text{m}^3 \cdot \text{Pa} & f_l &= V_l/V = 0.08 \end{aligned}$$

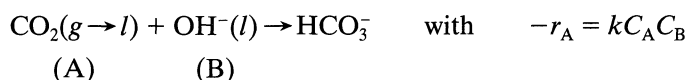
For the agitated tank

$$\begin{aligned} F_l &= 9000 \text{ mol/hr} & k_{Al}a &= 144 \text{ hr}^{-1} \\ C_{Bin} &= 5556 \text{ mol/m}^3 \text{ (about 10\% B)} & a &= 200 \text{ m}^2/\text{m}^3 \\ k_{Ag}a &= 0.72 \text{ mol/hr} \cdot \text{m}^3 \cdot \text{Pa} & f_l &= V_l/V = 0.9 \end{aligned}$$

Note that  $F_l$  and  $C_{Bin}$  are very different in packed beds and tank contactors, and here is the reason why. Packed columns need  $F_l/F_g \cong 10$  for satisfactory operations. This means large  $F_l$ , and so as not to waste reactant B, it is introduced in low concentration. On the other hand, tank contactors do not have this flow restriction. Thus we can use low  $F_l$  and high  $C_{Bin}$ , as long as we introduce sufficient B to react with A.

	Henry's Law Constant: $H_A$ , $\text{Pa} \cdot \text{m}^3/\text{mol}$	For Reaction: $k$ , $\text{m}^3/\text{mol} \cdot \text{hr}$	Type of Contactor T = Tower, Countercurrent A = Agitated Tank	
24.2.	0.0	0	In these problems of straight mass transfer assume that no B is present in the system.	A
24.3.	18	0		T
24.4.	1.8	0		T
24.5.	$10^5$	$\infty$		T
24.6.	$10^5$	$2.6 \times 10^7$		A
24.7.	$10^5$	$2.6 \times 10^5$		A
24.8.	$10^3$	$2.6 \times 10^3$		T
24.9.	$10^5$	$2.6 \times 10^7$		T
24.10.	$10^3$	$2.6 \times 10^5$		T

24.11. Danckwerts and Gillham, in *Trans. I. Chem. E.*, **44**, 42, March 1966, studied the rate of  $\text{CO}_2$  absorption into an alkaline buffered solution of  $\text{K}_2\text{CO}_3$  and  $\text{KHCO}_3$ . The resulting reaction can be represented as



In the experiment pure  $\text{CO}_2$  at 1 atm was bubbled into a packed column irrigated by rapidly recirculating solution kept at  $20^\circ\text{C}$  and close to constant  $C_B$ . Find the fraction of entering  $\text{CO}_2$  absorbed.

### Data

Column:  $V_r = 0.6041 \text{ m}^3$                        $f_l = 0.08$                        $a = 120 \text{ m}^2/\text{m}^3$   
 Gas:  $\pi = 101\,325 \text{ Pa}$                        $H_A = 3500 \text{ Pa} \cdot \text{m}^3/\text{mol}$                        $v_0 = 0.0363 \text{ m}^3/\text{s}$   
 Liquid:  $\bar{C}_B = 300 \text{ mol}/\text{m}^3$                        $\mathcal{D}_{Al} = \mathcal{D}_{Bl} = 1.4 \times 10^{-9} \text{ m}^2/\text{s}$   
 Rates:  $k = 0.433 \text{ m}^3/\text{mol} \cdot \text{s}$                        $k_{Al}a = 0.025 \text{ s}^{-1}$

This problem is by Barry Kelly.

24.12. A column packed with 5-cm polypropylene saddles ( $a = 55 \text{ m}^2/\text{m}^3$ ) is being designed for the removal of chlorine from a gas stream ( $G = 100 \text{ mol}/\text{s} \cdot \text{m}^2$ , 2.36%  $\text{Cl}_2$ ) by countercurrent contact with an NaOH solution

( $L = 250 \text{ mol/s} \cdot \text{m}^2$ , 10% NaOH,  $C_B = 2736 \text{ mol/m}^3$ ) at about 40–45°C and 1 atm.

How high should the tower be for 99% removal of chlorine? Double the calculated height to take care of deviations from plug flow.

### Data

The reaction  $\text{Cl}_2 + 2\text{NaOH} \rightarrow \text{product}$  is very very fast and irreversible. For these very high flow rates (close to the limits allowed) an extrapolation of the correlations in Perry 6th ed., section 14, gives

$$\begin{aligned} k_g a &= 133 \text{ mol/hr} \cdot \text{m}^3 \cdot \text{atm} & H_A &= 125 \times 10^6 \text{ atm} \cdot \text{m}^3/\text{mol} \\ k_l a &= 45 \text{ hr}^{-1} & \mathcal{D} &= 1.5 \times 10^{-9} \text{ m}^2/\text{s} \end{aligned}$$

Repeat Example 24.6 with the following two changes

	Henry's Law Constant $H_A$ , $\text{Pa} \cdot \text{m}^3/\text{mol}$	Second-Order Reaction Rate, Constant $k$ , $\text{m}^3/\text{mol} \cdot \text{hr}$
<b>24.13.</b>	$10^5$	$2.6 \times 10^5$
<b>24.14.</b>	$10^5$	$2.6 \times 10^9$
<b>24.15.</b>	$10^5$	$2.6 \times 10^3$
<b>24.16.</b>	$10^3$	$2.6 \times 10^{11}$