Chapter 23

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:

$$NH_3(g) + Na(l) \xrightarrow{250°C} NaNH_2(s) + \frac{1}{2}H_2$$

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[a]

Solute Gas	Reagent
CO_2	Carbonates
CO_2	Hydroxides
CO_2	Ethanolamines
CO	Cuprous amine complexes
CO	Cuprous ammonium chloride
SO_2	$Ca(OH)_2$
SO_2	Ozone-H_2O
SO_2	$HCrO_4$
SO_2	KOH
Cl_2	H_2O
Cl_2	$FeCl_2$
H_2S	Ethanolamines
H_2S	$Fe(OH)_3$
SO_3	H_2SO_4
C_2H_4	KOH
C_2H_4	Trialkyl phosphates
Olefins	Cuprous ammonium complexes
NO	$FeSO_4$
NO	$Ca(OH)_2$
NO	H_2SO_4
NO_2	H_2O

[a] 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 use 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

$$A(g \rightarrow l) + bB(l) \rightarrow R(s \text{ or } l \text{ or } g), \qquad -r_A = kC_AC_B$$

present in gas, but soluble in liquid with solubility given by $p_{Ai} = H_AC_{Ai}$

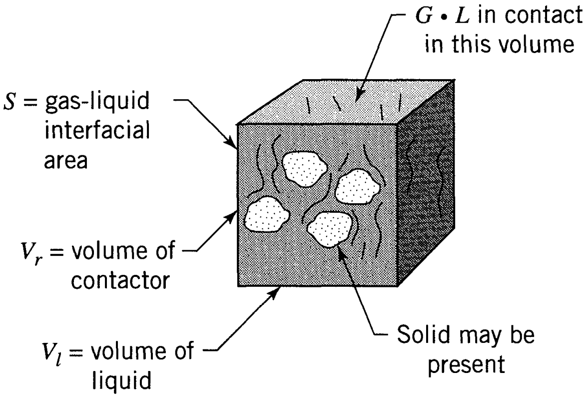
present in liquid and unable to enter the gas phase

reaction occurs in liquid only, maybe close to the interface (in the liquid film), maybe in the main body of liquid

For notation consider a unit volume of contactor V_r with its gas, liquid, and solid

$$f_l = \frac{V_l}{V_r}, \quad f_g = \frac{V_g}{V_r}, \quad \epsilon = f_l + f_g,$$

$$a_l = \frac{S}{V_l}, \qquad a = \frac{S}{V_r}$$



The rate of reaction is usefully written in a number of ways, as follows:

$$\left.\begin{aligned} -r_A'''' &= -\frac{1}{V_r}\frac{dN_A}{dt} \\ -r_{Al} &= -\frac{1}{V_l}\frac{dN_A}{dt} \\ -r_A'' &= -\frac{1}{S}\frac{dN_A}{dt} \end{aligned}\right\} \tag{1}$$

These rates are related by

$$r''''V_r = r_lV_l = r''S$$

or

$$r'''' = f_lr_l = ar''$$

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

$$r''_{\mathrm{A}} = \overset{\frac{\text{mol}}{\text{m}^2\cdot\text{Pa}\cdot\text{s}}}{\overset{\downarrow}{k_{\mathrm{A}g}}}(p_{\mathrm{A}} - p_{\mathrm{A}i}) \quad \ldots\text{or}\quad -r''''_{\mathrm{A}} = \overset{\frac{\text{mol}}{\text{m}^3\text{ contactor}\cdot\text{Pa}\cdot\text{s}}}{\overset{\downarrow}{\overline{k_{\mathrm{A}g}a}}}(p_{\mathrm{A}} - p_{\mathrm{A}i}) \qquad \textbf{(2)}$$

and for the liquid film

$$r''_{\mathrm{A}} = \underset{\frac{\text{m}^3\text{ liquid}}{\text{m}^2\text{ surface}\cdot\text{s}}}{\underset{\uparrow}{k_{\mathrm{A}l}}}(C_{\mathrm{A}i} - C_{\mathrm{A}}) \quad \ldots\text{or}\quad -r''''_{\mathrm{A}} = \underset{\frac{\text{m}^3\text{ liquid}}{\text{m}^3\text{ contactor}\cdot\text{s}}}{\underset{\uparrow}{\underline{k_{\mathrm{A}l}a}}}(C_{\mathrm{A}i} - C_{\mathrm{A}}) \qquad \textbf{(3)}$$

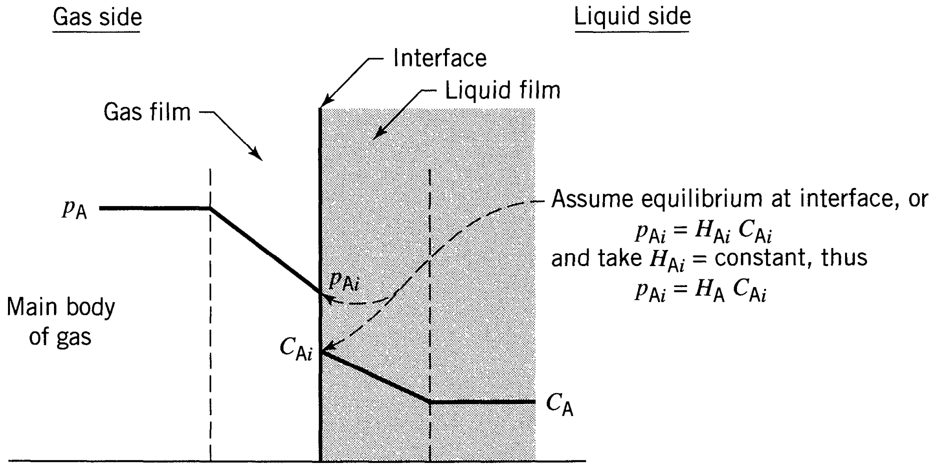
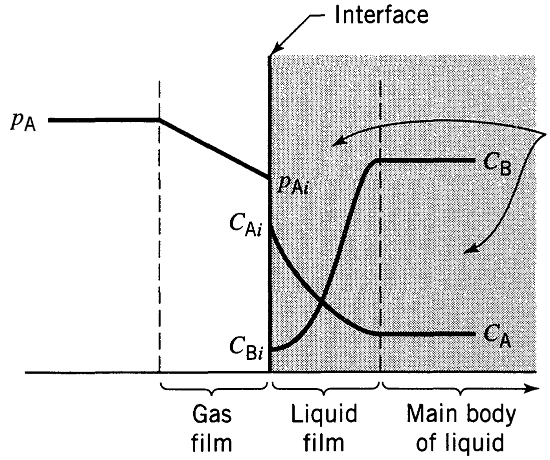


Figure 23.1 Setting up the rate equation for straight mass transfer based on the two film theory.



Reaction can take place in both the liquid film and in the main body of liquid. Fast reactions occur in a narrow zone within the film, slow reactions spread through the film and main body of liquid.

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.

$$\boxed{-r''''_A = \frac{1}{\dfrac{1}{k_{Ag}a} + \dfrac{H_A}{k_{Al}a}} (p_A - \underset{\uparrow \; \frac{\text{Pa}\cdot\text{m}^3\,\text{liquid}}{\text{mol}}}{H_A} C_A)} \tag{4}$$

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

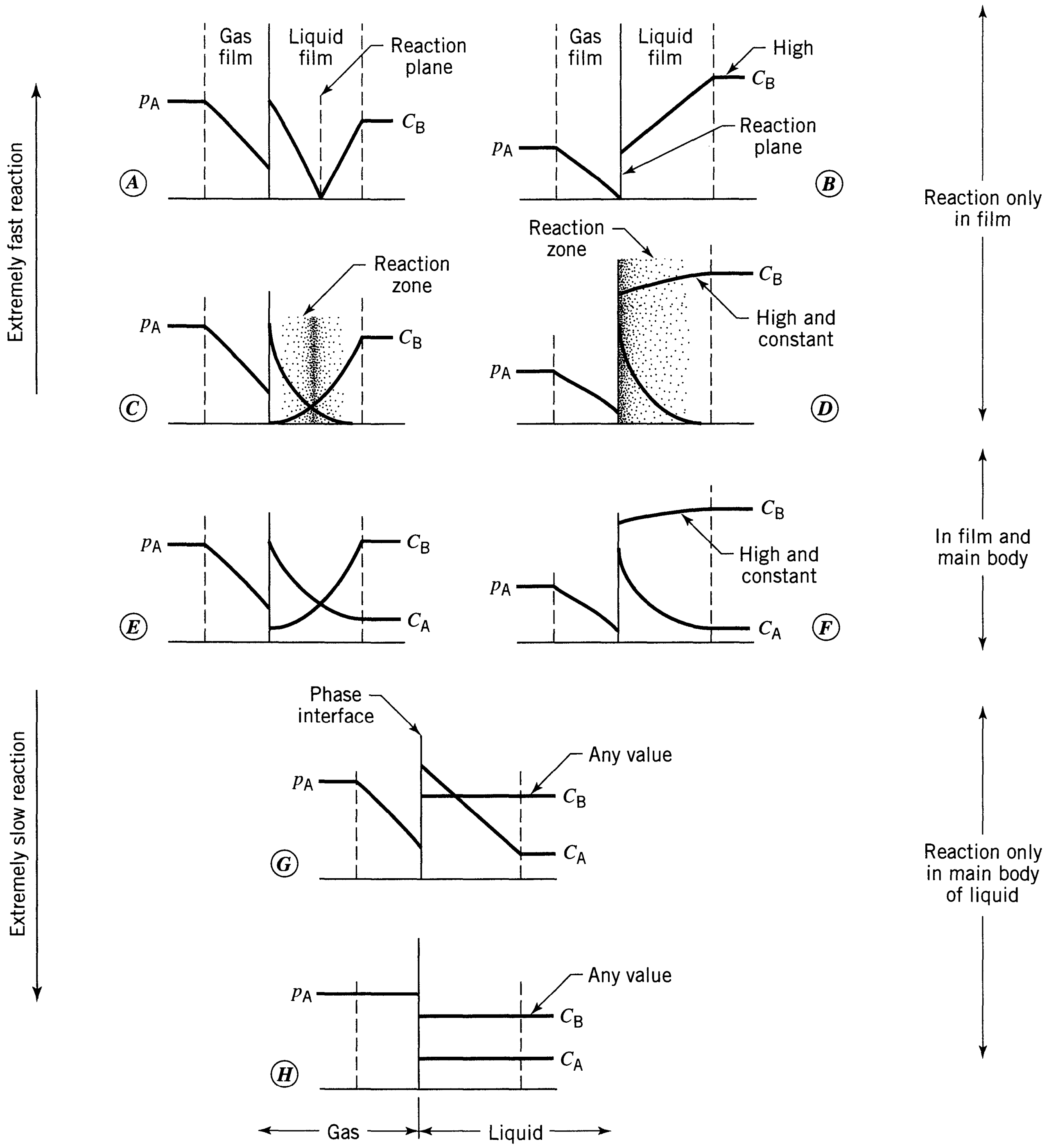


Figure 23.3 Interface behavior for the liquid-phase reaction

$$\text{A (from gas)} + b\text{B (liquid)} \rightarrow \text{products (liquid)}$$

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.

$$\boxed{-r_A'''' = \frac{1}{\underbrace{\frac{1}{k_{Ag}a}}_{\substack{\text{gas film}\\ \text{resistance}}} + \underbrace{\frac{H_A}{k_{Al}aE}}_{\substack{\text{liquid film}\\ \text{resistance}}} + \underbrace{\frac{H_A}{kC_Bf_l}}_{\substack{\text{liquid bulk}\\ \text{resistance}}}}\, p_A} \tag{5}$$

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

$$\begin{pmatrix}\text{Liquid film}\\ \text{enhancement}\\ \text{factor}\end{pmatrix}, E = \left(\frac{\begin{matrix}\text{rate of take up of A}\\ \text{when reaction occurs}\end{matrix}}{\begin{matrix}\text{rate of take up of A for}\\ \text{straight mass transfer}\end{matrix}}\right)_{\substack{\text{same } C_{Ai},\, C_A,\, C_{Bi},\, C_B\\ \text{in the two cases}}} \tag{6}$$

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:

$$E_i = \begin{pmatrix}\text{the enhancement factor for}\\ \text{an infinitely fast reaction}\end{pmatrix} \tag{7}$$

$$M_H^2 = \begin{pmatrix}\text{maximum possible conversion in the}\\ \text{film compared with maximum transport}\\ \text{through the film}\end{pmatrix} \tag{8}$$

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

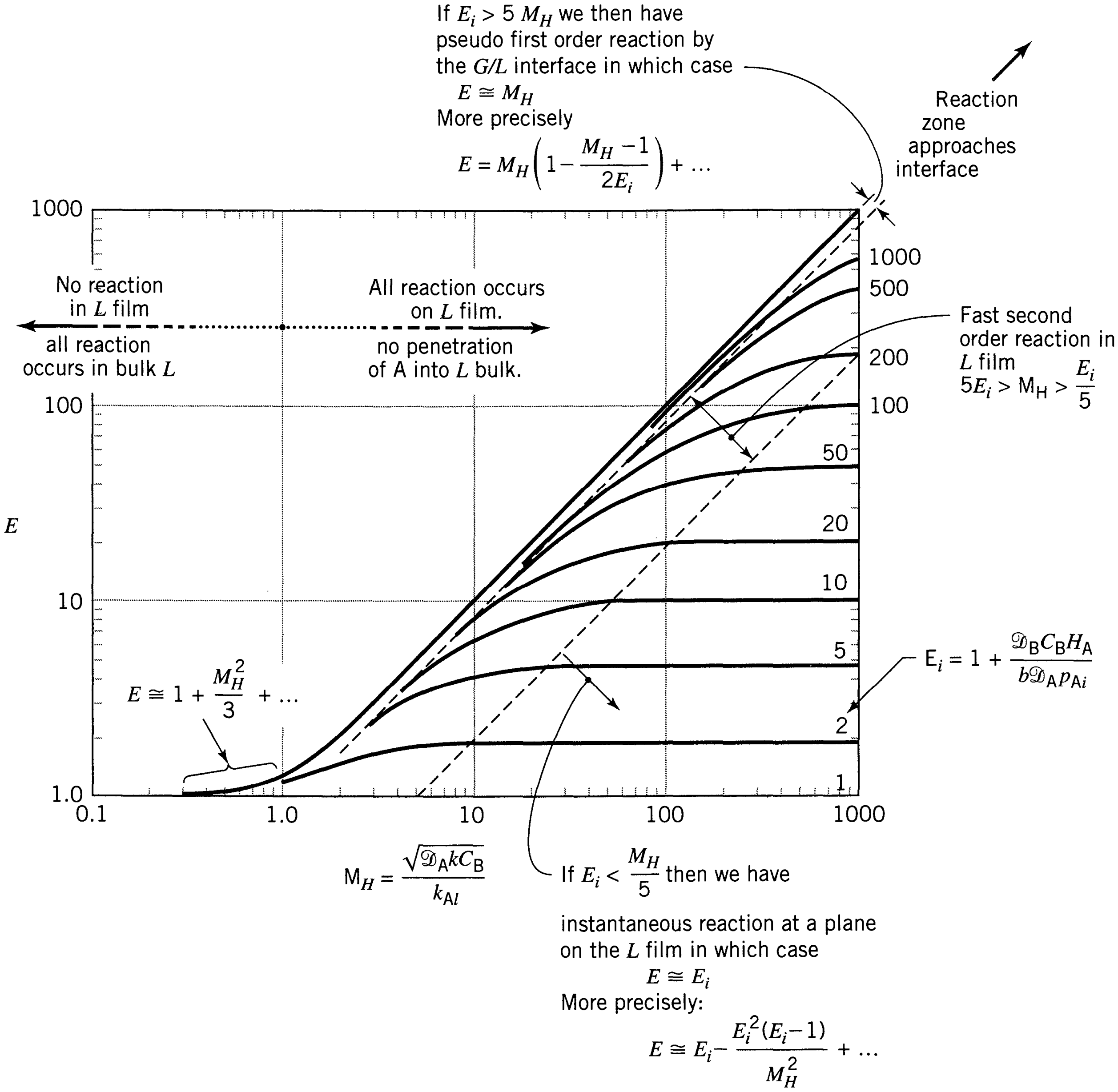


Figure 23.4 The enhancement factor for fluid-fluid reactions as a function of M_H and E_i, modified from the numerical solution of van Krevelens and Hoftijzer (1954).

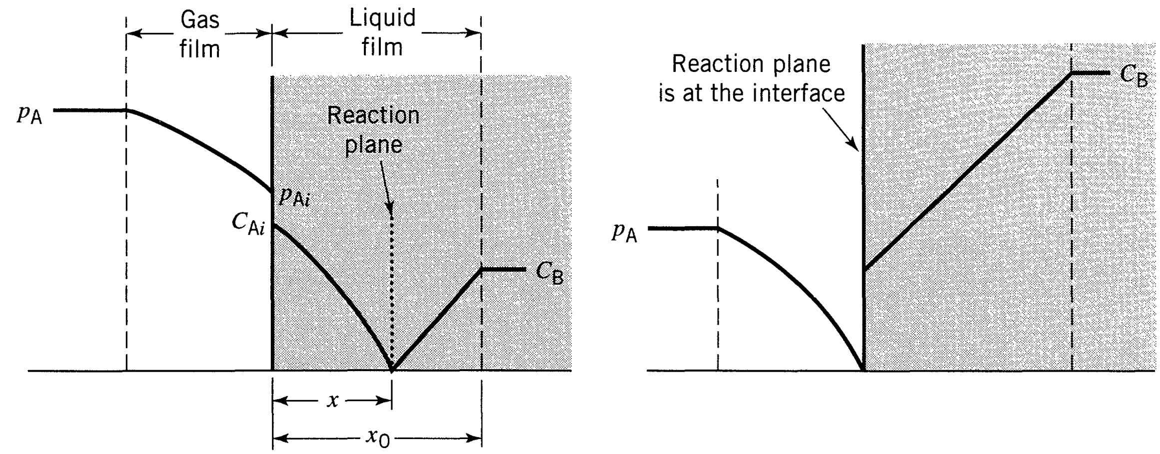
times the flow rate of A toward the reaction zone. Thus,

$$-r''_A = -\frac{r''_B}{b} = \underbrace{k_{Ag}(p_A - p_{Ai})}_{\text{A in gas film}} = \underbrace{k_{Al}(C_{Ai} - 0)\frac{x_0}{x}}_{\text{A in liquid film}} = \underbrace{\frac{k_{Bl}}{b}(C_B - 0)\frac{x_0}{x_0 - x}}_{\text{B in liquid film}} \tag{9}$$

where k_{Ag} and k_{Al}, k_{Bl} 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,

$$p_{Ai} = H_A C_{Ai} \tag{10}$$



Case *A*
Eq. 13

Case *B*
Eq. 16

Figure 23.5 Concentration of reactants as visualized by the two-film theory for an infinitely fast irreversible reactions of any order, A + *b*B → 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[1]

$$\frac{k_{Al}}{k_{Bl}} = \frac{\mathscr{D}_{Al}/x_0}{\mathscr{D}_{Bl}/x_0} = \frac{\mathscr{D}_{Al}}{\mathscr{D}_{Bl}} \tag{12}$$

Eliminating the unmeasured intermediates x, x_0, p_{Ai}, C_{Ai} by Eqs. 9, 10, and 12, we obtain

$$\text{for Case } \boldsymbol{A}\text{:} \quad \left(k_{Ag}p_A > \frac{k_{Bl}C_B}{b}\right) \quad \boxed{-r''_A = -\frac{1}{S}\frac{dN_A}{dt} = \frac{\dfrac{\mathscr{D}_{Bl}}{\mathscr{D}_{Al}}\dfrac{C_B}{b} + \dfrac{p_A}{H_A}}{\dfrac{1}{H_A k_{Ag}} + \dfrac{1}{k_{Al}}}} \tag{13}$$

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.

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[1] 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

$$\frac{k_{Al}}{k_{Bl}} = \sqrt{\frac{\mathscr{D}_{Al}}{\mathscr{D}_{Bl}}} \tag{11}$$

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

$$-r''_{\mathrm{A}} = k_{\mathrm{A}l}C_{\mathrm{A}i}\left(1 + \frac{\mathscr{D}_{\mathrm{B}l}C_{\mathrm{B}}}{b\mathscr{D}_{\mathrm{A}l}\,C_{\mathrm{A}i}}\right) \tag{14}$$

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

$$k_{\mathrm{A}g}p_{\mathrm{A}} \le \frac{k_{\mathrm{B}l}}{b}C_{\mathrm{B}} \tag{15}$$

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

$$\text{for Case } \boldsymbol{B}\text{:}\quad \left(k_{\mathrm{A}g}p_{\mathrm{A}} \le \frac{k_{\mathrm{B}l}C_{\mathrm{B}}}{b}\right) \quad \boxed{-r''_{\mathrm{A}} = -\frac{1}{S}\frac{dN_{\mathrm{A}}}{dt} = k_{\mathrm{A}g}p_{\mathrm{A}}} \tag{16}$$

Equation 17 tells whether Case ***A*** or Case ***B*** applies in any situation. Thus,

$$\boxed{\begin{array}{l} \text{if } k_{\mathrm{A}g}p_{\mathrm{A}} \ge \dfrac{k_{\mathrm{B}l}}{b}C_{\mathrm{B}}\text{, then use Eq. 13: Case } \boldsymbol{A} \\[2ex] \text{if } k_{\mathrm{A}g}p_{\mathrm{A}} \le \dfrac{k_{\mathrm{B}l}}{b}C_{\mathrm{B}}\text{, then use Eq. 16: Case } \boldsymbol{B} \end{array}} \tag{17}$$

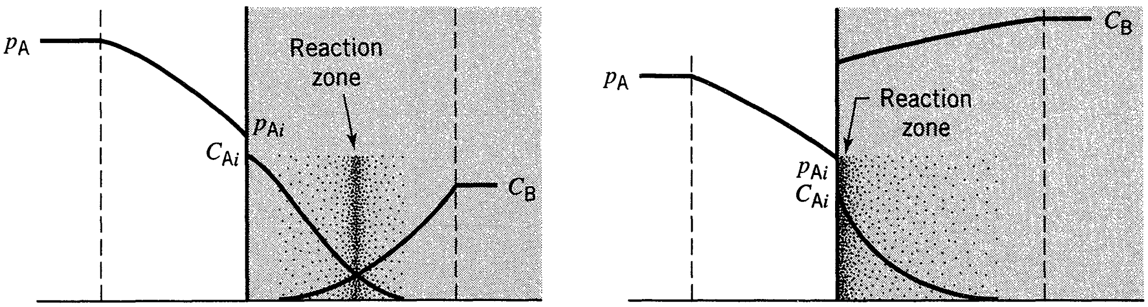
Let us now look at the other cases.

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

$$-r''''_{\mathrm{A}} = \frac{1}{\dfrac{1}{k_{\mathrm{A}g}a} + \dfrac{H_{\mathrm{A}}}{k_{\mathrm{A}l}aE}}p_{\mathrm{A}} \tag{18}$$

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,



Case *C*
(fast second order)
Eq. 18

Case *D*
(pseudo-first order)
Eq. 19

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

$$-r_A'''' = \frac{1}{\dfrac{1}{k_{Ag}a} + \dfrac{H_A}{a\sqrt{\mathscr{D}_A k C_B}}}\, p_A \tag{19}$$

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.

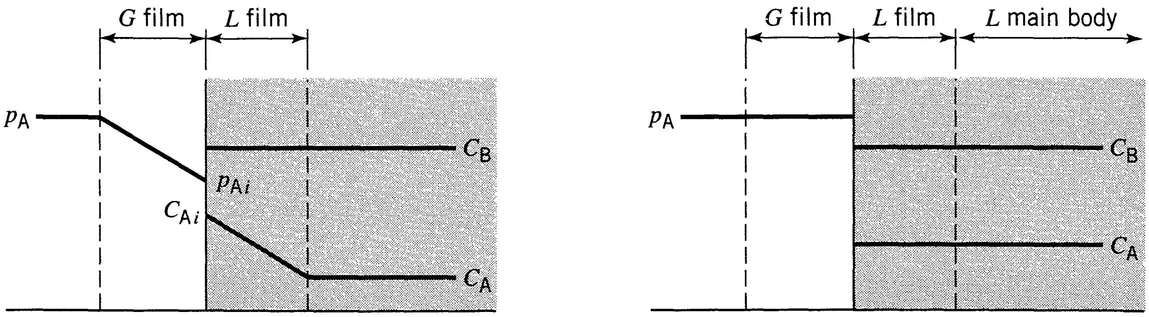
Case *G*: Slow Reaction with Respect to Mass Transfer. This represents the somewhat curious case where all reaction occurs in the main body of the liquid; however, the film still provides a resistance to the transfer of A into the main body of liquid. Thus, three resistances enter into the rate expression, and Eq. 5 reduces to

$$-r_A'''' = \frac{1}{\dfrac{1}{k_{Ag}a} + \dfrac{H_A}{k_{Al}a} + \dfrac{H_A}{kC_B f_l}}\, p_A \tag{20}$$

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.

$$-r_A'''' = \frac{kf_l}{H_A} p_A C_B = kf_l C_A C_B \tag{21}$$

Figure 23.7 shows cases *G* and *H*.



Case ***G***
Eq. 20

Case ***H***
Eq. 21

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

$$M_H^2 = \frac{\text{maximum possible conversion in the film}}{\text{maximum diffusional transport through the film}} = \frac{kC_{Ai}C_Bx_0}{\frac{\mathscr{D}_{Al}}{x_0}\cdot C_{Ai}} = \frac{kC_B\mathscr{D}_{Al}}{k_{Al}^2} \tag{22}$$

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

$$-\frac{1}{S}\frac{dN_A}{dt}=\frac{1}{\underbrace{\frac{1}{k_{Ag}}}_{\text{gas film}}+\underbrace{\frac{H_A}{k_{Al}}}_{\text{liquid film}}}\Delta p_A \tag{23}$$

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^3/mol, for Common Gases in Water

	N_2	H_2	O_2	CO	CO_2	NH_3
20°C	1.45×10^5	1.23×10^5	0.74×10^5	0.96×10^5	2600	0.020
60°C	2.16×10^5	1.34×10^5	1.13×10^5	1.48×10^5	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:

$$\mathrm{A}(g \rightarrow l) + 2\mathrm{B}(l) \rightarrow \mathrm{R}(l), \quad -r_{\mathrm{A}} = kC_{\mathrm{A}}C_{\mathrm{B}}^2, \quad k = 10^6\ \mathrm{m^6/mol^2 \cdot hr}$$

For this system

$$\begin{aligned} &k_{\mathrm{A}g}a = 0.01\ \mathrm{mol/hr \cdot m^3 \cdot Pa} && f_l = 0.98 \\ &k_{\mathrm{A}l}a = 20\ \mathrm{hr^{-1}} && H_{\mathrm{A}} = 10^5\ \mathrm{Pa \cdot m^3/mol}, \text{ very low solubility} \\ &\mathscr{D}_{\mathrm{A}l} = \mathscr{D}_{\mathrm{B}l} = 10^{-6}\ \mathrm{m^2/hr} && a = 20\ \mathrm{m^2/m^3} \end{aligned}$$

For a point in the absorber-reactor where

$$p_{\mathrm{A}} = 5 \times 10^3\ \mathrm{Pa} \quad \text{and} \quad C_{\mathrm{B}} = 100\ \mathrm{mol/m^3}$$

(a) locate the resistance to reaction (what % is in the gas film, in the liquid film, in the main body of liquid)
(b) locate the reaction zone
(c) determine the behavior in the liquid film (whether pseudo first-order reaction, instantaneous, physical transport, etc.)
(d) calculate the rate of reaction (mol/m^3 · 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,

$$kC_{\mathrm{A}}C_{\mathrm{B}}^2 \Rightarrow (kC_{\mathrm{B}})C_{\mathrm{A}}C_{\mathrm{B}}$$

To find the rate from the general expression (Eq. 5), we need to first evaluate E_i and M_H. Let us do this:

$$\left.\begin{aligned} M_H &= \frac{\sqrt{\mathscr{D}_{\mathrm{A}}kC_{\mathrm{B}}^2}}{k_{\mathrm{A}l}} = \frac{\sqrt{10^{-6}\,10^6\,100^2}}{1} = 100 \\ (E_i)_{\text{first guess}} &= 1 + \frac{\mathscr{D}_{\mathrm{B}}C_{\mathrm{B}}H_{\mathrm{A}}}{b\mathscr{D}_{\mathrm{A}}p_{\mathrm{A}i}} = 1 + \frac{100 \times 10^5}{2(\underset{\underset{\text{guess } p_{\mathrm{A}i} = p_{\mathrm{A}}}{\uparrow}}{5} \times 10^5)} = 10^3 \end{aligned}\right\}$$

Since $(E_i)_{\text{first guess}} > 5\ M_H$, then for any other smaller guess for $p_{\mathrm{A}i}$ 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,

$$-r_A'''' = \frac{p_A}{\dfrac{1}{k_{Ag}a} + \dfrac{H_A}{k_{Al}aE} + \dfrac{H_A}{kC_B^2 f_l}}$$

$$= \frac{5 \times 10^3}{\underset{\uparrow\,\frac{2}{3}}{\dfrac{1}{0.01}} + \underset{\uparrow\,\frac{1}{3}}{\dfrac{10^5}{20(100)}} + \underset{\uparrow\,\sim 0}{\dfrac{10^5}{(10^6)(100^2)(.098)}}} = 33 \text{ mol/hr} \cdot \text{m}^3 \text{ reactor}$$

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 $-r_A'''' = 33 \text{ mol/hr} \cdot \text{m}^3$ ←

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PROBLEMS

Gaseous A absorbs and reacts with B in liquid according to

$$A(g \rightarrow l) + B(l) \rightarrow R(l), \qquad -r_A = kC_AC_B$$

in a packed bed under conditions where

$k_{Ag}a = 0.1$ mol/hr · m² of reactor · Pa $\quad f_l = 0.01$ m³ liquid/m³ reactor

$k_{Al}a = 100$ m³ liquid/m³ reactor · hr $\quad \mathscr{D}_{Al} = \mathscr{D}_{Bl} = 10^{-6}$ m²/hr

$a = 100$ m²/m³ reactor

At a point in the reactor where $p_A = 100$ Pa and $C_B = 100$ mol/m³ liquid

(a) calculate the rate of reaction in mol/hr · m³ 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, m³ liquid/mol · hr	H_A, Pa · m³ 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 CO_2 is absorbed into a solution of NaOH in a packed column. The reaction is as follows:

$$\underset{(A)}{\underline{CO_2}} + \underset{(B)}{\underline{2NaOH}} \rightarrow Na_2CO_3 + H_2O \text{ with } -r_{Al} = kC_AC_B$$

Find the rate of absorption, the controlling resistance, and what is happening in the liquid film, at a point in the column where $p_A = 10^5$ Pa and $C_B = 500$ mol/m³.

Data: $k_{Ag}a = 10^{-4}$ mol/m² · s · Pa $\quad H_A = 25\,000$ Pa · m³/mol

$k_{Al} = 1 \times 10^{-4}$ m/s $\quad \mathscr{D}_A = 1.8 \times 10^{-9}$ m²/s

$a = 100$ m⁻¹ $\quad \mathscr{D}_B = 3.06 \times 10^{-9}$ m²/s

$k = 10$ m³/mol · s $\quad f_l = 0.1$

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 H_2S, while the absorbent contains 250 mol/m^3 of free MEA. The diffusivity of MEA in solution is 0.64 times that of H_2S. The reaction is normally regarded as irreversible and instantaneous.

$$\underset{(A)}{\underline{H_2S}} + \underset{(B)}{\underline{RNH_2}} \rightarrow HS^- + RNH_3^+$$

For the flow rates and packing used

$k_{Al}a = 0.03\ \text{s}^{-1}$

$k_{Ag}a = 60\ \text{mol/m}^3 \cdot \text{s} \cdot \text{atm}$

$H_A = 1 \times 10^{-4}\ \text{m}^3 \cdot \text{atm/mol}$, Henry's law constant for H_2S in water.

(a) Find the rate of absorption of H_2S 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).