

fairly wide range of  $b_1$  the ratio  $N^*$  is indeed very nearly unity, and Eq. 17.4-15 may be used to describe the absorption rate merely by setting  $\Gamma = 0$ . Similar simplification is possible for more realistic mass-transfer models.<sup>1</sup>

§17.5 DIFFUSION INTO A FALLING LIQUID FILM:  
FORCED-CONVECTION MASS TRANSFER

In this section we present an illustration of forced-convection mass transfer in which viscous flow and diffusion occur under such conditions that the

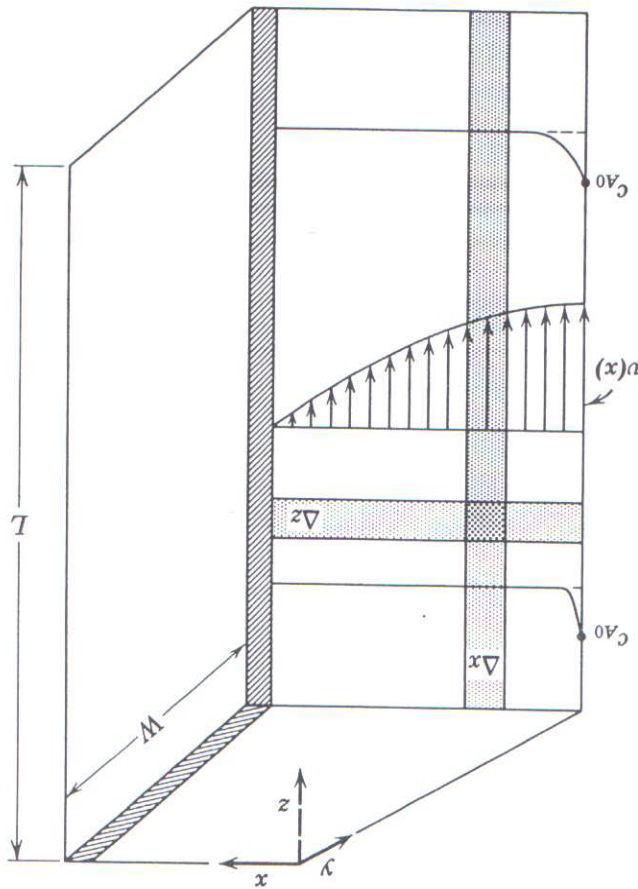


Fig. 17.5-1. Absorption into a falling film.

velocity field can be considered virtually unaffected by the diffusion. Specifically, we consider the absorption of gas  $A$  by a laminar falling film of liquid  $B$ . The material  $A$  is only slightly soluble in  $B$ , so that the viscosity of the liquids is not changed appreciably. We shall make the further restriction that the diffusion take place so slowly in the liquid film that  $A$  will not "penetrate" very far into  $B$ —that the penetration distance be small in comparison with the film thickness. The system is sketched in Fig. 17.5-1. Let us now set up the differential equations describing the process. First of all we have to solve the momentum transfer problem to obtain the velocity profile  $v_z(x)$  for the film; this has already been worked out in §2.2 in the

absence of mass transfer at the fluid surface, and we know that the result is

$$(17.5-1) \quad v^z(x) = v_{\max} \left[ 1 - \left( \frac{\delta}{x} \right)^2 \right]$$

provided that "end effects" are not considered.

Next we have to establish a mass balance on component *A*. We note that *c<sub>F</sub>* will be changing both with *x* and with *z*. Hence as the element of volume over which we set up the mass balance we select the volume formed by the intersection of a slab of thickness  $\Delta z$  with a slab of thickness  $\Delta x$ . Then the mass balance on *A* is simply

$$(17.5-2) \quad N_{Az}^z W \Delta x - N_{Az}^{z+\Delta z} W \Delta x + N_{Ax}^x W \Delta z - N_{Ax}^{x+\Delta x} W \Delta z = 0$$

in which *W* is the width of the film. By dividing by *W*  $\Delta x$   $\Delta z$  and performing the usual limiting process as the volume element becomes infinitesimally small, we get

$$(17.5-3) \quad \frac{\partial N_{Az}^z}{\partial x} + \frac{\partial N_{Ax}^x}{\partial z} = 0$$

Into this equation we now have to insert the expressions for *N<sub>Fz</sub>* and *N<sub>Fx</sub>* by making appropriate simplifications of Eq. 17.0-1. For the molar flux in the *z*-direction, we write, assuming constant *c*

$$(17.5-4) \quad N_{Az}^z = -\mathcal{G}_{AB} \frac{\partial c_A}{\partial z} + x_A(N_{Az}^z + N_{Bz}^z) \approx c_F v^z(x)$$

That is, *A* moves in the *z*-direction primarily because of the flow of the film, the diffusive contribution being negligible. The molar flux in the *x*-direction will be

$$(17.5-5) \quad N_{Ax}^x = -\mathcal{G}_{AB} \frac{\partial c_A}{\partial x} + x_A(N_{Ax}^x + N_{Bx}^x) \approx -\mathcal{G}_{AB} \frac{\partial c_A}{\partial x}$$

That is, in the *x*-direction *A* is transported primarily by diffusion, there being almost no convective transport because of the very slight solubility of *A* in *B*. Substitution of these expressions for *N<sub>Fx</sub>* and *N<sub>Fz</sub>* into Eq. 17.5-3 gives

$$(17.5-6) \quad v^z \frac{\partial c_A}{\partial z} = \mathcal{G}_{AB} \frac{\partial^2 c_A}{\partial x^2}$$

which is the differential equation describing *c<sub>F</sub>*(*x*, *z*).

The forced-convection mass transfer is then described by Eqs. 17.5-1 and 17.5-6. When these two equations are combined, we get finally

$$(17.5-7) \quad v_{\max} \left[ 1 - \left( \frac{\delta}{x} \right)^2 \right] \frac{\partial c_A}{\partial z} = \mathcal{G}_{AB} \frac{\partial^2 c_A}{\partial x^2}$$

This partial differential equation is to be solved with the following boundary conditions:

- B. C. 1: at  $z = 0$ ,  $c_A = 0$  (17.5-8)
- B. C. 2: at  $x = 0$ ,  $c_A = c_{A0}$  (17.5-9)
- B. C. 3: at  $x = \delta$ ,  $\frac{\partial c_A}{\partial x} = 0$  (17.5-10)

when the fluid film begins as pure B, and the interface concentration in the liquid is taken to be the solubility of A in B, here designated as  $c_{A0}$ . This problem has been solved by Pigford,<sup>1</sup> but we do not give that solution here. Instead, we solve to obtain only a limiting expression valid for "short contact times"—that is, small values of  $L/v_{max}$ .

If, as is indicated in Fig. 17.5-1, the substance A has penetrated only a short distance into the film, then the A species for the most part has the impression that the film is moving throughout with a velocity equal to  $v_{max}$ . Furthermore, if A does not penetrate very far, it does not "feel" the presence of the solid wall at  $x = \delta$ . Hence, if the film were of infinite thickness moving with the velocity  $v_{max}$ , the diffusing material would not know the difference. This physical argument suggests then that we replace Eq. 17.5-7 and its boundary conditions by

$$\frac{\partial^2 c_A}{\partial z^2} = \mathcal{G}_{AB} \frac{\partial^2 c_A}{\partial x^2} \quad (17.5-11)$$

- B. C. 1: at  $z = 0$ ,  $c_A = 0$  (17.5-12)
- B. C. 2: at  $x = 0$ ,  $c_A = c_{A0}$  (17.5-13)
- B. C. 3: at  $x = \infty$ ,  $c_A = 0$  (17.5-14)

The solution to Eq. 17.5-11 with these boundary conditions is<sup>2</sup>

$$\frac{c_A}{c_{A0}} = 1 - \frac{\sqrt{\pi}}{2} \int_0^{\sqrt{4\mathcal{G}_{AB}z/v_{max}}} e^{-\xi^2} d\xi$$

$$= 1 - \operatorname{erf} \frac{\sqrt{4\mathcal{G}_{AB}z/v_{max}}}{x}$$

or

$$\frac{c_A}{c_{A0}} = \operatorname{erfc} \frac{\sqrt{4\mathcal{G}_{AB}z/v_{max}}}{x} \quad (17.5-15)$$

<sup>1</sup> R. L. Pigford, doctoral dissertation, University of Illinois (1941).  
<sup>2</sup> The solution is worked out in detail in Example 4.1-1 by the "method of combination of variables."

Here  $erf\ y$  is the "error function" defined in §4.1 and  $erfc\ y = 1 - erf\ y$  is the "complementary error function"; both are standard tabulated functions. Once the concentration profiles are known, the total mass-transfer rate may be found by either of the following two methods:

Integration of Mass Flux over Length of Film

The local mass flux at the surface  $x = 0$  at a position  $z$  down the plate is

$$N_{Ax}(z)|_{x=0} = -\mathcal{D}_{AB} \left. \frac{\partial c_A}{\partial x} \right|_{x=0} = c_{A0} \sqrt{\frac{\pi z}{\mathcal{D}_{AB} v_{max}}} \quad (17.5-16)$$

The total moles of  $A$  transferred per unit time from the gas to the liquid film is

$$\mathcal{M}_A = \int_0^L \int_0^T N_{Ax}|_{x=0} dz dy$$

$$= W c_{A0} \sqrt{\frac{\mathcal{D}_{AB} v_{max}}{\pi}} \int_0^T z^{-1/2} dz$$

$$= W L c_{A0} \sqrt{\frac{\pi L}{4 \mathcal{D}_{AB} v_{max}}} \quad (17.5-17)$$

Integration of Concentration Profile over (Infinite) Film Thickness at  $z = L$

According to an over-all mass balance on the film, the total moles of  $A$  transferred per unit time across the gas-liquid interface must be the same as the total molar rate of flow of  $A$  across the plane  $z = L$ , which may be calculated by multiplying the volume rate of flow across the plane  $z = L$  by the average concentration at that plane:

$$\mathcal{M}_A = \lim_{\delta \rightarrow 0} (W \delta v_{max}) \left( \frac{1}{\delta} \int_0^{\delta} c_A|_{z=L} dz \right) x p$$

$$= W v_{max} c_{A0} \int_0^{\infty} erfc \left( \frac{z}{\sqrt{4 \mathcal{D}_{AB} L / v_{max}}} \right) dz$$

$$= W v_{max} c_{A0} \frac{\sqrt{4 \mathcal{D}_{AB} L / v_{max}}}{x} \int_0^{\infty} erfc \left( \frac{z}{x} \right) dz$$

$$= W v_{max} c_{A0} \frac{\sqrt{4 \mathcal{D}_{AB} L / v_{max}}}{2} \int_0^{\infty} \frac{\pi}{2} \cdot \left( \int_0^{\infty} e^{-\xi^2} d\xi \right) dz$$

$$= W v_{max} c_{A0} \sqrt{\frac{4 \mathcal{D}_{AB} L}{v_{max}}} \cdot \frac{\sqrt{\pi}}{2} \cdot \int_0^{\infty} \int_0^{\infty} e^{-\xi^2} d\xi dz \quad (17.5-18)$$

In the last line the new variable  $u = x / \sqrt{4 \mathcal{D}_{AB} L / v_{max}}$  has been introduced.

At this juncture we change the order of integration<sup>3</sup> in the double integral, which procedure enables us to evaluate the double integral analytically and to obtain Eq. 17.5-17 thus:

$$\begin{aligned}
 W_A &= W L c_{A0} \sqrt{\frac{4 \mathcal{D}_{AB} v_{\max}}{\pi L}} \cdot 2 \int_0^\infty e^{-\xi^2} \left( \int_\xi^0 du \right) d\xi \\
 &= W L c_{A0} \sqrt{\frac{4 \mathcal{D}_{AB} v_{\max}}{\pi L}} \cdot 2 \int_0^\infty e^{-\xi^2} \xi d\xi \\
 &= W L c_{A0} \sqrt{\frac{4 \mathcal{D}_{AB} v_{\max}}{\pi L}}
 \end{aligned}
 \tag{17.5-19}$$

From this development it is seen that the mass transfer rate is directly proportional to the square root of the diffusivity and inversely proportional to the square root of the "exposure time,"  $t^{\text{exp}} = L/v_{\max}$ . This approach for studying gas absorption was apparently first proposed by Higbie.<sup>4</sup>

### Example 17.5-1. Gas Absorption from Rising Bubbles

Estimate the rate at which gas bubbles of *A* are absorbed by liquid *B* as the gas bubbles rise at their terminal velocity  $v_t$  through a "clean" quiescent liquid.

**Solution.** For bubbles of moderate size rising in liquids with no surface-active agents, the gas in the bubble undergoes a toroidal circulation as shown in Fig. 17.5-2. As the gas circulates, it encounters fresh liquid at the top of the bubble. As the bubble rises, the liquid moves downward in relation to the bubble and leaves when it reaches the bottom of the bubble. The liquid near the interface is usually in laminar flow and appears to maintain its identity. Thus the liquid behaves much like the liquid at the surface of the falling film just discussed. The contact time is certainly short, so that the penetration of the dissolved gas is slight and the assumptions introduced in §17.5 are valid. Therefore, to a first approximation, we can use the result in Eq. 17.5-17 (or 19) to estimate the rate of gas absorption and the change in bubble size.

The average rate of mass transfer of *A* is

$$(N_A)_{\text{avg}} = \sqrt{\frac{4 \mathcal{D}_{AB}}{\pi t^{\text{exp}}}} c_{A0}
 \tag{17.5-20}$$

in which  $c_{A0}$  is the solubility of gas *A* in liquid *B*. The exposure time  $t^{\text{exp}}$  is the time required for the liquid to slide along the bubble from top to bottom. This can be taken to be approximately  $t^{\text{exp}} = D/v_t$ , in which  $D$  is the bubble diameter and

<sup>3</sup> See, for example, G. B. Thomas, Jr., *Calculus and Analytic Geometry*, Addison-Wesley Reading, Mass. (1953), Chapter 15.

<sup>4</sup> R. Higbie, *Trans. A.I.Ch.E.*, **31**, 365-389 (1935).

<sup>5</sup> R. Higbie, *op. cit.*

$v_t$  is the terminal velocity of the rising bubble. Hence the absorption rate through the bubble-liquid interface is

$$(N_A)_{\text{avg}} = \sqrt{\frac{4D_{AB} v_t}{\pi D}} c_{A0} \quad (17.5-21)$$

This result has been substantiated<sup>6</sup> for gas bubbles of about 0.3–0.5 cm in diameter rising through carefully purified water; small amounts of surface-active agents cause a marked decrease in  $(N_A)_{\text{avg}}$  because of the formation of a "skin" around

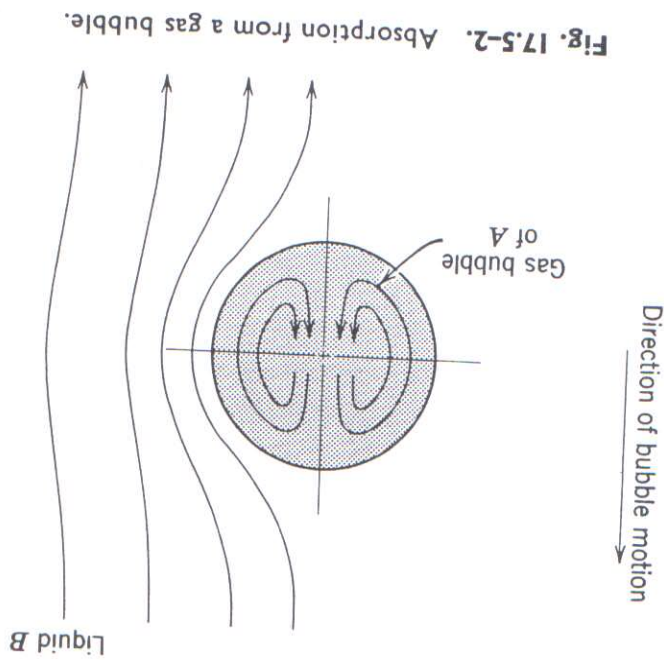


Fig. 17.5-2. Absorption from a gas bubble.

the bubble that effectively prevents mass transfer rates during drop-formation at a capillary tip.<sup>7</sup> A similar approach has been

### §17.6 DIFFUSION AND CHEMICAL REACTION INSIDE A POROUS CATALYST: THE "EFFECTIVENESS FACTOR"<sup>1,2,3</sup>

Up to this point we have discussed diffusion in gases and liquids in systems of simple geometry. We now wish to apply the shell mass-balance method and Fick's first law to describe diffusion on the inside of a porous catalyst pellet. We make no attempt to describe the diffusion inside the tortuous void passages in the medium. Instead, we describe the "average" diffusion of the chemical species in terms of an effective diffusion coefficient.

<sup>6</sup> D. Hammett and F. H. Garner, *Trans. Inst. Chem. Engrs. (London)*, **32**, 518 (1954).  
<sup>7</sup> H. Groothuis and H. Kramers, *Chem. Eng. Sci.*, **4**, 17-25 (1955).  
<sup>1</sup> E. W. Thiele, *Ind. Eng. Chem.*, **31**, 916-920 (1939).  
<sup>2</sup> R. Arts, *Chem. Eng. Sci.*, **6**, 265-268 (1957).  
<sup>3</sup> A. Wheeler, *Advances in Catalysis*, Academic Press, New York (1950), Vol. 3, pp. 250-326.