

3. Mass Transfer at Fluid Boundaries

3.1 Introduction of Mass-Transfer Coefficient

Case 1.

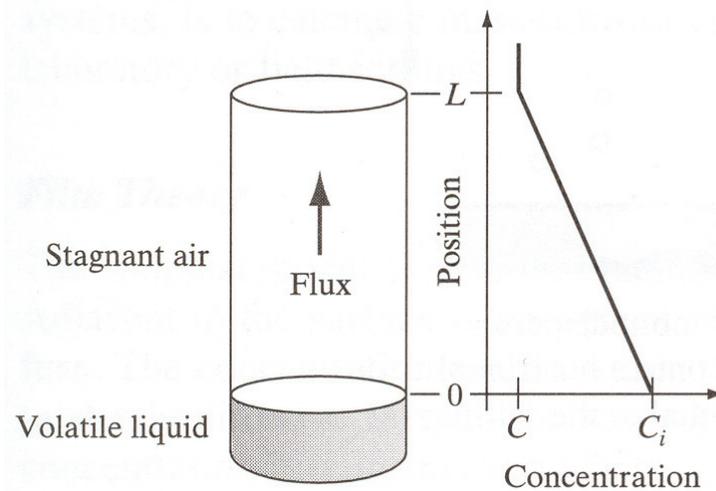


Figure 4.C.1 A simple system in which a mass-transfer coefficient can be directly determined.

$$J_b \propto (C - C_i)$$

Put

where J_b = net flux to the boundary (amount of species per area per time);

k_m = mass-transfer coefficient; and

C and C_i = concentration terms.

The diffusive flux through the tube, J_d is given by Fick's law as,

at a steady state, the net transport rate from the air to the liquid is equal to the negative of the diffusive flux and

Case 2.

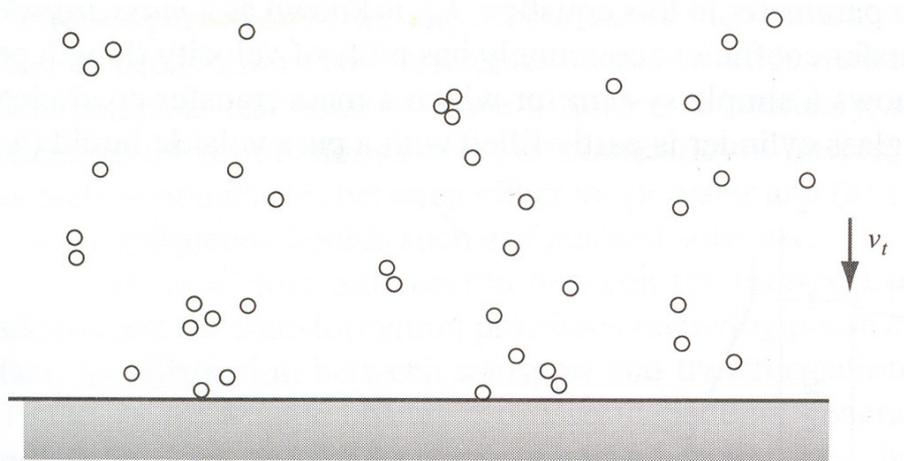


Figure 4.C.2 In a uniform suspension of monodisperse particles settling through a stagnant fluid onto a horizontal surface, the mass-transfer coefficient is equal to the settling velocity.

Particles are suspended in a fluid above a horizontal boundary. All particles are assumed to have the same terminal velocity, v_t . The gravitational flux from air to the fluid, J_b is

$$J_g = v_t \cdot C$$

The concentration of the particle at the boundary, C_i can be assigned to be 0 if no resuspension of particles is assumed (i.e., once particles strike the boundary, they are no longer suspended in the fluid). Then, the mass transfer coefficient is equal to the particle settling velocity.

Discussions on concentrations, i.e., C_i , C

- (1) The concentration at the boundary, C_i can be taken to be "0" when a transformation process that is fast and irreversible occurs at the boundary rather than surface-reaction kinetics is the rate-limiting step. In the other hand, C_i can be determined by assuming local equilibrium at the interface.
- (2) When the fluid is well mixed outside of a thin boundary layer, the concentration in bulk fluid, C is easily defined. Only rough approximation of C can be possible for practical environmental engineering problem because C vary strongly with position and time.

3.1.1 Film Theory

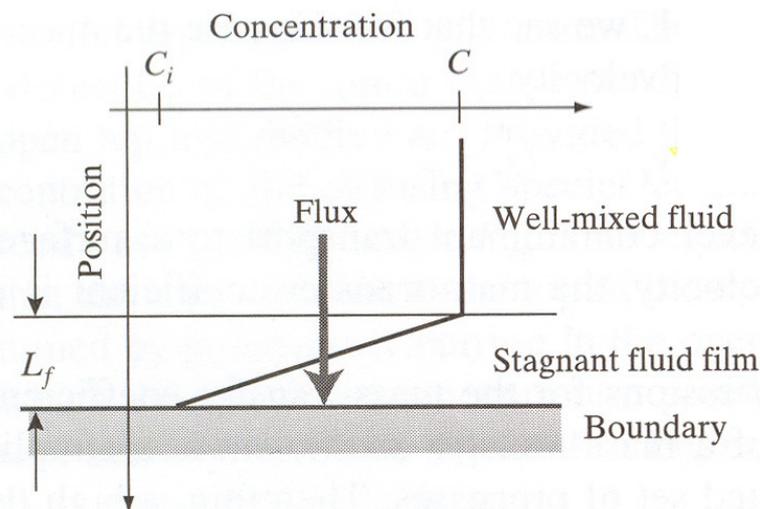


Figure 4.C.3 Schematic of mass transfer to a surface according to film theory

and

- Usually a higher diffusion coefficient, D results in a greater film thickness, L_f .
For example,
As $D_{air} \uparrow$, $L_f \uparrow$ and As $D_{air} = 0$, $L_f = 0$ (no diffusion in water)
- The key weakness of film theory is its dependence on the film thickness, L_f because there is no practical way to measure L_f .
- In this model, the diffusion in the water is not considered. Practically, for a compound with enough high diffusivity in the water, L_f becomes constant.

3.1.2 Penetration Theory

- In some circumstances, the contact time between a boundary and a fluid is not long enough for the concentration profile to approach the constant slope condition in Figure 4.C.3 and for film theory to apply.

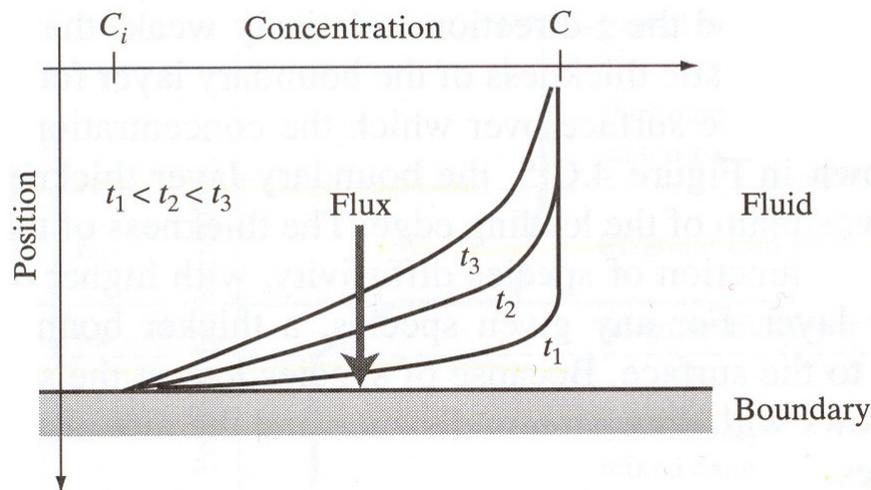


Figure 4.C.4 Schematic of mass transfer to a surface according to penetration theory

- The penetration theory is based on transient diffusion in one dimension (Figure 4.C.4). Since the distance through which species must diffuse increase with time, k_m decreases as time increases.

$$k_m(t) = \sqrt{\frac{D}{\pi \cdot t}} \text{ instantaneous mass transfer coefficient}$$

$$k_m = \frac{1}{t^*} \int_0^{t^*} \{k_m(t)\} dt = 2\sqrt{\frac{D}{\pi \cdot t^*}} \text{ time-averaged mass transfer coefficient}$$

where t^* = time interval concerned.

- The penetration theory predicts that the mass-transfer coefficient increase in proportional to the square root of diffusivity (power of 0.5). In contrast, the film theory predicts that the mass transfer coefficient is proportional to diffusivity (power of 1.0). In film theory, the film thickness is assumed to be constant and is independent of D. In penetration theory, the diffusion distance increases with time and the rate of growth depends on D.
- In the view point of the Film theory, as time passes, L_f increases and k_m decreases.

3.1.3 Boundary-layer Theory: Laminar Flow along a Flat Surface

- For transport from moving fluids to boundaries (Figure. 4.C.5)

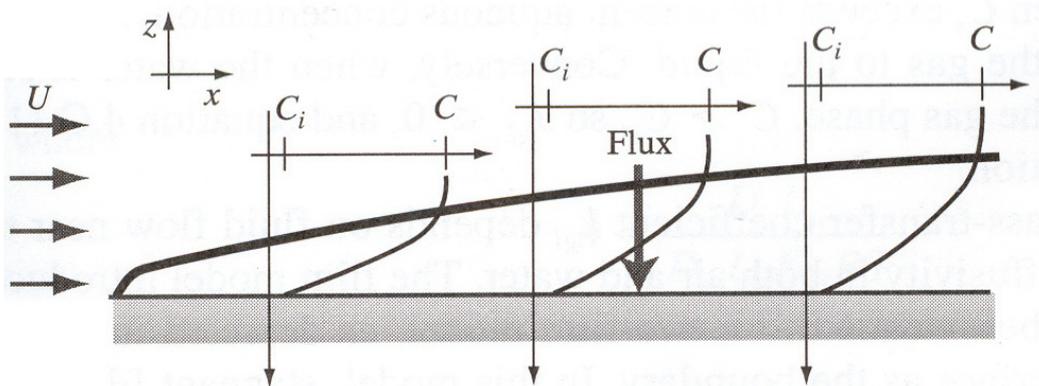


Figure 4.C.5 Schematic of mass transfer to a surface according to boundary-layer theory for a case of a flat surface parallel to a uniform, laminar fluid flow.

- The boundary-layer thickness grows and the rate of mass transfer

correspondingly decreases with increasing distance downstream of the leading edge because species loss at the surface.

$$k_m(x) = 0.323 \sqrt{\left(\frac{U}{x}\right)} \cdot \nu^{-1/6} \cdot D^{2/3} \quad \text{local (Cussler, 1984; and Bejan, 1984)}$$

$$k_m = \frac{1}{L} \int_0^L \{k_m(x)\} dx = 0.646 \sqrt{\left(\frac{U}{L}\right)} \cdot \nu^{-1/6} \cdot D^{2/3} \quad \text{average}$$

(Integration from the leading edge to a distance “L” downstream)

- The mass transfer coefficient in the boundary-layer theory is proportional to 2/3 power of D (between 0.5 for penetration theory and 1.0 for film theory)
- In terms of the Film theory, the thick solid line in Figure 4.C.5 implies the boundary layer thickness, e.g., L_f .

3.2 Two Film Model for Transport across the Air-Water Interface

- Two resistance model for interfacial mass transfer

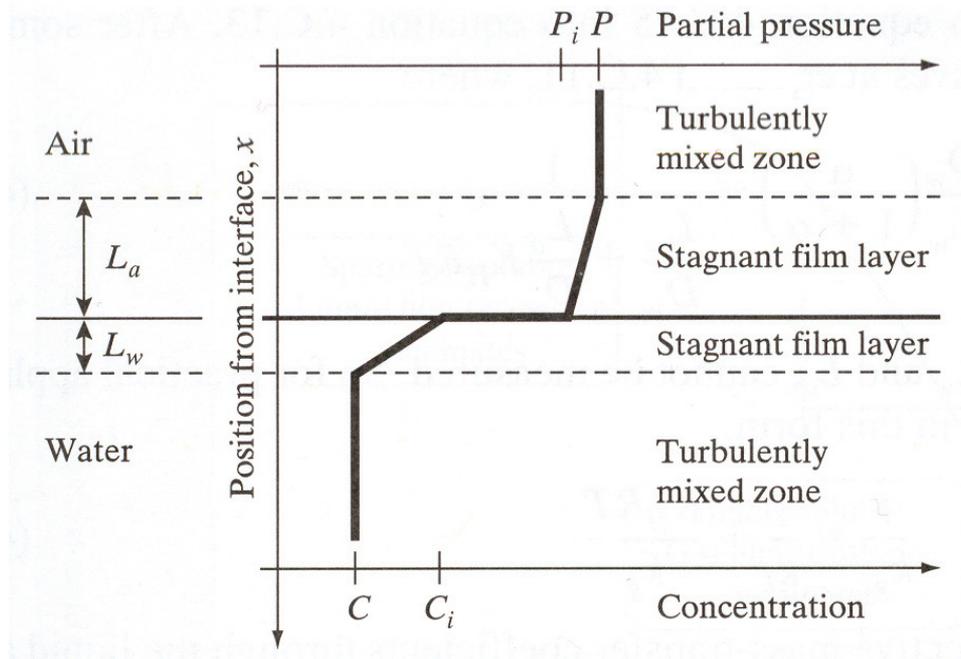


Figure 4.C.6 Schematic of the two-film model for estimating mass transfer across an air-water interface.

Applying Fick's law, the gas-side flux (from air to the interface), J_{gl} can be written as

where D_a = diffusivity of the species through air;
 L_a = thickness of the stagnant film layer in the air
 P = partial pressure in the gas phase; and
 P_i = partial pressure at the interface.

Likewise, the liquid-side flux (from the interface into the water), J_{wl} is

where D_w = diffusivity of the species in water;

L_w = thickness of the stagnant film layer in the water

C = aqueous concentration; and

C_i = aqueous concentration at the interface.

$J_{gl} = J_{wl}$ (conservation law without accumulation in the interface)

and $C_i = K_H \cdot P_i$

Then, we can solve 3 variables, i.e., J_{gl} , C_i , and P_i using the previous 3 equations.

$$C_i = \frac{\alpha \cdot C_s + C}{1 + \alpha}$$

where C_s = saturation concentration of species in the aqueous phase

$$\alpha = \frac{D_a \cdot L_w}{D_w \cdot L_a \cdot K_H \cdot R \cdot T}$$

and $C_s = K_H \cdot P$

$$J_{gl} = \frac{D_w}{L_w} \cdot (C_i - C) = \frac{D_w}{L_w} \cdot \frac{\alpha}{1 + \alpha} \cdot (C_s - C) \quad \text{and}$$

$$J_{gl} = k_{gl} \cdot (C_s - C)$$

Thus,

$$k_{gl} = \frac{D_w}{L_w} \cdot \left(\frac{\alpha}{1 + \alpha} \right) = \frac{1}{\frac{L_w}{D_w} + \frac{L_a}{D_a} \cdot K_H \cdot R \cdot T} \quad \text{and}$$

$$\frac{1}{k_{gl}} = \frac{1}{k_l} + \frac{K_H \cdot R \cdot T}{k_g}$$

where k_{gl} = overall mass transfer coefficient;

k_l = mass transfer coefficient through the liquid boundary layer ($=D_w/L_w$); and

k_g = mass transfer coefficient through the gas boundary layer ($=D_a/L_a$).

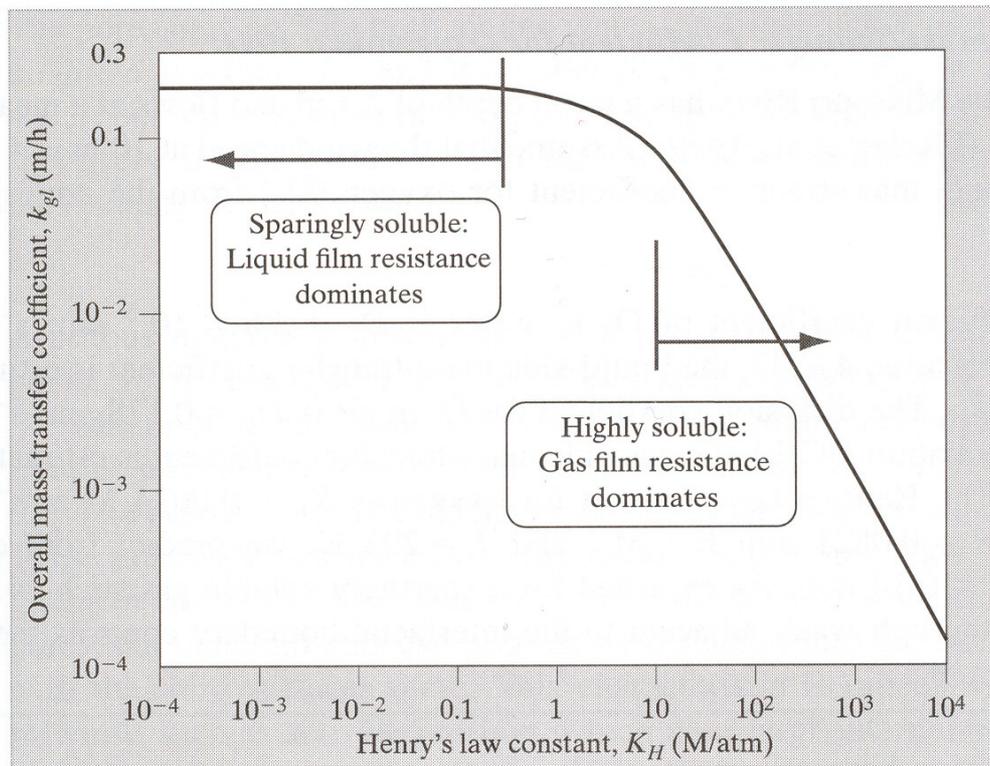


Figure 4.C.7 Dependence of the overall mass-transfer coefficient on the Henry's law constant for average conditions in large bodies of water. The curve traces equation 4.C.19 with $k_l = 0.2 \text{ m h}^{-1}$, $k_g = 30 \text{ m h}^{-1}$, and $T = 293 \text{ K}$ (Liss and Slater, 1974).

For natural bodies of water, the following expressions can be applied to estimate mass transfer coefficients, k_g and k_l .

$$k_g \text{ (m/hr)} = \left[\frac{D_a \text{ (cm}^2/\text{sec)}}{0.26} \right]^{2/3} \cdot (7 \cdot U_{10} + 11)$$

for oceans, lakes, and other slowly flowing waters,

$$k_l \text{ (m/hr)} = \left[\frac{D_w \text{ (cm}^2/\text{sec)}}{2.6 \times 10^{-5}} \right]^{0.57} \cdot (0.0014 \cdot U_{10}^2 + 0.014)$$

for rivers,

$$k_1 \text{ (m/hr)} = 0.18 \cdot \left[\frac{D_w \text{ (cm}^2 \text{ / sec)}}{2.6 \times 10^{-5}} \right]^{0.57} \cdot \left(\frac{U_w}{d_w} \right)^{1/2}$$

where U_{10} = mean wind speed measured at 10m above the water surface (m/sec)

U_w = mean velocity in the river (m/sec); and

d_w = mean stream depth (m).