4.5 Evaporation and Diffusion

4.5.4 Evaporation and Diffusion through Quiescent Air (page 286)

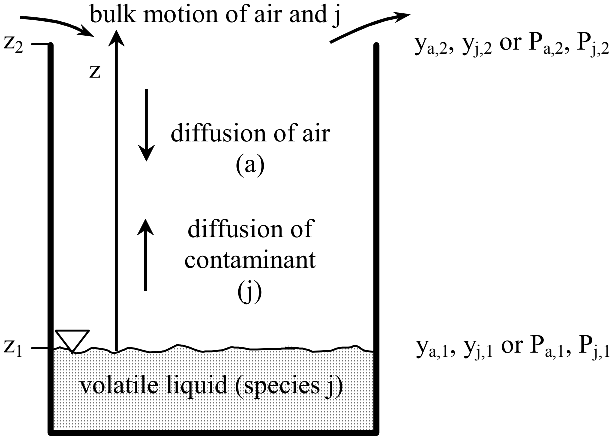

Figure 4.10 Evaporation of a volatile liquid (species j) from a container open at the top, partially filled with the volatile liquid.

The ***evaporation mass flow rate*** (mass per time) is given in all cases by

$$\boxed{\dot{m}_{evap,j} = N_j M_j A} \tag{4-46}$$

A ***log mean mol fraction*** (y_{am}) and a ***log mean partial pressure ratio*** (P_{am}) are defined as

$$\boxed{y_{am} = \frac{y_{a,2} - y_{a,1}}{\ln\left(\frac{y_{a,2}}{y_{a,1}}\right)}} \tag{4-53}$$

and

$$\boxed{P_{am} = \frac{\left(P_{a,2} - P_{a,1}\right)}{\ln\left(\frac{P_{a,2}}{P_{a,1}}\right)}} \tag{4-54}$$

The ***mass transfer coefficient*** is defined as k_G. For pure diffusion, k_G is

$$\boxed{k_G = \frac{D_{ja}}{R_u T\left(z_2 - z_1\right) y_{am}}} \tag{4-59}$$

or,

$$\boxed{k_G = \frac{P D_{ja}}{R_u T\left(z_2 - z_1\right) P_{am}}} \tag{4-60}$$

The molar flux (N_j) can be expressed as

$$\boxed{N_j = k_G P\left(y_{j,1} - y_{j,2}\right)} \tag{4-61}$$

Alternatively, the molar flux (N_j) can be written instead as

$$\boxed{N_j = k_G R_u T\left(c_{molar,j,1} - c_{molar,j,2}\right) = k_G\left(P_{j,1} - P_{j,2}\right)} \tag{4-62}$$

Usually, points 1 and 2 correspond to the liquid-gas interface (subscript i) and the top of the container or tank (subscript 2 in Figure 4.10) respectively.

Example 4.10 - Evaporation of PERC from a Nearly Empty Drum

Given: A dry cleaning establishment uses perchloroethylene, commonly called PERC or "perk" ($Cl_2C{=}CCl_2$, CAS 127-18-4), as the fluid to clean clothes. PERC is a colorless liquid with a chloroform-like odor and a PEL of 100 PPM. The liquid arrives in a 55-gallon drum and is transferred to the cleaning equipment. A nearly empty drum with an open top is improperly stored inside the facility and a small pool of PERC in the bottom of the drum evaporates into the workplace. The drum has a cross-sectional area of 0.25 m^2 and a height, $(z_2 - z_1)$, of 0.813 m. From the MSDS and Appendices A.8, A.9, and A.20, PERC has the following properties:

- M = 165.8, $\rho = 1.62\ g/cm^3$
- odor recognition threshold (high value) = 69. PPM
- boiling point (BP) = 250. °F
- vapor pressure, P_v(at 20 °C) = 14.0 mm Hg
- $D_{ja} = 0.74 \times 10^{-5}\ m^2/s$

To do: Estimate the rate at which PERC evaporates.

Solution: In the far-field, $P_{a,2} = P$, since $P_{j,2} \approx 0$. At the liquid interface, the partial pressure of the PERC is equal to the vapor pressure at standard atmospheric conditions, $P_{j,1}$ = 14.0 mm Hg. Thus,

$$P_{a,1} = P - P_{j,1} = (760. - 14.0)\ \text{mm Hg} = 746.\ \text{mm Hg}$$

From Eq. (4-54),

$$P_{am} = \frac{(P_{a,2} - P_{a,1})}{\ln\left(\frac{P_{a,2}}{P_{a,1}}\right)} = \frac{(760. - 746.)\ \text{mm Hg}}{\ln\left(\frac{760.}{746.}\right)} = 753.0\ \text{mm Hg}$$

The mass transfer coefficient (k_G) can be obtained from Eq. (4-60),

$$k_G = \frac{P\,D_{ja}}{R_u T (z_2 - z_1) P_{am}} = \frac{(760.\ \text{mm Hg})\left(0.74 \times 10^{-5}\ \frac{m^2}{s}\right)}{8.314\ \frac{kJ}{kmol \cdot K}(293.15.\ K)0.813\ m(753.0\ \text{mm Hg})}\left(\frac{kJ}{kN \cdot m}\right)\left(\frac{kN}{kPa \cdot m^2}\right)$$

$$k_G = 3.769 \times 10^{-9}\ \frac{kmol}{kPa \cdot m^2 \cdot s}$$

The molar flux is then found from Eq. (4-62),

$$N_j = k_G\left(P_{j,1} - P_{j,2}\right) =$$

$$= 3.769 \times 10^{-9}\ \frac{kmol}{kPa \cdot m^2 \cdot s}\left[(14.0 - 0)\ \text{mm Hg}\right]\left(\frac{101.3\ kPa}{760.0\ \text{mm Hg}}\right) = 7.034 \times 10^{-9}\ \frac{kmol}{m^2 s}$$

Finally, the mass flow rate of the PERC is obtained from Eq. (4-46),

$$\dot{m}_{evap,j} = N_j M_j A = \left(7.034 \times 10^{-9}\ \frac{kmol}{m^2 s}\right)\left(166.0 \frac{kg}{kmol}\right)\left(0.25\ m^2\right) = \mathbf{2.92 \times 10^{-7}\ \frac{kg}{s}}$$

which is approximately 1.03 g/hr.

4.5.5 Evaporation of Single Component Liquids (page 291)

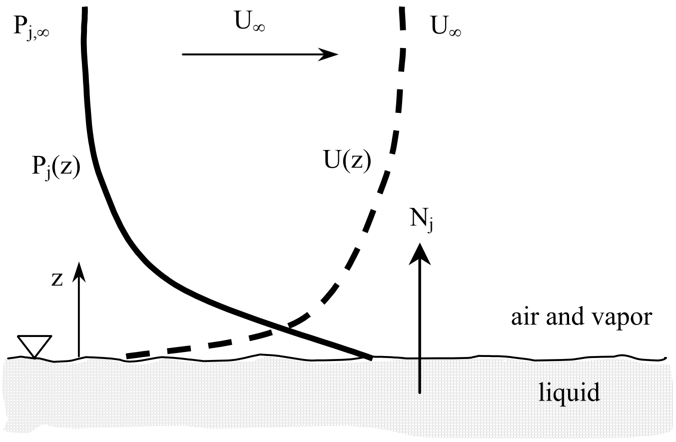

Figure 4.12 Mass transfer through a single-film; concentration and velocity profiles in air passing over a volatile single molecular species liquid.

We still use the same equation for the ***evaporation mass flow rate***,

$$\boxed{\dot{m}_{evap,j} = N_j M_j A} \qquad (4\text{-}46)$$

And we still use the same expression for ***molar flux*** (N_j), i.e.,

$$\boxed{N_j = k_G \left(P_{j,i} - P_{j,\infty}\right)} \qquad (4\text{-}67)$$

where the variables are defined (along with typical units) as

- N_j = molar flux [kmol/(m^{2}s)]
- k_G = ***gas phase mass transfer coefficient*** [kmol/(m^{2}s kPa)]
- $P_{j,i}$ = partial pressure of species j at the liquid-gas interface (mm Hg or kPa)
- $P_{j,\infty}$ = partial pressure of species j in the far-field (mm Hg or kPa)

Now, however, the expression for k_G becomes more complicated, and Reynolds analogy is used. We introduce

$$\boxed{\text{Re (Reynolds number)} = \frac{LU_\infty \rho}{\mu} = \frac{LU_\infty}{\nu}} \qquad (4\text{-}70)$$

$$\boxed{\text{Sc (Schmidt number)} = \frac{\mu}{D_{ja}\,\rho} = \frac{\nu}{D_{ja}}} \qquad (4\text{-}71)$$

Characteristic length (L) is chosen by the user or defined in a particular empirical equation. It is the practice in heat transfer to also express the film coefficient in dimensionless form as

$$\boxed{\text{Nu} = C_2 \left(\text{Re}\right)^{a_2} \left(\text{Pr}\right)^{b_2}} \qquad (4\text{-}72)$$

where C_2, a_2, and b_2 are dimensionless constants that depend on the geometry of the surface and the range of Reynolds numbers under consideration. The two new parameters, ***Nusselt number*** and ***Prandtl number***, are also dimensionless and are defined as

$$\boxed{\text{Nu (Nusselt number)} = \frac{Lh}{k}} \qquad (4\text{-}73)$$

$$\boxed{\text{Pr (Prandtl number)} = \frac{\mu c_P}{k}} \qquad (4\text{-}74)$$

where h is the ***heat transfer coefficient***. In all of the above equations, the dynamic viscosity (μ), kinematic viscosity (ν), density (ρ), and thermal conductivity (k) pertain to the *air*, not the liquid. Since the contaminant concentration is usually very small, the properties of pure air can be used.

The ratio of the Schmidt and Prandtl numbers is called the ***Lewis number*** (Le),

$$\boxed{\mathrm{Le} = \frac{\mathrm{Sc}}{\mathrm{Pr}} = \frac{k}{\rho c_P D_{ja}}} \tag{4-77}$$

We also introduce the ***Sherwood number*** (Sh),

$$\boxed{\mathrm{Sh} = \mathrm{Nu}\left(\frac{\mathrm{Sc}}{\mathrm{Pr}}\right)^{b_1}} \tag{4-79}$$

Finally, an empirical expression for the ***gas-phase mass transfer coefficient*** k_G can be written as

$$\boxed{k_G = \mathrm{Nu}\frac{D_{ja}}{L}\left(\frac{\mathrm{Sc}}{\mathrm{Pr}}\right)^{b_1}\frac{P}{P_{am}}\frac{1}{R_u T}} \tag{4-80}$$

Example 4.12 - Estimating Evaporation Rate from Fundamental Principles

Given: Ethyl mercaptan (CH_3CH_2SH, CAS 75-08-1) is a liquid with an unpleasant skunk-like odor. The material is a strong oxidizer with a PEL of 0.5 PPM. A 55-gallon drum of the material is handled roughly and a small leak develops in a seam. A circular pool, approximately 10. m in diameter develops. The wind speed over the pool is estimated to be around 3.0 m/s.

To do: Estimate the evaporation rate from the spill (S_s, in kg/hr), using first principles rather than empirical equations such as Eq. (4-14).

Solution: It is assumed that the partial pressure of the contaminant at the liquid-gas interface is equal to the vapor pressure of the contaminant, $P_{v,j}$ the value of which can be found in Appendix A.8. It is also assumed that the characteristic length is the diameter of the pool, i.e. L = D. The temperature is 17.7 °C (290.85 K) and the total pressure is 1.00 atm (760. mm Hg).

ethyl mercaptan	**air**
$P_{j,i} = P_{v,j} = 400.$ mm Hg	$\nu = 15.89 \times 10^{-6}\ m^2/s$
$\mathcal{D}_{ja} = 0.9 \times 10^{-5}\ m^2/s$	Pr = 0.707
$M_j = 62.1$	$U_\infty = 3.0$ m/s
	$P_{a,i} = 760. - P_{j,i} = 360.$ mm Hg

The presence of ethyl mercaptan in air just above the interface influences the Prandtl (Pr) and Schmidt (Sc) numbers. For a first approximation, this influence is neglected because the concentrations are not large. The following parameters are computed:

$$P_{am} = \frac{(760.-360.)\ \text{mm Hg}}{\ln\left(\frac{760.}{360.}\right)} = 535.3\ \text{mm Hg} \qquad \text{Re} = \frac{U_\infty D}{\nu} = \frac{3.0\frac{\text{m}}{\text{s}}(10.0\ \text{m})}{1.589\times10^{-5}\ \frac{\text{m}^2}{\text{s}}} = 1.888\times10^6$$

The criteria in Table 4.3 show that the flow is turbulent. Table 4.3 indicates that the Nusselt number can be calculated as

$$\text{Nu} = \left[0.037(\text{Re})^{0.8} - 871\right](\text{Pr})^{0.33} = \left[0.037\left(1.888\times10^6\right)^{0.8} - 871\right](0.707)^{0.33} = 2685.$$

The Schmidt number is

$$\text{Sc} = \frac{\mu}{\mathcal{D}_{ja}\,\rho} = \frac{\nu}{\mathcal{D}_{ja}} = \frac{1.589\times10^{-5}\ \frac{\text{m}^2}{\text{s}}}{9.0\times10^{-6}\ \frac{\text{m}^2}{\text{s}}} = 1.766$$

The mass transfer coefficient (k_G) can be computed from Eq. (4-80), where $b_1 = 0.33$,

$$k_G = \text{Nu}\frac{\mathcal{D}_{ja}}{D}\left(\frac{\text{Sc}}{\text{Pr}}\right)^{0.33}\frac{P}{P_{am}}\frac{1}{R_u T}$$

$$= 2685\frac{9.0\times10^{-6}\ \frac{\text{m}^2}{\text{s}}}{10.0\ \text{m}}\left(\frac{1.766}{0.707}\right)^{0.33}\frac{760.\ \text{mm Hg}}{535.3\ \text{mm Hg}}\frac{1}{8.314\frac{\text{kJ}}{\text{kmol}\cdot\text{K}}(290.85\ \text{K})}\left(\frac{\text{kJ}}{\text{m}^3\text{kPa}}\right)$$

which yields

$$k_G = 1.92\times10^{-6}\ \frac{\text{kmol}}{\text{m}^2\text{s}\cdot\text{kPa}}$$

The molar flux (N_j) can be computed from Eq. (4-67), assuming that the ethyl mercaptan partial pressure in the far field is zero ($P_{j,\infty} = 0$),

$$N_j = k_G\left(P_{j,i} - P_{j,\infty}\right) = 1.92\times10^{-6}\ \frac{\text{kmol}}{\text{m}^2\text{s}\cdot\text{kPa}}\left(400.\ \text{mm Hg} - 0\right)\left(\frac{101.3\ \text{kPa}}{760.\ \text{mm Hg}}\right) = 1.02\times10^{-4}\ \frac{\text{kmol}}{\text{m}^2\text{s}}$$

Finally, the total evaporation rate from the pool is obtained from Eq. (4-46),

$$\dot{m}_{\text{evap},j} = N_j M_j A = 1.02\times10^{-4}\ \frac{\text{kmol}}{\text{m}^2\text{s}}\, 62.1\frac{\text{kg}}{\text{kmol}}\,\frac{\pi}{4}\ \left(10.0\ \text{m}\right)^2\left(\frac{3600\ \text{s}}{\text{hr}}\right) = 1.79\times10^3\ \frac{\text{kg}}{\text{hr}}$$

or approximately 1800 kg/hr.

Discussion: If the empirical equation, Eq. (4-14), were used instead to estimate the evaporation rate, a value of 1670 kg/hr would have been obtained. The evaporation rate computed from fundamental principles is about 5% larger than the value computed from the empirical equation. This agreement is excellent, considering the numerous approximations and assumptions! An explanation for the discrepancy may lie in the fact that the equation used to compute the Nusselt number assumes that the velocity and concentration boundary layers begin at the leading edge of the pool. In the actual case, air passing over the ground has a fully established boundary layer at the leading edge of the pool, and the equation for the Nusselt number may not apply to the actual case.

4.5.6 Single Film Theory for Multi-Component Liquids (page 297)

We still use the same equation for the ***evaporation mass flow rate***,

$$\boxed{\dot{m}_{evap,j} = N_j M_j A} \tag{4-46}$$

And we still use the same expression for ***molar flux*** (N_j), i.e.,

$$\boxed{N_j = k_G \left(P_{j,i} - P_{j,\infty}\right)} \tag{4-67}$$

But now we need to be careful how to determine the partial pressure of species j at the interface. We use either ***Raoult's law***,

$$\boxed{P_j = y_j P \qquad P_{j,i} = y_{j,i} P = x_{j,i} P_{v,j}} \tag{4-82}$$

where $P_{v,j}$ is the vapor pressure (see Appendix A.8) of pure species j at the temperature of the liquid, and $x_{j,i}$ is the mol fraction at the interface in the liquid phase, or we use ***Henry's law***, which can be expressed in several forms depending on the units chosen to represent the solute concentration.

$$\boxed{P_j = Hc_{molar,j} = Hx_j c_{molar,L} = H'x_j} \tag{4-97}$$

where

$$\boxed{H' = c_{molar,L} H} \tag{4-98}$$

See text for equations for the ***gas-phase mass transfer coefficient*** k_G. For example, for large spills of petroleum on bodies of water, spills of the order of hundreds of meters in diameter, Drivas (1982) recommends the expression

$$\boxed{k_G = \frac{0.0292 U_\infty^{0.78}}{R_u T_\infty D_0^{0.11} Sc^{0.67}}} \tag{4-95}$$

for all the evaporating species, where

- k_G = mass transfer coefficient [mol/(m^2 atm hr)]
- U_∞ = air velocity (m/hr)
- D_0 = diameter of the spill (m)
- Sc = gas-phase Schmidt number, using a mass weighted average for the liquid mixture (unitless)
- R_u = universal gas constant [8.206 x 10^{-5} (atm m^3)/(mol K)]
- T_∞ = air temperature (K)

4.5.7 Two-Film Evaporation of Multi-Component Liquids (page 302)

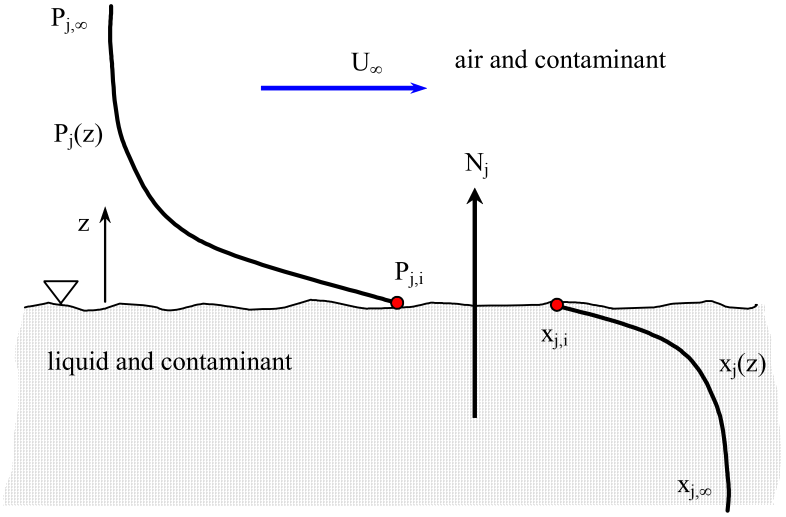

Figure 4.13 Concentration profiles for two-film mass transfer; x_j is the mol fraction in the liquid phase, and P_j is the partial pressure in the vapor phase.

We still use the same equation for the ***evaporation mass flow rate***,

$$\boxed{\dot{m}_{evap,j} = N_j M_j A} \qquad (4\text{-}46)$$

But see text for empirical expressions for **molar flux** N_j.

Example 4.16 - Evaporation of Volatile Compounds from a Stagnant Waste Lagoon

Given: A waste lagoon is 25. m x 40. m x 3.5 m deep. It contains 100. mg/L of benzene (M_b = 78.0) and 100. mg/L of chloroform (M_c = 119.0) in water. The air and liquid temperatures are 25.0 °C and the wind speed is 1.70 m/s at z = 10. m.

To do: Estimate the evaporation rate (kg/hr) of benzene and chloroform.

Solution: First, the Schmidt numbers are listed:

Sc (benzene-water) = 1,000	Sc (benzene-air) = 1.76
Sc (chloroform-water) = 1,100	Sc (chloroform-air) = 2.14

The total molar density ($c_{molar,L}$) is

$$c_{molar,L} = \frac{\rho_{total}}{M_{total}} \approx \frac{\rho_{water}}{M_{water}} = \frac{1000.\dfrac{kg}{m^3}}{18.0\dfrac{kg}{kmol}}\left(\frac{1000.\ mol}{kmol}\right) = 5.556\times10^4\ \frac{mol}{m^3}$$

Henry's law constants for the two chemicals in the water can be looked up:

- benzene: $H'_b = 3.05 \times 10^7\ N/m^2$ $\quad H_b = H'_b/c_{molar,L} = 5.5 \times 10^{-3}\ (atm\ m^3)/gmol$
- chloroform: $H'_c = 2.66 \times 10^7\ N/m^2$ $\quad H_c = H'_c/c_{molar,L} = 3.39 \times 10^{-3}\ (atm\ m^3)/gmol$

The overall mass transfer coefficient $K_{L,j}$ is given by Eq. (4-106), and the mass transfer coefficients for the gas and liquid phases are calculated from Eqs. (4-109) through (4-111). The friction velocity U* can be found from Eq. (4-113),

$$U^* = U_{10}\sqrt{6.1+0.63U_{10}} = \left(1.7\ \frac{m}{s}\right)\sqrt{6.1+0.63(1.7)} = 4.55\ \frac{m}{s}$$

Since U^* is greater than 0.3 m/s, Eq. (4-110) is relevant for this example problem. Summarizing the mass transfer coefficients for the two chemicals,

<u>Benzene (subscript b)</u>:

$k_{G,b} = 4.1 \times 10^{-2} + (1.9)(4.55)/1.76^{0.67} = 5.959 \cong 5.96\ mol/(m^2\ s\ atm)$

$k_{L,b} = 10^{-6} + 34.1 \times 10^{-4}(4.55)/1{,}000^{0.5} = 10^{-6} + 490.6 \times 10^{-6} = 4.92 \times 10^{-4}\ m/s$

$K_{L,b} = 4.85 \times 10^{-4}\ m/s$

<u>Chloroform (subscript c)</u>:

$k_{G,c} = 4.1 \times 10^{-2} + (1.9)(4.55)/2.14^{0.67} = 5.233 \cong 5.23\ mol/(m^2\ s\ atm)$

$k_{L,c} = 10^{-6} + 34.1 \times 10^{-4}\ (4.55)/1{,}100^{0.5} = 10^{-6} + 467.8 \times 10^{-6} = 4.69 \times 10^{-4}\ m/s$

$K_{L,c} = 4.57 \times 10^{-4}\ m/s$

The molar flux (N_j) for species j is given by Eq. (4-107) where $c_{molar,j,\infty}$ is the molar concentration of the species in the liquid far-field and $P_{j,\infty}$ is the partial pressure of species j in the gas far-field. In the liquid far-field (near the bottom of the lagoon),

$$c_{molar,b,\infty} = 100.\frac{mg}{L}\frac{1}{M_b} \qquad c_{molar,c,\infty} = 100.\frac{mg}{L}\frac{1}{M_c}$$

but in the gas far-field (distances far above the liquid-air interface) there is only pure air, so

$$P_{b,\infty} = P_{c,\infty} = 0$$

Eq. (4-107) then simplifies to

$$N_j = K_{L,j}\left(c_{\text{molar},j,\infty} - \frac{P_{j,\infty}}{H}\right) \approx K_{L,j}c_{\text{molar},j,\infty}$$

The mass transfer rate of benzene (j = b) and that of chloroform (j = c) from the lagoon (in kg/hr) for surface area A = 1,000 m^2 are thus

$$\dot{m}_b = N_b M_b A = K_{L,b} c_{\text{molar},b,\infty} M_b A$$

$$= 4.85\times10^{-4}\,\frac{\text{m}}{\text{s}}\left(100.\frac{\text{mg}}{\text{L}}\frac{1}{M_b}\right)M_b\left(1000\ \text{m}^2\right)\left(\frac{\text{kg}}{10^6\ \text{mg}}\right)\left(\frac{3600\ \text{s}}{\text{hr}}\right)\left(\frac{1000\ \text{L}}{\text{m}^3}\right) = 175.\frac{\text{kg}}{\text{hr}}$$

and

$$\dot{m}_c = N_c M_c A = K_{L,c} c_{\text{molar},c,\infty} M_c A$$

$$= 4.57\times10^{-4}\,\frac{\text{m}}{\text{s}}\left(100.\frac{\text{mg}}{\text{L}}\frac{1}{M_c}\right)M_c\left(1000\ \text{m}^2\right)\left(\frac{\text{kg}}{10^6\ \text{mg}}\right)\left(\frac{3600\ \text{s}}{\text{hr}}\right)\left(\frac{1000\ \text{L}}{\text{m}^3}\right) = 164.\frac{\text{kg}}{\text{hr}}$$

Discussion: Comparing the resistance of the liquid and gas films to mass transfer, it is clear that the liquid film resistance is nearly one hundred times larger than the gas film resistance (for either chemical).