Fundamentals of mass diffusion

1 Errata

- Slide 11 has an incorrect species subscript in the mass-fraction denominator. Use

$$w_A = \frac{x_A M_A}{x_A M_A + x_B M_B}$$

- Slide 13 retains species subscripts on the summed mixture fluxes. Use the total fluxes

$$n = \sum_i \rho_i v_i, \qquad N = \sum_i c_i v_i$$

  The molar-flux description should say molar flow rate per unit area.

- Slide 14 mislabels the second velocity heading. Use “Molar-average velocity” with

$$v^* = \frac{\sum_i c_i v_i}{c}$$

2 Reading list

- Bird et al. (2006), chapters 17 and 18.
- Geankoplis (2003), chapter 6.
- Welty et al. (2001), chapter 24.

Use consistent kmol units with $R_u = 8314\ \mathrm{Pa\,m^3\,kmol^{-1}\,K^{-1}}$.

3 Choose a steady-diffusion model

Given conditions	Model and checks
Equal and opposite molar fluxes	Set total molar flux to zero and use Eq. 8.
Carrier B has zero net flux	Retain bulk molar motion and use the stagnant-carrier logarithmic relation, Eq. 9.
Radial transfer through a cylinder or sphere	Write an area-weighted shell balance; conserve molar rate rather than radial flux.
A liquid boundary moves slowly	Use a pseudo-steady gas profile plus the interface inventory balance, Eq. 11.
Concentration changes through time inside a body	Move to the transient-diffusion topic; a steady film model alone is insufficient.

4 Fick's law of diffusion

DEFINITION
Molecular diffusion

Species transport relative to the bulk mixture caused by molecular motion and a thermodynamic driving force. In the simple Fickian models used here, the driving force is a concentration gradient.

When two gases with different compositions meet, random molecular motion mixes them even if there is no imposed flow. Across a plane in the gas, molecules of A arrive from both sides. More arrive from the side with the greater concentration of A, so their random motion produces a net transfer towards the lower concentration.

Fick's law relates that net transfer to the concentration gradient. For a binary mixture at constant total molar concentration, the molar diffusive flux relative to the mixture's molar-average velocity is

$$J_A = -D_{AB}\frac{dc_A}{dz} \tag{1}$$

J_A is in $\mathrm{kmol\,m^{-2}\,s^{-1}}$, c_A in $\mathrm{kmol\,m^{-3}}$, z in m and D_{AB} in $\mathrm{m^2\,s^{-1}}$. The gradient has units $\mathrm{kmol\,m^{-4}}$, so the dimensions close. The minus sign predicts transport down the gradient. The specified reference frame matters. A moving mixture can also transport A past the tube wall, so the flux measured by a fixed observer may differ from J_A.

QUIZ
1. The sign of diffusion
At constant total molar concentration, c_A decreases as z increases and $D_{AB} > 0$. What is the direction of the molar diffusive flux J_A?

1. It is negative because the gradient is negative.
2. It is zero unless the bulk fluid moves.
3. It points in positive z, down the concentration gradient.
4. It cannot be determined from the gradient.

See solution for Quiz 1

4.1 Examples: estimating diffusion times

Diffusion smooths a concentration difference over a distance L on the time scale

$$t_{\mathrm{diff}} \sim \frac{L^2}{D_{AB}}$$

The estimate follows by comparing the accumulation term c_A/t with the diffusion term $D_{AB}c_A/L^2$ in the transient species balance. It estimates how quickly a profile changes, rather than the exact time to reach a specified concentration.

For $L = 1\ \mathrm{mm} = 10^{-3}\ \mathrm{m}$, the estimate gives

$$\text{Gas:} \quad t_{\text{diff}} \sim \frac{(10^{-3})^2}{10^{-5}} = 0.1\ \text{s}$$

$$\text{Liquid:} \quad t_{\text{diff}} \sim \frac{(10^{-3})^2}{10^{-9}} = 1000\ \text{s}$$

$$\text{Solid:} \quad t_{\text{diff}} \sim \frac{(10^{-3})^2}{10^{-14}} = 10^{8}\ \text{s}$$

The values of D are illustrative. Diffusivity depends on the species pair, phase and temperature. Over the same distance, molecular diffusion can mix a gas in a fraction of a second while taking years in a solid. Doubling the distance multiplies the estimated time by four.

For modest dilute-gas extrapolations, kinetic theory gives

$$\frac{D_1}{D_2} = \frac{P_2}{P_1}\left(\frac{T_1}{T_2}\right)^{3/2} \tag{2}$$

Use absolute temperatures and matching pressure units. Doubling temperature at fixed pressure predicts a factor 2.83 with this estimate, compared with 3.36 using a $T^{1.75}$ fit. Measured data take precedence.

For hydrogen in nickel, $D_1 = 1.2 \times 10^{-12}$ at $T_1 = 358\,\text{K}$ and $D_2 = 10^{-11}\ \text{m}^2\,\text{s}^{-1}$ at $T_2 = 438\,\text{K}$. Solid-state diffusion is often represented by the Arrhenius relation,

$$D = D_0 \exp\left(-\frac{E_a}{R_u T}\right)$$

Taking logarithms at the two temperatures eliminates the unknown prefactor D_0. The activation energy is therefore

$$E_a = \frac{R_u \ln\left(\frac{D_2}{D_1}\right)}{\frac{1}{T_1} - \frac{1}{T_2}} = \frac{8.314 \ln\left[\frac{10^{-11}}{1.2\times10^{-12}}\right]}{\frac{1}{358} - \frac{1}{438}} = 3.46 \times 10^4\ \text{J mol}^{-1}$$

Thus the two supplied values imply $E_a \simeq 35\ \text{kJ mol}^{-1}$. The gas constant here is on a molar basis, $R_u = 8.314\ \text{J mol}^{-1}\,\text{K}^{-1}$.

For a porous medium using

$$D_{\text{eff}} = \frac{D\epsilon}{\tau},$$

$\epsilon = 0.4$ and $\tau = 3$ give $D_{\text{eff}} = 0.133D$.

DEFINITION
Diffusivity

Diffusivity, D_{AB}, is the material property relating the molar diffusive flux of A to its concentration gradient in the binary Fickian model at constant total concentration, $J_A = -D_{AB} dc_A/dz$. Its SI unit is $\text{m}^2\,\text{s}^{-1}$. It depends on the species pair, temperature, pressure and composition.

QUIZ

2. Diffusion time scale

A species has constant diffusivity $D = 10^{-9}\ \mathrm{m^2\,s^{-1}}$. What is the diffusion time scale across 1 mm?

1. 1000 s.
2. 1 s.
3. 10^{-3} s.
4. 10^{6} s.

See solution for Quiz 2

5 Units of concentration terms

DEFINITION

Mass fraction

The mass of a species divided by the total mixture mass. It is dimensionless, and all species mass fractions sum to one.

DEFINITION

Mole fraction

The molar amount of a species divided by the total molar amount of the mixture. It is dimensionless, and all species mole fractions sum to one.

Let ρ_i be species mass concentration in $\mathrm{kg\,m^{-3}}$, c_i molar concentration in $\mathrm{kmol\,m^{-3}}$, M_i molecular weight in kg kmol⁻¹, and w_i the dimensionless mass fraction. The source also writes ω_i for the same fraction. Use y_i for gas mole fraction and x_i for liquid mole fraction; a general mixture mole fraction below is denoted χ_i. The source shell balance uses x_i even for gas, which denotes the same quantity as our y_i.

$$\rho_i = c_i M_i$$

The total mass and molar concentrations are sums over the species,

$$\rho = \sum_i \rho_i$$

$$c = \sum_i c_i$$

The mass fraction and mole fraction are the corresponding species-to-total ratios,

$$w_i = \frac{\rho_i}{\rho}$$

$$\chi_i = \frac{c_i}{c}$$

Both sets of fractions sum to one,

$$\sum_i w_i = \sum_i \chi_i = 1 \tag{3}$$

For an ideal gas $c_i = p_i/(R_u T)$, $c = P/(R_u T)$ and $y_i = p_i/P$. Here p_i is partial pressure and P total pressure in Pa; $R_u = 8314\ \mathrm{Pa\,m^3\,kmol^{-1}\,K^{-1}}$. For a liquid, $c = \rho/\overline{M}$, where $\overline{M} = \sum_i \chi_i M_i$ is the mixture molecular weight, not the solute's molecular weight. Conversion between mass and mole fractions follows

$$\begin{aligned} \chi_A &= \frac{\frac{w_A}{M_A}}{\frac{w_A}{M_A} + \frac{w_B}{M_B}} \\ w_A &= \frac{\chi_A M_A}{\chi_A M_A + \chi_B M_B} \end{aligned} \tag{4}$$

In a binary mixture $\chi_B = 1 - \chi_A$, so the gradients are opposite. At constant c, this identity and $J_A + J_B = 0$ require the same mutual diffusivity for the pair. They do not imply that laboratory-frame total molar flux is zero.

QUIZ

3. Mass fraction and mole fraction

A binary mixture contains equal moles of A and B, but A has the greater molar mass. Which statement is true?

1. Both mass fractions must be one half.
2. A has the smaller mass fraction.
3. Mole fractions cannot be found without density.
4. Both mole fractions are one half, but A has the greater mass fraction.

See solution for Quiz 3

6 Component velocity in a mixture

A species velocity v_i in m s⁻¹ is a local average of many random molecular velocities, leaving a small drift. It is not a molecule's thermal speed. A fixed observer measures mass flux $n_i = \rho_i v_i$ in $\mathrm{kg\,m^{-2}\,s^{-1}}$ or molar flux $N_i = c_i v_i$ in $\mathrm{kmol\,m^{-2}\,s^{-1}}$. Their sums $n = \sum_i n_i$ and $N = \sum_i N_i$ describe the mixture.

The two mixture averages weight different quantities:

$$\begin{aligned} v &= \frac{\sum_i \rho_i v_i}{\rho} \\ v^* &= \frac{\sum_i c_i v_i}{c} \end{aligned} \tag{5}$$

v is the mass-average velocity used in overall mass continuity; v^* is the molar-average velocity natural for molar diffusion. In an equal-mole hydrogen/nitrogen mixture with $v_B = -v_A$ and molecular weights 2 and 28, $v^* = 0$ but

$$v = \frac{(2-28)v_A}{30} = -0.867v_A.$$

These averages coincide when molecular weights are equal.

A fixed observer sees v_i, a mass-average observer sees $v_i - v$, and a molar-average observer sees $v_i - v^*$. A diffusion velocity measures the species drift relative to the chosen mixture average. It can be positive, negative or zero. Weighted sums of diffusion velocities vanish by construction.

7 Bulk flux and diffusion flux

DEFINITION
Diffusive flux

Species transport rate per unit area relative to a specified mixture-average velocity. Its definition must identify both the mass or molar basis and the reference frame.

DEFINITION
Total molar flux

Molar transport rate of a species per unit area past a fixed observer. It includes transport by bulk motion and diffusion, and has units such as $\mathrm{mol\,m^{-2}\,s^{-1}}$.

By Eq. 5, $cv^* = N_A + N_B$. Expanding $J_A = c_A(v_A - v^*)$ gives

$$J_A = N_A - \chi_A(N_A + N_B),$$

so

$$N_A = \chi_A(N_A + N_B) + J_A \tag{6}$$

Figure 1 shows how transport by bulk motion and diffusion add to give the total molar flux in Eq. 6. For stagnant B, the bulk contribution is the fraction χ_A of N_A. For arbitrary N_B, use the full sum $N_A + N_B$ to determine the bulk contribution. At dilute A the stagnant-carrier correction is small because A makes up only a small fraction of the moving mixture. At higher concentrations, it must be included.

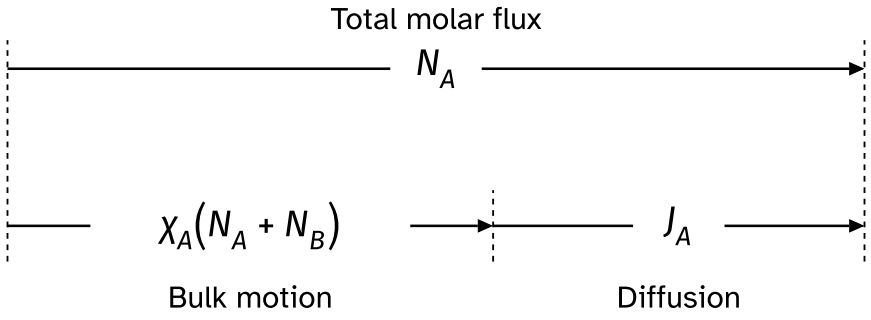


Figure 1: Total molar flux is the sum of transport by bulk motion and diffusion, shown here in the same direction. Dashed guides align the component arrows with the total.

QUIZ

4. Separating transport by bulk motion from diffusion

In a binary mixture, the molar-frame diffusive fluxes satisfy $J_A + J_B = 0$. What follows about the total molar flux $N_A + N_B$ past a fixed observer?

1. It must always be zero.
2. It can be nonzero because bulk motion carries moles past the observer.
3. It must equal the total mass flux numerically.
4. It must be negative.

See solution for Quiz 4

8 Diffusion flux

Substituting Eq. 1 into Eq. 6 gives

$$\begin{aligned} N_A &= \frac{c_A}{c}(N_A + N_B) - D_{AB}\frac{dc_A}{dz} \\ N_A &= \chi_A(N_A + N_B) - cD_{AB}\frac{d\chi_A}{dz} \end{aligned} \tag{7}$$

The product derivative

$$\frac{dc_A}{dz} = c\,\frac{d\chi_A}{dz} + \chi_A\,\frac{dc}{dz}$$

explains the constant-c restriction. In an isothermal isobaric ideal gas it is exact. A liquid may need a composition-dependent model or a justified average concentration. Positive flux means motion in positive z; a negative result reports the direction rather than an arithmetic failure.

9 Diffusion flux: two limiting cases

Equimolar counter-diffusion imposes $N_A + N_B = 0$. Burning solid carbon to only carbon dioxide consumes one oxygen molecule for one carbon dioxide molecule produced, so this is a useful gas-film model. Formation of CO changes the ratio and invalidates the equimolar assumption. Binary distillation with equal molar latent heats is another approximate example.

A crossing stagnant B imposes $N_B = 0$. Water absorbed into concentrated acid crosses the interface while insoluble carrier air does not. Air can still diffuse towards the interface: bulk motion cancels its diffusion exactly. This is zero net flux, not zero microscopic motion. Other stoichiometric ratios or imposed flows must be inserted into Eq. 7 explicitly.

10 Equimolar counter-diffusion of gases A and B

DEFINITION

Equimolar counter-diffusion

Binary transport with equal and opposite total molar fluxes, $N_A = -N_B$. The net mixture molar flux is zero.

Take steady, one-dimensional, nonreacting transfer across $0 \le z \le L$ with constant D, T and P. Conservation makes N_A constant. Since $c_A = p_A/(R_u T)$,

$$\begin{aligned} N_A &= -\frac{D_{AB}}{R_u T}\frac{dp_A}{dz} \\ N_A L &= -\frac{D_{AB}}{R_u T}\int_{p_{A1}}^{p_{A2}} dp_A \\ N_A &= \frac{D_{AB}(p_{A1}-p_{A2})}{R_u T L} \end{aligned} \tag{8}$$

Partial pressures and concentrations are linear, with $p_A + p_B = P$. The pressure-based resistance is $R_u T L/D$, with units $\mathrm{Pa\,m^2\,s\,kmol^{-1}}$, while concentration-based resistance L/D has units s m⁻¹. Use the same driving-force basis when adding resistances in series.

11 A diffusing through stagnant, non-diffusing B

DEFINITION
Stagnant carrier

A species with zero total flux past the chosen fixed observer, such as $N_B = 0$. Its diffusive and bulk contributions can still be nonzero and cancel each other.

Now set $N_B = 0$ in Eq. 7. Rearranging and separating gives

$$\begin{aligned} N_A(1-y_A) &= -cD_{AB}\frac{dy_A}{dz} \\ N_A\int_0^L dz &= -cD_{AB}\int_{y_{A1}}^{y_{A2}}\frac{dy_A}{1-y_A} \\ N_A &= \frac{cD_{AB}}{L}\ln\frac{1-y_{A2}}{1-y_{A1}} \end{aligned} \tag{9}$$

Equivalently

$$N_A = \frac{D_{AB}P}{R_u T L}\ln\left(\frac{P-p_{A2}}{P-p_{A1}}\right).$$

When $y_{A1} > y_{A2}$, the logarithm is positive. The local multiplier $1/(1-y_A)$ is 2 at $y_A = 0.5$ and 10 at 0.9. At low concentration the logarithm approaches $y_{A1} - y_{A2}$ and Eq. 8 returns.

Define the log-mean stagnant-species partial pressure and mole fraction:

$$\begin{aligned} p_{BM} &= \frac{p_{B2}-p_{B1}}{\ln\left(\frac{p_{B2}}{p_{B1}}\right)}, \quad y_{BM} = \frac{p_{BM}}{P} \\ N_A &= \frac{D_{AB}(p_{A1}-p_{A2})}{R_u T L}\frac{P}{p_{BM}} \\ N_A &= \frac{cD_{AB}(y_{A1}-y_{A2})}{L y_{BM}} \end{aligned} \tag{10}$$

DEFINITION

Stefan-flow enhancement factor

For A diffusing through stagnant B in the stated binary gas film,

$$F_S = \frac{1}{y_{BM}} = \frac{P}{p_{BM}}$$

multiplies the equimolar-diffusion flux based on the same endpoint concentration difference. It accounts for bulk molar motion. The local multiplier $1/(1 - y_A)$ is distinct from this integrated factor.

If the endpoints coincide, take the common value as the log mean. The exact enhancement is P/p_{BM}, not an arbitrarily chosen local fraction. The logarithm follows from integrating $1/(1 - y_A)$ and the profile is curved. Its gradient magnitude increases towards the low-A end because

$$\left|\frac{dy_A}{dz}\right| = \frac{N_A(1 - y_A)}{cD}.$$

The smaller fraction of A at that end means that a steeper gradient is needed to maintain the same total flux.

As A becomes dilute, F_S approaches one; when B's log-mean fraction is 0.5, $F_S = 2$. This correction needs the stagnant-B model. A change in reaction stoichiometry or imposed bulk flow changes the multiplier.

QUIZ

5. A stagnant carrier

A diffuses through stagnant B with $N_B = 0$. What does stagnant mean here?

1. B molecules have no random motion.
2. The mixture molar-average velocity must be zero.
3. B has zero total molar flux, while its bulk and diffusive contributions can cancel.
4. The concentration gradient of B must be zero.

See solution for Quiz 5

11.1 Pseudo-steady-state analysis with a moving boundary

Let $L(t)$ be the distance from a falling pure-liquid surface to a fixed swept tube mouth. The surface equilibrium composition and the mouth composition remain constant. The gas adjusts over L^2/D while the liquid retreats much more slowly, so approximate the gas profile as steady at each instantaneous length. Liquid molar density is $c_L = \rho_L/M_A$, with ρ_L a mass density, not a molar density.

$$c_L \frac{dL}{dt} = \frac{cD_{AB}\Lambda}{L}, \quad \Lambda = \ln \frac{1 - y_{A2}}{1 - y_{A1}}$$
$$\int_0^t dt = \frac{c_L}{cD_{AB}\Lambda} \int_{L_0}^{L_f} L \, dL \tag{11}$$
$$t = \frac{c_L (L_f^2 - L_0^2)}{2cD_{AB}\Lambda}$$

Since

$$\Lambda = \frac{y_{A1} - y_{A2}}{y_{BM}},$$

this also reproduces the source's log-mean form. Only L changes during integration. Plotting L^2 against time is the Stefan-tube method of estimating diffusivity. Its slope is $2cD\Lambda/c_L$. Maintaining temperature, a dry mouth and negligible convection is necessary.

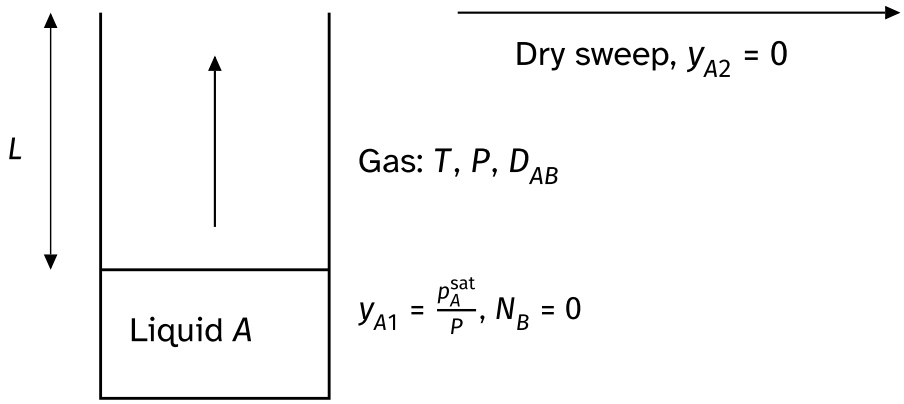


Figure 2: A Stefan tube with a liquid surface below a dry swept mouth. Vapour moves upwards through air with zero net air flux.

12 Classroom example 1: water evaporation

EXERCISE
Exercise 1. Water evaporation

Water in the bottom of a narrow metal tube is held at a constant temperature of 293 K. The total pressure of air (assumed dry) is 1.01325×10^5 Pa and the temperature is 293 K. Water evaporates and diffuses through the air in the tube, and the diffusion path $z_2 - z_1$ is 0.1524 m. Calculate the rate of evaporation at steady state in $\mathrm{kgmol}/(\mathrm{s} \cdot \mathrm{m}^2)$. The diffusivity of water vapour at 293 K and 1 atm pressure is 0.250×10^{-4} m^2/s. Assume that the system is isothermal. The vapour pressure of water at 1 atm and 293 K is 17.535 mmHg.

Additional note: Moving boundaries or pseudo-steady state diffusion. How long would it take for the water level to decrease by 0.1 m?

See solution for Exercise 1

13 Classroom example 2: butanol in water

EXERCISE
Exercise 2. Butanol in water

Calculate the rate of diffusion of butanol at 20 °C under unidirectional steady state conditions through a 0.1 cm thick film of water when the concentrations of butanol at the opposite sides of the film are, 10% and 4% butanol by weight, respectively.

D_{AB} (butanol in water solution)=5.9×10^{-6} cm^2/s. The densities of 10% and 4% butanol solutions at 20 °C may be taken as 0.971 and 0.992 g/cc, respectively. Molecular weight of Butanol is 74, and that of water is 18.

See solution for Exercise 2

14 Steady-state mass transport: shell balance approach

14.1 Species balance and homogeneous reaction

At steady state, species inflow minus outflow plus generation is zero. Total N_A already includes convection and diffusion. For a plane shell of area $A_s = \Delta x \Delta y$ and thickness Δz,

$$\begin{aligned} A_s[N_A(z) - N_A(z+\Delta z)] + A_s \Delta z R_A = 0 \\ \frac{dN_A}{dz} = R_A \end{aligned} \tag{16}$$

R_A is net production in $\mathrm{kmol\,m^{-3}\,s^{-1}}$, negative for consumption. A homogeneous nth-order rate may be written $R_A = \pm k_n''' c_A^n$, with k_n''' units $(\mathrm{kmol\,m^{-3}})^{1-\mathrm{n}}\,\mathrm{s^{-1}}$. Multiplying by volume produces kmol s⁻¹, while multiplying N_A by face area produces the same units. A heterogeneous reaction acts at a boundary, so it sets a surface-flux condition instead of a volumetric source. A porous catalyst can distribute internal reacting area throughout its modelled volume, requiring an effective volumetric rate and diffusivity.

14.2 Setting interface conditions

Use the equilibrium relation appropriate to the example, such as Raoult's law $p_A = x_{A,L} p_A^{\mathrm{sat}}$ or Henry's law $p_A = H x_{A,L}$, with H in Pa for this convention. An impermeable face has $N_A = 0$; a reacting face has a flux condition from its stoichiometry.

15 Case study 1: diffusion through stagnant gas film

15.1 Balance and constitutive law

Consider the same straight tube at an instant, with interface z_1 and mouth z_2. B cannot cross the liquid surface; steadiness without reaction then requires $N_B = 0$ throughout. A's balance

is Eq. 16 with $R_A = 0$, so $dN_A/dz = 0$. Every mole leaving the liquid reaches the mouth. Substitute Eq. 7:

$$\begin{aligned} N_A &= -\frac{cD_{AB}}{1-y_A}\frac{dy_A}{dz} \\ \frac{d}{dz}\left[\frac{cD_{AB}}{1-y_A}\frac{dy_A}{dz}\right] &= 0 \end{aligned} \tag{17}$$

The isothermal isobaric gas has constant c, and constant diffusivity is assumed. Remove these constants before integrating. If properties vary strongly they must stay inside the derivative.

15.2 Two integrations and boundary conditions

Integrating Eq. 17 once and then again gives

$$\begin{aligned} \frac{1}{1-y_A}\frac{dy_A}{dz} &= C_1 \\ -\ln(1-y_A) &= C_1 z + C_2 \end{aligned} \tag{18}$$

C_1 has units m^{-1} and C_2 is dimensionless. At z_1 and z_2, impose y_{A1} and y_{A2}. Subtraction yields

$$\begin{aligned} \Lambda &= \ln\frac{1-y_{A2}}{1-y_{A1}} \\ L &= z_2 - z_1 \\ C_1 &= -\frac{\Lambda}{L} \\ C_2 &= -\ln(1-y_{A1}) - C_1 z_1 \end{aligned} \tag{19}$$

Write the profile using a dimensionless distance measured from the liquid surface:

$$\begin{aligned} \eta &= \frac{z - z_1}{L} \\ 1 - y_A &= (1-y_{A1})\left(\frac{1-y_{A2}}{1-y_{A1}}\right)^{\eta} \\ N_A &= -cD_{AB}C_1 = \frac{cD_{AB}}{L}\Lambda \end{aligned} \tag{20}$$

The endpoints give the specified values, and differentiating the profile reproduces Eq. 9 at every position. This is the benefit of shell balance: the profile is now known, rather than only a resistance formula. Dilute A makes it approximately linear.

16 Case study 2: steady-state diffusion from a suspended droplet

Take a spherical liquid droplet of radius a surrounded by a gas film ending at radius b. Radial coordinate r points outward. Assume quasi-steady spherical symmetry, constant c and D, no reaction or external flow, interface gas fraction y_{A1} and outer fraction y_{A2}, and insoluble B. At a pure-liquid interface Raoult's law sets the surface vapour fraction at the droplet temperature.

A shrinking droplet is only instantaneously steady; neglect thermal cooling or include it in a coupled model.

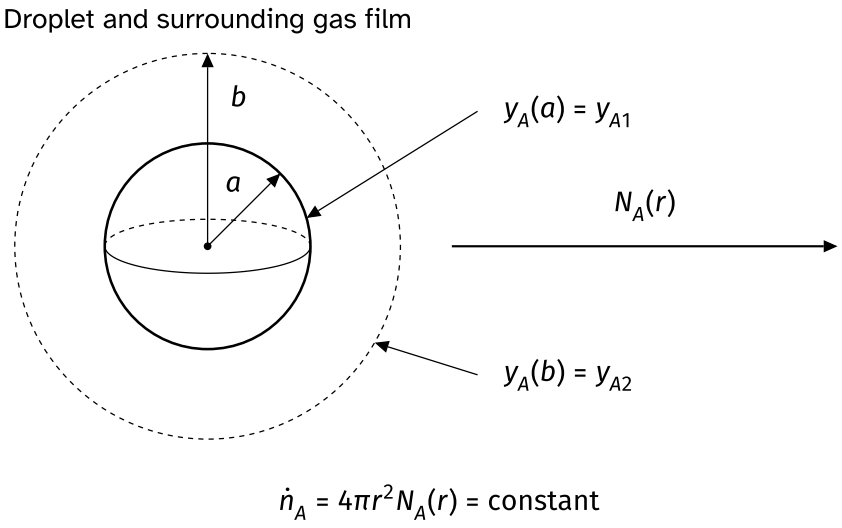


Figure 4: Spherical diffusion from a liquid droplet of radius a to the outer edge of a gas film at radius b.

A shell has different inner and outer areas. Conservation gives

$$\begin{aligned} 4\pi\left[r^2 N_A(r) - (r+\Delta r)^2 N_A(r+\Delta r)\right] &= 0 \\ \frac{d}{dr}(r^2 N_A) = 0, \qquad r^2 N_A &= C_N \\ N_A = -\frac{cD_{AB}}{1-y_A}\frac{dy_A}{dr} & \end{aligned} \tag{21}$$

Thus the flux falls as $1/r^2$ while total molar rate stays fixed. Substituting and integrating gives

$$\begin{aligned} \frac{r^2}{1-y_A}\frac{dy_A}{dr} &= C_1 \\ -\ln(1-y_A) &= -\frac{C_1}{r} + C_2 \\ C_1 &= \frac{\Lambda}{\frac{1}{b}-\frac{1}{a}} \\ C_2 &= -\ln(1-y_{A1}) + \frac{C_1}{a} \end{aligned} \tag{22}$$

Here C_1 has units m, unlike the plane integration constant. Subtract the surface equation to avoid dimensioned exponents:

$$\begin{aligned} \ln\frac{1-y_A(r)}{1-y_{A1}} &= \Lambda\frac{\frac{1}{a}-\frac{1}{r}}{\frac{1}{a}-\frac{1}{b}} \\ N_A(a) &= \frac{cD_{AB}\Lambda}{a^2\left(\frac{1}{a}-\frac{1}{b}\right)} \\ \dot{n}_A = 4\pi a^2 N_A(a) &= \frac{4\pi cD_{AB}\Lambda}{\frac{1}{a}-\frac{1}{b}} \end{aligned} \tag{23}$$

$\dot{n}_A$ is a total molar rate in kmol s^{-1}; n_i earlier was a mass flux, so the overdot and A label matter. The source calls this rate W_A. Both boundary fractions are recovered by Eq. 23. For $b \to \infty$, $N_A(a) = cD\Lambda/a$ and $\dot{n}_A = 4\pi acD\Lambda$.

DEFINITION
Sherwood number

The dimensionless mass transfer coefficient $\mathrm{Sh} = k_c L/D_{AB}$, comparing surface transfer with diffusion across the fluid length L. The coefficient k_c must use a concentration difference on the same basis as the species diffusivity. It is the mass counterpart of Nusselt number.

Large Sh means a steep interfacial concentration gradient relative to the reference gradient across L. Values of order one mean that reference diffusion scale is comparable. A stagnant sphere gives Sh two with diameter as L, as derived below, rather than a universal value of one. For $k_c = 0.01\ \mathrm{m\,s^{-1}}$, $L = 0.02\ \mathrm{m}$ and $D_{AB} = 2 \times 10^{-5}\ \mathrm{m^2\,s^{-1}}$, $\mathrm{Sh} = 10$. Using radius instead halves it; use the length required by the correlation. For a local coefficient use the matching local length; for a surface average use the average coefficient and the specified overall length. The convective topic derives these local and average forms.

For dilute A, $\Lambda \simeq y_{A1} - y_{A2}$. Compare the surface flux with $N_A = k_c(c_{A1} - c_{A2})$ to obtain

$$\begin{aligned} k_c &= \frac{D_{AB}}{a}, \quad d_p = 2a \\ \mathrm{Sh} &= \frac{k_c d_p}{D_{AB}} = 2 \end{aligned} \tag{24}$$

The leading two in sphere correlations is this diffusion limit, analogous to the heat-transfer $\mathrm{Nu} = 2$ limit. At concentrated A, Stefan flow increases the coefficient based on the simple concentration difference, so Sh equals two only for the stated dilute limit. Combining $\dot{n}_A$ with the liquid balance

$$-\left(\frac{\rho_L}{M_A}\right) 4\pi a^2 \frac{da}{dt} = \dot{n}_A$$

gives

$$\frac{d(a^2)}{dt} = -\frac{2M_A cD\Lambda}{\rho_L}$$

in the infinite-film constant-property approximation. Diameter squared then decreases linearly. Real droplets can cool, encounter flow or change properties; those effects change the model. For a flowing gas, a suitable mass-transfer correlation accounts for the changed concentration field.

QUIZ

6. Flux from a spherical droplet

In steady spherically symmetric diffusion with no volumetric reaction, which quantity stays constant as radius increases?

1. $4\pi r^2 N_{Ar}$, the total molar rate.
2. N_{Ar}, the local flux.
3. rN_{Ar} in every spherical problem.
4. The concentration c_A.

See solution for Quiz 6

17 Additional examples

EXERCISE

Exercise 3. Compare equimolar diffusion and a stagnant carrier

A binary ideal gas is at 300 K and 100 kPa. Across a 5.0 mm plane film, the mole fraction of A falls from 0.30 to zero. Use $D_{AB} = 2.0 \times 10^{-5}$ m² s⁻¹ and $R = 8.314$ J mol⁻¹ K⁻¹. Compare the steady molar flux of A for equimolar counter-diffusion and for zero net flux of B. Take positive flux from the high-A face to the low-A face. Explain the difference and determine the flux ratio if the high-face mole fraction is reduced to 0.010, with all other data unchanged.

See solution for Exercise 3

18 What you should now be able to calculate

Convert concentration and flux bases, distinguish equimolar from stagnant-carrier diffusion, and calculate plane or radial rates and slow interface motion.

Practice: Workshop 8 for evaporation and shrinking droplets.

19 Report an error

Email Ranjeet Utikar with the title Fundamentals of mass diffusion, the URL `/mass-transport/diffusion-fundamentals/`, and the equation or passage to check.

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Bird, R. Byron, Warren E. Stewart, and Edwin N. Lightfoot. 2006. *Transport Phenomena.* Revised 2nd. John Wiley & Sons. https://www.wiley-vch.de/en/areas-interest/engineering/transport-phenomena-978-0-470-11539-8.

Geankoplis, Christie J. 2003. *Transport Processes and Separation Process Principles.* 4th ed. Prentice Hall.

Shah, Milinkumar. n.d. “CHEN3001-TP: Mass Transport 1.” Curtin University. Unpublished.

Welty, James R., Charles E. Wicks, Robert E. Wilson, and Gregory L. Rorrer. 2001. *Fundamentals of Momentum, Heat, and Mass Transfer*. 4th ed. John Wiley & Sons.

Solutions

Quiz solutions

Quiz 1. The sign of diffusion

Correct choice: 3.

Fick's law gives

$$J_A = -D_{AB}\frac{dc_A}{dz}$$

The concentration gradient is negative, so the diffusive flux is positive. A moves toward increasing position, from higher to lower concentration. Bulk motion can make the total flux different from this diffusive flux.

Back to Quiz 1

Quiz 2. Diffusion time scale

Correct choice: 1.

First convert the diffusion distance:

$$L = 1\ \text{mm} = 10^{-3}\ \text{m}$$

Then estimate the diffusion time:

$$t_{\text{diff}} \sim \frac{L^2}{D} = \frac{(10^{-3})^2}{10^{-9}} = 1000\ \text{s}$$

Back to Quiz 2

Quiz 3. Mass fraction and mole fraction

Correct choice: 4.

Mole fraction counts moles, while mass fraction weights those moles by molar mass. Equal molar amounts therefore give equal mole fractions and unequal mass fractions when molar masses differ.

Back to Quiz 3

Quiz 4. Separating transport by bulk motion from diffusion

Correct choice: 2.

The diffusive fluxes sum to zero in the molar-average frame. Past a fixed observer, bulk motion also transports material:

$$N_A + N_B = cv^*$$

The total molar flux can therefore be nonzero. It is zero only if the molar-average velocity is zero, as in equimolar counter-diffusion.

Back to Quiz 4

Quiz 5. A stagnant carrier

Correct choice: 3.

Stagnant B means that no net amount of B crosses a fixed surface. B can still diffuse in one direction while bulk motion carries it in the opposite direction. These contributions cancel. It does not mean that B molecules stop moving or that the mixture has zero bulk velocity.

Back to Quiz 5

Quiz 6. Flux from a spherical droplet

Correct choice: 1.

The same molar rate crosses every sphere surrounding the droplet:

$$\dot{n}_A = 4\pi r^2 N_{Ar} = \text{constant}$$

Thus,

$$N_{Ar} = \frac{\dot{n}_A}{4\pi r^2}$$

The area increases with the square of radius, so the local flux decreases as the inverse square. The total rate stays constant.

Back to Quiz 6

Exercise solutions

Exercise 1. Water evaporation

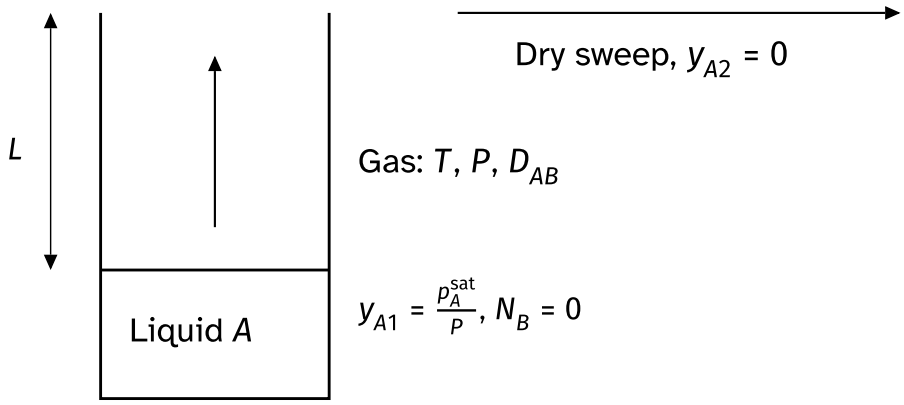


Figure 3: Water vapour diffuses through the gas above the liquid to the tube mouth. As the liquid surface falls, the gas diffusion distance increases.

The evaporation path is the gas space between the water surface and the tube mouth, as shown in Figure 2. Water vapour moves upwards. Air has zero net flux across the liquid interface.

Data

Quantity	Value
Initial gas diffusion length	$L_0 = 0.1524\ \mathrm{m}$
Temperature	$T = 293\ \mathrm{K}$
Pressure	$P = 101325\ \mathrm{Pa}$
Diffusivity	$D_{AB} = 2.50 \times 10^{-5}\ \mathrm{m^2\,s^{-1}}$
Surface vapour pressure	$p_{A,s} = 17.535\ \mathrm{mmHg}$
Liquid density for the moving-boundary calculation	$\rho_L = 1000\ \mathrm{kg\,m^{-3}}$
Water molar mass	$M_A = 18\ \mathrm{kg\,kmol^{-1}}$
Final gas diffusion length	$L_f = 0.1524 + 0.1000 = 0.2524\ \mathrm{m}$

The source unit kgmol is equivalent to kmol. Liquid density and molar mass are supplementary inputs needed to convert liquid-depth loss to an amount evaporated.

Assumptions

- Unidirectional diffusion through the gas space.
- Steady gas profile for the initial flux calculation.
- Pseudo-steady gas profile as the liquid surface recedes.

- Ideal gas behaviour.
- Constant temperature, pressure and diffusivity.
- Vapour-liquid equilibrium at the water surface.
- Zero net air flux through the liquid surface.
- Negligible natural convection.

Calculations

At the liquid surface, equilibrium fixes the vapour partial pressure. At the mouth, the dry air gives $p_{A2} = 0$. Converting the surface vapour pressure to Pa gives

$$p_{A1} = \frac{17.535}{760}(101325) = 2337.8\ \text{Pa}$$

The surface mole fraction and total gas concentration are

$$y_{A1} = \frac{p_{A1}}{P} = \frac{2337.8}{101325} = 0.0230724$$

$$c = \frac{P}{R_u T} = \frac{101325}{8314(293)} = 0.0415948\ \text{kmol m}^{-3}$$

Because air has zero net flux, the appropriate governing relation is the stagnant-carrier result, Eq. 9,

$$N_A = \frac{cD_{AB}}{L_0} \ln \frac{1 - y_{A2}}{1 - y_{A1}}$$

Substituting the boundary fractions and the initial gas length gives

$$N_A = \frac{0.0415948(2.50 \times 10^{-5})}{0.1524} \ln \frac{1}{1 - 0.0230724} = 1.593 \times 10^{-7}\ \text{kmol m}^{-2}\,\text{s}^{-1} \quad (12)$$

Multiplying by molar mass converts the molar flux to mass flux,

$$n_A = M_A N_A = 18(1.593 \times 10^{-7}) = 2.867 \times 10^{-6}\ \text{kg m}^{-2}\,\text{s}^{-1}$$

The initial rate is about $0.248\ \text{kg m}^{-2}$ per day. The stagnant-carrier flux is only 1.17 percent above the equimolar estimate because the water vapour is dilute.

For the falling liquid level, the gas length increases and the evaporation flux decreases. Define the constant logarithmic driving force,

$$\Lambda = \ln \frac{1 - y_{A2}}{1 - y_{A1}} = \ln \frac{1}{1 - 0.0230724} = 0.0233427$$

The liquid molar density is

$$c_L = \frac{\rho_L}{M_A} = \frac{1000}{18} = 55.5556\ \text{kmol m}^{-3}$$

A decrease in liquid depth dL removes $c_L dL$ kmol per unit tube area. Equating that loss to the instantaneous evaporation flux gives

$$c_L \frac{dL}{dt} = \frac{cD_{AB}\Lambda}{L}$$

Separating variables and integrating between the initial and final levels gives the moving-boundary relation, Eq. 11,

$$t = \frac{c_L(L_f^2 - L_0^2)}{2cD_{AB}\Lambda}$$

Substitute the consistent kmol-based concentrations,

$$t = \frac{55.5556(0.2524^2 - 0.1524^2)}{2(0.0415948)(2.50 \times 10^{-5})(0.0233427)} = 4.632 \times 10^7 \text{ s} = 536 \text{ days} \tag{13}$$

As a check, removing 0.1 m of water requires $5.556 \text{ kmol m}^{-2}$. Even if the initial flux stayed constant, evaporation would take

$$\frac{5.556}{1.593 \times 10^{-7}} = 3.49 \times 10^7 \text{ s}.$$

The falling level lengthens the diffusion path, so the calculated time must be greater than that lower bound.

The gas diffusion time is $L_0^2/D_{AB} \simeq 929$ s, much shorter than the liquid retreat time. This supports the pseudo-steady approximation. Maintaining the stipulated isothermal, convection-free conditions for 536 days would be difficult in an experiment.

Answer

The initial evaporation flux is $N_A = 1.59 \times 10^{-7} \text{ kgmol m}^{-2} \text{ s}^{-1}$, directed towards the tube mouth. The corresponding mass flux is $2.87 \times 10^{-6} \text{ kg m}^{-2} \text{ s}^{-1}$.

Under the pseudo-steady moving-boundary model, the water level takes 4.63×10^7 s, or about 536 days, to fall by 0.1 m.

Back to Exercise 1

Exercise 2. Butanol in water

Data

Quantity	Value
Film thickness	$L = 0.1\ \mathrm{cm}$
Diffusivity	$D_{AB} = 5.9 \times 10^{-6}\ \mathrm{cm^2\,s^{-1}}$
Butanol mass fraction at side 1	$w_{A1} = 0.10$
Density at side 1	$\rho_1 = 0.971\ \mathrm{g\,cm^{-3}}$
Butanol mass fraction at side 2	$w_{A2} = 0.04$
Density at side 2	$\rho_2 = 0.992\ \mathrm{g\,cm^{-3}}$
Butanol molar mass	$M_A = 74\ \mathrm{g\,mol^{-1}}$
Water molar mass	$M_B = 18\ \mathrm{g\,mol^{-1}}$

Assumptions

- Steady state.
- Unidirectional diffusion across the film.
- Isothermal conditions at 20 °C.
- No chemical reaction.
- Zero net water flux.
- Constant diffusivity.
- Total molar concentration approximated by its arithmetic mean across the film.

Calculations

Let A be butanol and B be water, with positive flux from the 10 percent side to the 4 percent side. The stagnant-water model uses mole fractions, so first convert the supplied mass fractions. On a 100 g basis, side 1 contains $10/74$ mol butanol and $90/18$ mol water. Hence

$$x_{A1} = \frac{\frac{10}{74}}{\frac{10}{74} + \frac{90}{18}} = 0.0263158$$

For side 2, the same conversion gives

$$x_{A2} = \frac{\frac{4}{74}}{\frac{4}{74} + \frac{96}{18}} = 0.0100334$$

The total molar concentration equals the total moles divided by the solution volume. Since a 100 g sample occupies $100/\rho_i\ \mathrm{cm^3}$,

$$c_1 = \frac{\frac{10}{74} + \frac{90}{18}}{\frac{100}{0.971}} = 0.0498622\ \mathrm{mol\,cm^{-3}}$$

$$c_2 = \frac{\frac{4}{74} + \frac{96}{18}}{\frac{100}{0.992}} = 0.0534429 \text{ mol cm}^{-3}$$

Their arithmetic mean is

$$\bar{c} = \frac{c_1 + c_2}{2} = \frac{0.0498622 + 0.0534429}{2} = 0.0516525 \text{ mol cm}^{-3} \tag{14}$$

The total molar concentration changes by about 7 percent across the film. Treating it as uniform is an approximation for this liquid mixture. Constant temperature and pressure alone do not make a liquid's molar concentration constant.

With zero net water flux, the governing total-flux relation is

$$N_A = -\frac{\bar{c} D_{AB}}{1 - x_A} \frac{dx_A}{dz}$$

Integrating over the film gives the liquid version of Eq. 9,

$$N_A = \frac{\bar{c} D_{AB}}{L} \ln \frac{1 - x_{A2}}{1 - x_{A1}}$$

Substituting in centimetre and mol units gives

$$\begin{aligned} N_A &= \frac{0.0516525(5.9 \times 10^{-6})}{0.1} \ln \frac{1 - 0.0100334}{1 - 0.0263158} \\ &= 5.054 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1} \\ &= 5.054 \times 10^{-7} \text{ kmol m}^{-2} \text{ s}^{-1} \end{aligned} \tag{15}$$

The mass flux follows by multiplying by the molar mass of butanol,

$$n_A = M_A N_A = 74(5.054 \times 10^{-8}) = 3.740 \times 10^{-6} \text{ g cm}^{-2} \text{ s}^{-1}$$

As a check, neglecting the stagnant-water correction gives

$$N_{A,\text{eq}} = \frac{\bar{c} D_{AB}(x_{A1} - x_{A2})}{L} = 4.962 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}.$$

The full result is 1.85 percent larger, consistent with dilute butanol.

The flux is about 3.23 kg m^{-2} per day. Comparing it with the water-evaporation example requires the concentration difference and film thickness as well as the diffusivity.

Answer

Butanol diffuses from the 10 percent side to the 4 percent side at $N_A = 5.05 \times 10^{-7} \text{ kmol m}^{-2} \text{ s}^{-1}$, equivalent to a mass flux of $3.74 \times 10^{-5} \text{ kg m}^{-2} \text{ s}^{-1}$.

Back to Exercise 2

Exercise 3. Compare equimolar diffusion and a stagnant carrier

Data

Quantity	Value
Temperature	$T = 300\ \mathrm{K}$
Pressure	$P = 100000\ \mathrm{Pa}$
Film thickness	$L = 0.0050\ \mathrm{m}$
Diffusivity	$D_{AB} = 2.0 \times 10^{-5}\ \mathrm{m^2\,s^{-1}}$
Gas constant	$R = 8.314\ \mathrm{J\,mol^{-1}\,K^{-1}}$
Side 1 mole fraction in the first comparison	$y_{A1} = 0.30$
Side 2 mole fraction	$y_{A2} = 0$
Side 1 mole fraction in the second comparison	$y_{A1} = 0.010$

Assumptions

- Steady state.
- One-dimensional diffusion across a plane film.
- Ideal gas behaviour.
- Constant temperature, pressure and diffusivity.
- No reaction in the film.

Calculations

Positive flux points from the high-A face towards the low-A face. The total concentration is

$$c = \frac{P}{RT} = \frac{100000}{8.314(300)} = 40.09\ \mathrm{mol\,m^{-3}}$$

For equimolar counter-diffusion, $N_A + N_B = 0$. As in Eq. 8, the bulk contribution vanishes and the governing relation is

$$N_A = -cD_{AB}\frac{dy_A}{dz}.$$

Integrating between the film faces gives

$$\begin{aligned} N_{A,\mathrm{eq}} &= \frac{cD_{AB}}{L}(y_{A1} - y_{A2}) \\ &= \frac{40.09(2.0 \times 10^{-5})}{0.0050}(0.30 - 0) \\ &= 0.04811\ \mathrm{mol\,m^{-2}\,s^{-1}} \end{aligned}$$

For zero net flux of B, the total flux satisfies

$$N_A = -\frac{cD_{AB}}{1-y_A}\frac{dy_A}{dz}.$$

Integrating this relation gives

$$\begin{aligned} N_{A,\mathrm{stag}} &= \frac{cD_{AB}}{L}\ln\frac{1-y_{A2}}{1-y_{A1}} \\ &= \frac{40.09(2.0\times10^{-5})}{0.0050}\ln\frac{1}{0.70} \\ &= 0.05720\ \mathrm{mol\,m^{-2}\,s^{-1}} \end{aligned}$$

A enters the film without a compensating net flux of B, producing molar flow in A's direction. That bulk flow transports additional A. B still diffuses towards the high-A side, but its bulk contribution cancels its diffusion.

With $y_{A2} = 0$, dividing the two fluxes gives

$$\frac{N_{A,\mathrm{stag}}}{N_{A,\mathrm{eq}}} = \frac{-\ln(1-y_{A1})}{y_{A1}}$$

The common concentration, diffusivity and film thickness cancel. The ratios at the two supplied compositions are

$$\left[\frac{N_{A,\mathrm{stag}}}{N_{A,\mathrm{eq}}}\right]_{y_{A1}=0.30} = \frac{-\ln(0.70)}{0.30} = 1.189$$

$$\left[\frac{N_{A,\mathrm{stag}}}{N_{A,\mathrm{eq}}}\right]_{y_{A1}=0.010} = \frac{-\ln(0.990)}{0.010} = 1.0050$$

As a dilute-limit check,

$$-\ln(1-y) = y + \frac{y^2}{2} + \cdots,$$

so the ratio approaches one as $y \to 0$. The two models then give nearly the same flux.

Answer

At $y_{A1} = 0.30$, the equimolar flux is $0.0481\ \mathrm{mol\,m^{-2}\,s^{-1}}$ and the stagnant-carrier flux is $0.0572\ \mathrm{mol\,m^{-2}\,s^{-1}}$. The latter is 18.9 percent larger. At $y_{A1} = 0.010$, their ratio falls to 1.005.

Back to Exercise 3